

**ABSTRACTS**  
OF  
**CHEMICAL PAPERS**  
ISSUED BY THE  
**BUREAU OF CHEMICAL ABSTRACTS**

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**A. PURE CHEMISTRY**

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**ORGANIC CHEMISTRY AND BIOCHEMISTRY.**

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### A. PURE CHEMISTRY.

#### PART I.

#### Organic Chemistry.

**Substitution Reactions in Organic Chemistry.** B. N. MENSCHUTKIN (*Ann. Inst. Analyse Physico-Chim.*, 1922, 2, 61—95).—A theoretical paper in which the nature of substitution reactions is first discussed and it is pointed out that the study of binary mixtures by the thermal method often gives valuable indications regarding the mechanism of such reactions. The mechanism of Friedel and Crafts' reaction, and more especially the part played by the aluminium chloride, is then examined in detail. G. A. R. K.

**Number of Atomic Rings in Molecules.** H. DECKER (*Z. physikal. Chem.*, 1923, 107, 111—118).—A theoretical paper in which the author deduces equations to give the number of rings contained in organic and other compounds of stated molecular formula. The consideration is based on MendeléeV's formula for the relationship between the number of primary, quaternary, and tertiary carbon atoms in the members of the ethylene series of hydrocarbons, namely,  $pr = te + 2qu$ , where  $pr$ ,  $te$ , and  $qu$  represent, respectively, the number of primary, tertiary, and quaternary carbon atoms. If  $R$  represents the number of rings, ethylene itself, and all double linkings being regarded as two-membered rings, then  $R = 1 - 1/2pr + 1/2te + qu$ . The number of rings in any hydrocarbon of the formula  $C_nH_m$  is given by  $R = 1 - 1/2m + n$ . In any organic compound of the formula  $C_nH_mO_pN_q^{III}N_r^V$ , where the oxygen is all bi-valent, the number of rings is given by  $R = 1 - 1/2m + 1/2p + n + 3/2q$ . In a compound of the molecular formula  $E_m^I E_o^II E_p^{III} E_n^{IV} E_q^V E_r^{VI} E_s^{VII} E_t^{VIII}$ , where  $E^I E^{II}$ , etc., represent elements of one, two, three . . . eight valencies and  $m, n, . . .$  represent the number of atoms of such elements, the number of rings is given by the formula  $R = 1 - 1/2m + 1/2p + n + 3/2q + 2r + 5/2s + 3t$ . For open-chain compounds the

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relationship  $m=6t+5s+4r+3q+2n+p+2$  is true. The usual formula for the paraffins  $C_nH_{2n+2}$  corresponds with the formula  $E_t^{VIII}E_s^{VII}E_r^{VI}E_q^{V}E_n^{IV}E_p^{III}E_o^{II}E_m^I$ , where  $m=6t+5s+4r+3q+2n+p+2$  for compounds of any elements. The formula for hydrogen derivatives of any element  $E^x$ , which is an open chain and contains  $y$  atoms of  $E^x$ ,  $x$  being the valency, is  $E^xH_{(x+2)y+2}$ . The formula of the polycyclic hydrogen derivative is given by  $E^xH_{(y-2)y+2-2R}$ , where  $R$  is the number of rings. The entrance of two univalent atoms into a molecule ruptures a ring, the entrance and removal of bivalent atoms do not affect the number of rings, the entrance of two trivalent atoms brings about the formation of a ring, the entrance of one quadrivalent atom forms one ring, the entrance of two quinquivalent atoms produces three rings, the entrance of one sexavalent atom produces two rings, the entrance of two septavalent atoms produces five rings, and the entrance of one octavalent atom produces three rings.

J. F. S.

**The Preparation of Pure Ethylene.** L. MOSER and F. LINDINGER (*Monatsh.*, 1923, **44**, 141—150).—The effect of adding various catalysts to mixtures in various proportions of 96% alcohol and concentrated sulphuric acid has been examined. Using molecular proportions of alcohol and acid, evolution of gas begins at 140°, but in presence of small quantities of foreign substances, evolution may begin at 125°. The purity of the gas and the proportions of ether, sulphur dioxide, and carbon dioxide were determined under various conditions, the best results being obtained by using 1 mol. of alcohol to 2 mols. of acid, adding 1.5—2.0% of copper sulphate; the yield is 15—20% at a temperature of 145—150°, the gas after careful purification containing 99.2% of ethylene.

By allowing alcohol to drop on to orthophosphoric acid ( $d$  1.70) heated at 220°, the yield is raised to 30%, but the gas after washing contains 5% of impurities, chiefly butane. If alcohol vapour is passed over pumice saturated with pyrophosphoric acid heated at 300°, a yield of about 90% of nearly pure ethylene is obtained. Using kaolin at a temperature of 400° in place of the pumice saturated with pyrophosphoric acid, the yield is 50—60%, and the gas contains, after washing, 2.8—3.6% of impurities.

The action of zinc on ethylene dibromide, which gives the purest gas, is conveniently carried out by warming granulated zinc with a solution of the dibromide in alcohol (15% by volume) at 40°, more dibromide being allowed to trickle in from a dropping funnel when the first evolution of gas slackens.

S. I. L.

**Catalytic Dehydrations and Dehydrogenations by Means of Anhydrous Zinc Sulphate.** G. BRUS (*Bull. Soc. chim.*, 1923, **33**, [iv], 1433—1440).—Anhydrous zinc sulphate behaves towards alcohols as a mixed catalyst, its action being both dehydrating and dehydrogenating. The latter action preponderates as in the case of zinc oxide and it is suggested that the sulphate may function as a basic salt. Its action is more marked than that of the oxide. A proportion of the aldehyde formed is condensed, but *isobutaldehyde* and *isovaleraldehyde* may be obtained readily and in good yield,

whilst glycerol yields acetaldehyde by internal dehydration. The action on acetone results in the formation of a small quantity of mesityl oxide and of phorone.  
H. J. E.

**Trichloro- and Tribromo-ethyl Alcohols.** R. WILLSTÄTTER and W. DUISBERG (*Ber.*, 1923, **56**, [B], 2283—2286).—The phytochemical reduction of chloral and bromal is described.

A dilute solution of bromal hydrate in water containing carbon dioxide is added gradually to a solution of sucrose in water which is in the process of active fermentation by bottom yeast. Poisoning of the ferment is avoided if the total concentration of bromal hydrate and brominated alcohol is maintained below 0.2%. The products of the reaction are dibromoethyl alcohol, b. p. 70—72°/10—11 mm.,  $d_4^{20}$  2.33 (*dibromoethylurethane*, prisms, m. p. 90—91°), possibly monobromoethyl alcohol and tribromoethyl alcohol, prisms, m. p. 80°, b. p. 92—94°/11 mm. (*tribromoethylurethane*, prisms, m. p. 86—87°).

Trichloroethyl alcohol is produced similarly from chloral hydrate. Since the yield of alcohol is 70% of that theoretically possible, its formation must be ascribed to the addition of hydrogen, and not to disproportionation of the aldehyde. *Trichloroethyl p-nitrobenzoate* crystallises in domatic prisms, m. p. 71°; it is reduced by ammonium sulphide in alcoholic solution to *trichloroethyl p-aminobenzoate*, slender, lustrous needles, m. p. 87°, whereas hydrogen sulphide and other reagents transform it readily into ethyl *p-aminobenzoate*. *Trichloroethyl carbamate* crystallises in needles, m. p. 64—65°.

H. W.

**Odour and Molecular Asymmetry.** J. VON BRAUN and W. KAISER (*Ber.*, 1923, **56**, [B], 2268—2274).—An instance is recorded in which the odour of an optically active substance differs appreciably from that of the corresponding *dl*-mixture.

*dl-γγ*-Dimethyloctanol,  $\text{CHMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , b. p. 104—105°/12 mm.,  $d_4^{25}$  0.838, is obtained in 80% yield by the catalytic hydrogenation of citral under medium pressure and in the presence of a nickel catalyst at about 150°. In accordance with the authors' experience of the hydrogenation of aldehydes (A., 1923, i, 1197) small amounts of a by-product, a pale yellow, viscous liquid, b. p. 189—194°/13 mm.,  $d_4^{25}$  0.892, are also produced which is regarded as the secondary *alcohol*,

$\text{CHMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{CHMe} \cdot [\text{CH}_2]_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CHMe} \cdot [\text{CH}_2]_3 \cdot \text{CHMe}_2$ . The primary alcohol is transformed into the corresponding *acetate*, b. p. 108—109°/14 mm.,  $d_4^{25}$  0.875, from which it is regenerated with unchanged physical constants. In a similar manner, *d*-citronellal, b. p. 86—89°/12 mm.,  $d_4^{20}$  0.855,  $\alpha_D$  about +12°, is hydrogenated to *d-γγ*-dimethyloctanol, b. p. 104—106°/12 mm.,  $d_4^{25}$  0.838,  $[\alpha]_D^{20} +2.23'$ , and a *substance*, b. p. about 200°/14 mm., of the approximate composition  $\text{C}_{20}\text{H}_{42}\text{O}$ . The possibility that racemisation occurs to a greater or less extent during the hydrogenation appears to be excluded by the observation that the properties of the product are not appreciably altered by wide variation of the experimental

conditions. The primary alcohol is transformed into its *acetate*, a liquid, b. p. 107—109°/14 mm.,  $d_4^{17}$  0.877,  $[\alpha]_D +0^\circ 28'$ , from which it is regenerated with unchanged physical properties. Its odour is more refreshing and penetrating than that of the inactive alcohol. The suspicion, however, that it is possibly contaminated with *isopulegol* has led the authors to continue their work in the following manner.

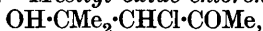
The alcohols are oxidised to the corresponding aldehydes. *dl- $\gamma$ -Dimethyloctanaldehyde* is a liquid, b. p. 79—82°/13 mm.,  $d_4^{22}$  0.823 (*semicarbazone*, needles, m. p. 92—93°), whereas the active *aldehyde* has b. p. 79—82°/13 mm.,  $d_4^{18}$  0.824,  $[\alpha]_D +10^\circ 2'$  (*semicarbazone*, m. p. 78—79°). Both aldehydes have a very pleasant odour of lemons, but that of the inactive compound is more pleasant and intense. They are oxidised with extreme ease when exposed to air; the inactive aldehyde yields thereby an acid, b. p. 134—137°/13 mm.,  $d_4^{18}$  0.897, which closely resembles Wallach's *decoic acid* (A., 1912, i, 878).

*dl*-Dimethyloctanol is converted by fuming hydrobromic acid at 110—120° into the corresponding *bromide*, b. p. 103°/14 mm., which is transformed successively into the corresponding *nitrile*,  $\text{CHMe}_2[\text{CH}_2]_3\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$ , a colourless liquid, b. p. 112—114°/14 mm.,  $d_4^{18}$  0.836, *dl-undecoic acid*, b. p. 149—152°/14 mm.,  $d_4^{18}$  0.897, and *ethyl dl-undecoate*, b. p. 120—122°/13 mm. In a similar series, *d*-dimethyloctanol is converted successively into the corresponding *bromide*, b. p. 103—105°/13 mm.,  $d_4^{19}$  1.083,  $[\alpha]_D -5^\circ 37'$ ; the *nitrile*, b. p. 111—114°/14 mm.,  $d_4^{18}$  0.836,  $[\alpha]_D +0^\circ 30'$ ; *d-undecoic acid*, b. p. 151—153°/14 mm.,  $d_4^{17}$  0.901,  $[\alpha]_D -0.35^\circ$ , and *ethyl d-undecoate*, b. p. 124—126°/14 mm.,  $d_4^{21}$  0.866,  $[\alpha]_D +0^\circ 12'$ . The possibility of racemisation during the sequence of changes is practically excluded by the observations that *d*-dimethyloctanol is regenerated unchanged from the bromide and by the hydrolysis of the nitrile and ester by acid or alkali to undecoic acid which is optically identical with the product obtained by acid hydrolysis of the nitrile. Reduction of the esters by sodium and alcohol under precisely similar conditions leads to the production of the corresponding  *$\delta$ -dimethylnonanols*, the yields being 75% and 25% in the cases of the *d*- and *dl*-compounds, respectively. The *dl*-alcohol has b. p. 110—113°/14 mm.,  $d_4^{18}$  0.834, whereas the dextrorotatory alcohol has b. p. 117—120°/15 mm.,  $d_4^{18}$  0.833,  $[\alpha]_D +2^\circ 7'$ . The physical constants of the racemic and dextrorotatory *acetates* are b. p. 124—126°/13 mm., and b. p. 124—126°/13 mm.,  $d_4^{17}$  0.866,  $[\alpha]_D +0^\circ 48'$ . The observation that the portion of the ethyl *d*-undecoate which is hydrolysed during the reduction yields an optically pure *d*-acid renders it improbable that the dimethylnanol is partly racemised. The alcohols have a very pleasant odour resembling that of geranium leaves; the smell of the optically inactive compound is, however, more intense and less delicate than that of the active compound.

*d- $\gamma$ -Dimethylnonaldehyde* is a liquid, b. p. 93—96°/13 mm.,  $d_4^{18}$  0.830,  $[\alpha]_D +1^\circ 12'$ ; the corresponding *semicarbazone* has m. p. 67—69°.

H. W.

**The Halohydrins of Mesityl Oxide.** PASTUREAU and H. BERNARD (*Bull. Soc. chim.*, 1923, [iv], **33**, 1440—1444).—Mesityl oxide readily yields halohydrins with hypochlorous, hypobromous, and hypoiodous acids. *Mesityl oxide chlorohydrin*,



a colourless, oily liquid, b. p.  $81^\circ/10$  mm., is obtained the most easily and with the best yield. The method employed consists in the addition of mesityl oxide to a mixture of calcium hypochlorite and boric acid and extraction of the product with ether. On saponification by means of potassium carbonate, the glycol of mesityl oxide is formed. Addition of mesityl oxide to bromine water which has been kept for two days yields *mesityl oxide bromohydrin*,  $\text{CMe}_2\text{Br} \cdot \text{CH}(\text{OH}) \cdot \text{COMe}$ , an oily, colourless, lachrymatory liquid, b. p.  $73\text{--}75^\circ/20$  mm. The different constitution, as compared with the chlorohydrin, is assigned to it by reason of its lower boiling point. With potassium carbonate, it behaves similarly to the chlorohydrin. The action on mesityl oxide dissolved in ether saturated with water of iodine in presence of yellow mercuric oxide yields a mixture from which a lachrymatory liquid containing the iodohydrin may be prepared, but separation by distillation under reduced pressure is not practicable, as the substance decomposes. It has a tendency to lose hydriodic acid. Its reactions with potassium carbonate, silver nitrate, and sodium benzoate produce the glycol of mesityl oxide; with the last-named reagent the mesityl homologue of ethylene oxide is formed in addition. This substance may also be prepared by the action of silver oxide on an ethereal solution of the iodohydrin.

H. J. E.

**Unsaturated Reduction Products of the Sugars and their Transformations. VII. The Anhydride of a Disaccharide from  $\delta$ -Hydroxy- $\delta$ -acetylbutyl Alcohol.** M. BERGMANN, A. MIEKELEY, and F. STATHER (*Ber.*, 1923, **56**, [B], 2255—2257).—The synthesis of a non-reducing disaccharide anhydride of the type which has been assumed to constitute the components of the complex polysaccharides is described.

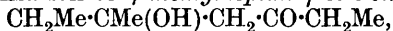
Anhydro- $\delta$ -enol-acetylbutyl alcohol,  $\begin{array}{c} \text{CH}_2\text{--O--CMe} \\ | \\ \text{CH}_2\text{--CH}_2\text{--CH} \end{array}$ , is converted

by an ethereal solution of perbenzoic acid into  $\delta$ -hydroxy- $\delta$ -acetylbutyl alcohol,  $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{COMe}$  (A., 1923, i, 1053). The ethereal solution is shaken with water and the aqueous extract is concentrated under diminished pressure; the residue is mixed with water, or preferably, with the condensate from the first distillation and the solvent is again evaporated, whereby the new *disaccharide anhydride*,  $\begin{array}{c} \text{CH}_2\text{--O--CMe} \cdot \text{O} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2\text{--CH}_2\text{--CH--O} \cdot \text{CMe--O--CH}_2 \end{array}$ , is obtained in colourless

crystals, m. p.  $195^\circ$ . The crude hydroxyacetylbutyl alcohol appears to be mixed with a substance which is somewhat volatile with steam and is responsible for the conversion of the sugar into the disaccharide anhydride; the pure sugar is not affected by evaporation with water under the experimental conditions adopted. The new anhydride is remarkably stable, and may be distilled

without decomposition (b. p. 268°) under atmospheric pressure. It does not reduce Fehling's or ammoniacal silver solution. It does not react with phenylhydrazine. It is hydrolysed with unusual difficulty, which may be partly due to its very sparing solubility in water. It is converted by treatment with hot 2·5*N*-sulphuric acid into a mixture of  $\delta$ -hydroxy- $\delta$ -acetylbutyl alcohol anhydride,  $\begin{array}{c} \text{CH}_2\text{--O--CMe} \\ | \\ \text{CH}_2\text{--CH}_2\text{--CH--} \end{array} \text{>O}$ , and  $\delta$ -hydroxy- $\delta$ -acetylbutyl alcohol. It is transformed by methyl-alcoholic hydrogen chloride into the methyl-*cycloacetal* of  $\delta$ -methoxy- $\delta$ -acetylbutyl alcohol,  $\begin{array}{c} \text{CH}_2\text{--O--CMe--OMe} \\ | \\ \text{CH}_2\text{--CH}_2\text{--CH--OMe} \end{array}$ .  
H. W.

**The Behaviour of some Homologues of Acetone with Alkaline Condensing Agents.** A. FRANKE and T. KÖHLER (*Annalen*, 1923, 433, 314—326).—In the presence of cold, concentrated, aqueous alkali hydroxide solution, methyl ethyl ketone undergoes condensation to  $\gamma$ -methylheptan- $\gamma$ -ol- $\epsilon$ -one,



a colourless, mobile oil, b. p. 187—192° (slight decomp.), or 80°/about 12 mm., *oxime*, an oil, b. p. 130—138°/10 mm. If the condensation is carried out using concentrated alcoholic alkali hydroxide or sodium ethoxide solution, the product is  $\Delta^6$ -hepten- $\gamma$ -one (cf. Becker and Thorpe, T., 1922, 121, 1303), *oxime*, an oil, b. p. 103—104°/10 mm.; the same compound is formed if boiling aqueous alkali hydroxide is employed. The action of cold, concentrated aqueous sodium hydroxide on methyl propyl ketone gives  $\delta$ -methylnonan- $\delta$ -ol- $\delta$ -one, a colourless, mobile oil, b. p. 99·5—100°/10 mm., whereas the product when sodium ethoxide is used is  $\delta$ -methyl- $\Delta^6$ -nonen- $\delta$ -one (cf. Descudé, A., 1903, i, 735), a clear, mobile oil, b. p. 198—204°, *oxime*, thick, colourless liquid, b. p. 120—122°/10 mm. Diethyl ketone does not undergo condensation in the presence of cold or boiling aqueous alkali, but in the presence of sodium ethoxide there is formed a slightly yellow oil, b. p. 247° (oily *oxime*, b. p. 148—149°/10 mm., from which a few crystals separate), together with a portion having b. p. 200—240°; the latter appears to be an unsaturated ketone, whilst the former only reacts slowly with bromine in chloroform solution.

Diethyl ketone condenses, but not readily, with acetaldehyde in the presence of a small quantity of dilute, aqueous alkali hydroxide, to give, apparently,  $\gamma$ -methylheptan- $\beta$ -ol- $\delta$ -one,



b. p. 84—85°/10 mm.; if isobutaldehyde is employed, the product is  $\beta\delta$ -dimethylheptan- $\gamma$ -ol- $\delta$ -one, an oil, b. p. 95—96°/15 mm., which is also formed by the use of alcoholic alkali hydroxide, and from which water is eliminated by warming with anhydrous oxalic acid, to give  $\beta\delta$ -dimethyl- $\Delta^7$ -hepten- $\delta$ -one, a colourless oil, b. p. 178—183° (decomp.), or 66—69°/16 mm., *oxime*, crystals, m. p. 83°, b. p. 112°/16 mm., giving an *acetate*, a colourless oil, b. p. 125—127°/16 mm.

The hydroxy-ketones described are practically odourless, but the unsaturated ketones have powerful, characteristic odours.

W. S. N.



**The Purity of  $\alpha\gamma$ -Dichlorohydrin Prepared by the Action of Hydrogen Chloride on Glycerol.** J. B. CONANT and O. R. QUAYLE (*J. Amer. Chem. Soc.*, 1923, **45**, 2771—2772).—It is shown that  $\alpha\gamma$ -dichlorohydrin prepared as stated contains very little of the isomeric  $\alpha\beta$ -dichlorohydrin. The *p*-nitrobenzoate is prepared from samples boiling over a range of 3° and 7°, respectively. From 5 g. of chlorohydrin, the yields of ester are, respectively, 10.2 g. and 10.0 g., and the m. p. 55—58° and 53—57.5°. The pure ester has m. p. 58—59°. The *p*-nitrobenzoate of  $\alpha\beta$ -dichlorohydrin has m. p. 35.5—37°. A mixture of 90% of the  $\alpha\gamma$ -ester and 10% of the isomeride melts between 26° and 48°. The crude products from the fractions above must contain less than 10% of the  $\alpha\beta$ -ester, and the original fractions must have contained at least 91% and 89% of  $\alpha\gamma$ -dichlorohydrin, respectively. Probably the  $\alpha\beta$ -dichlorohydrin is almost completely absent. W. S. N.

**Crystal Structure and Chemical Constitution of Basic Beryllium Acetate and Propionate.** SIR W. BRAGG and G. T. MORGAN (*Proc. Roy. Soc.*, 1923, [A], **104**, 437—451).—Results obtained by Wyckoff (A., 1922, ii, 573), by W. L. Bragg (A., 1914, ii, 181), and by Clark (A., 1923, ii, 469), supporting Werner's theory of chemical combination and molecular structure based on the conception of co-ordination are briefly referred to. The physical and chemical properties of basic beryllium acetate do not support the formulation of this substance as a molecular compound, but indicate a unitary structure similar to that ascribed to non-ionised organic compounds. The preparation of basic beryllium acetate, m. p. 285—286°, of basic beryllium propionate, m. p. 133—135°, and of basic beryllium acetate-propionate, m. p. 140—142°, is briefly described. These m. p. values are in all cases higher, and in the case of the last two considerably higher (about 15°), than the highest respective values of the melting point recorded for these substances. Particulars of the determination, by X-ray analysis, of the respective crystal structures of basic beryllium acetate and propionate are given. The results support the formulation of the acetate group on a co-ordination basis, and confirm the validity of the structure of basic beryllium acetate suggested by Morgan and others, viz., the oxygen atom is situated at the centre of a tetrahedron, and the four beryllium atoms on the four lines joining the centre to the vertices, whilst the atoms composing an acetate group are disposed so as to be symmetrical about a plane perpendicular to each tetrahedron edge and passing through the opposite edge, i.e., the six acetate groups span the edges of the tetrahedron. The crystal of basic beryllium propionate is, in accordance with anticipation, of lower symmetry, and is probably monoclinic prismatic with the following dimensions of the unit cell: *a*, 16.00 Å.; *b*, 9.76 Å.; *c*, 9.15 Å.;  $\beta$ , 116° 7'. Possibly the molecule of basic beryllium propionate, although approximately centrosymmetrical, has actually no symmetry at all. The crystal of basic beryllium acetate-propionate is not of high symmetry and is possibly analogous in structure to the propionate.

J. S. G. T.

**The Acids in Beeswax.** A. GASCARD and G. DAMOY (*Compt. rend.*, 1923, **177**, 1222—1224; cf. A., 1920, i, 418, 470).—Beeswax was saponified, and so converted into a mixture of acids. The mixture was fractionally crystallised from alcohol, using a method described previously (Gascard, *loc. cit.*). Four, and only four acids were present: *Neocerotic*,  $C_{25}H_{50}O_2$  (m. p.  $77.8^\circ$ ); *cerotic*,  $C_{27}H_{54}O_2$  (m. p.  $82.5^\circ$ ), identical with the acid from Chinese wax (Gascard, *loc. cit.*); *montanic*,  $C_{29}H_{58}O_2$  (m. p.  $86.8^\circ$ ) (cf. Tropsch and Kretzner, A., 1922, i, 317, 804), and *melissic*,  $C_{31}H_{62}O_2$  (m. p.  $90^\circ$ ).  
E. E. T.

**Preparation of Anhydrides of Fatty Acids of Low Molecular Weight.** CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (Brit. Pat. 194719).—Fatty acids of low molecular weight, particularly acetic acid, preferably diluted with inert gases or vapours, are led in rapid current over catalysts, such as the chlorides and sulphates of the alkalis and alkaline earths, boric acid, and borates, preferably mounted on porous carriers, at temperatures of about  $400$ — $700^\circ$ . Yields of from 30—60% of acid anhydride are in this way readily obtained. The gases coming from the reaction chamber must be quickly cooled, and it is of advantage to inject into them liquids which have a cooling effect. Suitable liquids are those which are able to precipitate the water formed, and have a low boiling point, as, for instance, a volatile hydrocarbon. From the crude product pure anhydride may be obtained by adding a solvent, which precipitates most of the water, after which the solution of the anhydride is dried and separated from acid and solvent by fractionation. Propionic and butyric anhydrides may be prepared similarly. It is essential that any catalyst, such as alumina, which tends to promote the formation of ketones or of hydrocarbons should be absent from the reaction chamber.

T. S. W.

**Addition to Compounds with Marked Conjugation. I. Addition of Hydrogen and Bromine to Sorbic Acid and Related Compounds.** K. VON AUWERS and J. HEYNA (*Annalen*, 1923, **434**, 140—165; cf. this vol., i, 44).—The addition of bromine to sorbic acid (ester) and its homologues (prepared from unsaturated aldehydes and  $\alpha$ -halogeno-esters) has been studied by effecting the ozonolysis of the resulting compounds, which are thus shown to be  $\gamma\delta$ -dibromides.

Sorbic acid forms a *p-toluidide*, m. p.  $168$ — $169^\circ$ , and a *p-nitrobenzyl* ester, m. p.  $70$ — $72^\circ$ . Dihydrosorbic acid ( $n_D^{20}$  1.4393,  $d_4^{20}$  0.965) forms an *anilide* (m. p.  $54$ — $56^\circ$ ) and a *p-bromophenacyl ether*, m. p.  $63$ — $65^\circ$ . Sorbic acid dibromide, on ozonolysis, affords  $\alpha\beta$ -dibromobutaldehyde, which at once passes into  $\alpha$ -bromocrotonaldehyde. [The semicarbazone decomposes at  $162^\circ$  (Viguier, A., 1913, i, 444, gives m. p.  $228$ — $230^\circ$ ). The phenylhydrazone has m. p.  $117^\circ$  (Viguier gives  $125^\circ$ ).]

Bromoacetaldehyde is converted by semicarbazide into glyoxal disemicarbazone.  $\alpha$ -Bromopropaldehyde with semicarbazide hydro-

chloride and sodium acetate gives either acetol-semicarbazone (m. p. 195°) or methylglyoxal disemicarbazone (m. p. 256°).

Ethyl sorbate with bromine gives *ethyl γδ-dibromo-Δ<sup>α</sup>-hexenoate*, yellow oil, b. p. 139°/11 mm. (with partial decomposition). The dibromo-ester affords the same products of ozonolysis as are given by the acid.

*Ethyl crotonylidenemalonate*, a yellow oil, b. p. 148—151°/15 mm., gives, with bromine, *ethyl γδ-dibromobutylidenemalonate* (yellow oil), this compound, when treated successively with ozone, etc., and a mixture of semicarbazide hydrochloride and sodium acetate, giving either *ethyl mesoxalate semicarbazone* (m. p. 55—56°), or the compound, 
$$\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} > \text{C} < \begin{matrix} \text{CO}_2\text{Et} \\ \text{CO}_2\text{Na} \end{matrix}$$
 m. p. 242°, the latter also being obtainable from ethyl mesoxalate and the above reagent.

α-Methylsorbic acid has m. p. 100—101° (Jaworsky and Reformatsky, A., 1903, i, 728, give 90—92°), forms an *ethyl ester* (a colourless oil, b. p. 207° or 100°/15 mm.), and on reduction gives α-methyl-Δ<sup>β</sup>-hexenoic acid, b. p. 113·5°/15 mm.,  $d_4^{20}$  0·942,  $n_D^{20}$  1·4395 (the latter giving a p-bromophenacyl ester, m. p. 41—42°, and a dibromide, m. p. 107—108°). α-Methylsorbic acid dibromide, needles, m. p. 114—115°, gives a yellow oily ozonide, which, on decomposition, affords α-bromocrotonaldehyde.

α-Ethylsorbic acid, needles, m. p. 85—86° (Jaworsky and Reformatsky give 75—77°) was obtained by the action of potassium hydrogen sulphate on *ethyl p-hydroxy-α-ethyl-Δ<sup>γ</sup>-hexenoate* (produced by a Reformatsky reaction), gives an *ethyl ester*, b. p. 103—103·5°/13 mm., and on reduction affords α-ethyl-Δ<sup>β</sup>-hexenoic acid, oil, b. p. 118—119°/12 mm.,  $d_4^{20}$  0·928,  $n_D^{20}$  1·4421 (p-bromophenacyl ester has m. p. 34°). The latter acid forms a dibromide, needles, m. p. 118—119°, and on ozonolysis affords a mixture of propionic and butyric acids with the corresponding aldehydes.

α-Ethylsorbic acid with bromine gives *γδ-dibromo-α-ethyl-Δ<sup>α</sup>-hexenoic acid* (needles, m. p. 130·5—131·5°), the latter on ozonolysis being converted into α-bromocrotonaldehyde.

γ-Methylsorbic acid (from the action of potassium hydrogen sulphate, etc., on β-hydroxy-γ-methyl-Δ<sup>γ</sup>-hexenoic ester, b. p. 112—120°/11 mm.), forms needles, m. p. 94—95° (*ethyl ester*, b. p. 98—99°/12 mm.), and on reduction affords γ-methyl-Δ<sup>β</sup>-hexenoic acid, a mobile, colourless oil, m. p. 111° [sic., ? b. p. 111°/12 mm.],  $d_4^{20}$  0·966,  $n_D^{20}$  1·4503. The latter acid, with 2% permanganate solution is converted into acetic acid and methyl ethyl ketone.

βδ-Dimethylsorbic acid, on esterification, gives a mixture of *ethyl ester* (b. p. 87°/9 mm.) and a lactone (cf. Rupe, A., 1909, i, 927), whilst it forms a brown, oily dibromide, and on reduction affords βγ-dimethyl-Δ<sup>β</sup>-hexenoic acid, which has  $n_D^{15}$  1·44800 and  $d_4^{20}$  0·932.

E. E. T.

**Bismuth Oxalates.** E. MOLES and R. PORTILLO (*Anal. Fis. Quím.*, 1923, 21, 401—408).—The preparation by different methods of normal bismuth oxalate,  $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$ , is described. On

heating at 130—150°, 6 mols. of water of crystallisation are lost. The salt thus obtained is red or pink and readily absorbs water, giving the salt with 7 mols. of water. Both salts give by hydrolysis an oxalate having the formula  $[(\text{BiO})\text{HC}_2\text{O}_4]_2 \cdot \text{H}_2\text{O}$ , in which the water molecule is closely combined and is supposed to be attached to two bismuth atoms. G. W. R.

**Salts of Maleic, Fumaric, and *i*-Malic Acids.** J. M. WEISS and C. R. DOWNS (*J. Amer. Chem. Soc.*, 1923, **45**, 2341—2349).—A number of salts of the above-mentioned acids are described, of which some are new, whilst others have properties different from those described in the literature.

Strontium fumarate, dried at 100°, is anhydrous. *Calcium hydrogen fumarate*, air-dried,  $+2\text{H}_2\text{O}$ . Calcium hydrogen *i*-malate, air-dried, is anhydrous. Magnesium *i*-malate is not obtained crystalline. *Cobalt maleate*,  $+11\text{H}_2\text{O}$ ; cobalt fumarate, air-dried,  $+4\text{H}_2\text{O}$ , dried at 100°,  $+2\text{H}_2\text{O}$ . *Cobalt i-malate*,  $+3\text{H}_2\text{O}$ . Nickel fumarate,  $+4\text{H}_2\text{O}$  or  $+5\text{H}_2\text{O}$ ; from concentrated solution,  $+5\text{H}_2\text{O}$ . *Nickel i-malate* is crystalline. *Manganous hydrogen maleate*, air-dried,  $+4.5\text{H}_2\text{O}$ ; *manganous maleate*, dried at 100°,  $+3\text{H}_2\text{O}$ ; manganous fumarate, dried at room temperature, is anhydrous. Zinc fumarate, air-dried,  $+5\text{H}_2\text{O}$ . Ferric maleate, dried at 100°, a nearly black, amorphous mass, is evidently the dihydrate. *Ferric ammonium i-malate* resembles ferric ammonium citrate, but is less stable. Copper fumarate, dried at 100°,  $+2\text{H}_2\text{O}$ ; *copper i-malate*, when air-dried, passes through the trihydrate to the dihydrate, but this result is not certain. *Cadmium fumarate*, dried at 100°, is anhydrous; *cadmium maleate*, air-dried,  $+2\text{H}_2\text{O}$ . A white, hard substance is described as *sodium antimonyl i-malate*. Lead fumarate, dried at 100°, is anhydrous, and so is lead maleate; lead *i-malate* softens at 100° to a dough-like mass, and is apparently the compound  $\text{PbC}_4\text{H}_4\text{O}_5 \cdot \frac{1}{2}\text{H}_2\text{O}$ . *Silver fumarate*, like silver maleate, deflagrates when heated. Other salts have been found to have the properties previously assigned to them. The solubilities in water of 22 salts are given. In general, fumarates are less soluble than the corresponding maleates. W. S. N.

**Preparation of Methylglycuronide by the Oxidation of Methylglucoside.** K. SMOLEŃSKI (*Roczniki Chemji*, 1923, **3**, 153—164).—Glycuronic acid cannot be obtained by the direct oxidation of dextrose because the aldehyde group is the first to be attacked and gluconic acid (and saccharic acid) are produced. It was suggested by Fischer (A., 1891, 677) that glycuronic acid is produced in the animal organism by the oxidation of dextrose in which the aldehyde group is protected and it is now shown that this supposition is justifiable. The oxidation of  $\alpha$ -methylglucoside by means of bromine and sodium carbonate or, better still, hydrogen peroxide with a trace of ferric hydroxide, leads to the formation of methylglycuronide, which is obtained in yields up to 30% and can be isolated in the form of its brucine salt. G. A. R. K.

**Autoxidations. I. Autoxidation of Cysteine and Poisoning by Hydrocyanic Acid.** E. ABDERHALDEN and E. WERTHEIMER (*Pflüger's Archiv*, 1923, **197**, 131—146; from *Chem. Zentr.*, 1923, iii, 463).—The autoxidation of cysteine is closely controlled by the reaction of the medium. An acid reaction depresses oxidation. Rapid oxidation occurs at litmus neutrality, whilst oxidation is appreciable with alkaline reaction. The temperature has an effect, since at 100° the nitroprusside reaction is no longer obtainable. Iron, copper, mercury, and arsenic favour oxidation, whilst lead, nickel, cobalt, uranium, thorium, and cadmium have no effect. Autoxidation is unaffected by light. In continuation of earlier experimental work on the effect of hydrocyanic acid (*Pflüger's Archiv*, 1922, **194**, 147), it was found that organs of animals poisoned by hydrocyanic acid retained the nitroprusside reaction twice as long as organs of normal animals. Potassium cyanide inhibits the autoxidation of cysteine. Alcohols, chloroform, and ethyl ether favour autoxidation. The reverse action, whereby the oxidised products are again reduced, was also studied. The thiol group of cysteine is again reduced by the tissues. It is supposed that in inhibition of autoxidation by hydrocyanic acid, the thio-group of the cysteine is the point of attack, and that cyanogen attached to the labile sulphur group reacts with oxygen. The normal reaction is represented by  $R\cdot SH\cdot R \rightleftharpoons S\cdot S\cdot R$ , whilst in the presence of alcohols the reaction is  $R\cdot SH\cdot R \rightarrow [R\cdot S\cdot S\cdot R]$ , and is irreversible. In the presence of hydrocyanic acid, the reverse reaction follows the course  $R\cdot S\cdot S\cdot R \rightarrow R\cdot SH + SS\cdot R$ .

G. W. R.

**Autoxidations. II. The Transformation of Cysteine into Cystine.** E. ABDERHALDEN and E. WERTHEIMER (*Pflüger's Archiv*, 1923, **198**, 122—127; from *Chem. Zentr.*, 1923, iii, 463; cf. preceding abstract).—The autoxidation of cysteine and also the inhibition of the reaction by hydrocyanic acid can take place in the absence of iron. Oxidation of cysteine is, however, accelerated by the addition of small quantities of ferric chloride solution. In this case, the iron acts simply as a catalyst. This is in contradiction to Warburg's view (*A.*, 1922, i, 190), that iron plays an essential part in the autoxidation of cysteine.

G. W. R.

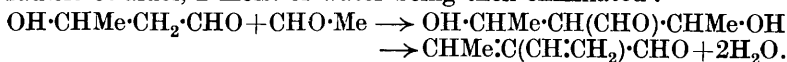
**Autoxidations. III.** E. ABDERHALDEN and E. WERTHEIMER (*Pflüger's Archiv*, 1923, **198**, 415—420; from *Chem. Zentr.*, 1923, iii, 690; cf. preceding abstracts).—In the reactions  $\text{alcohol} \rightleftharpoons \text{aldehyde} \rightleftharpoons \text{acid}$ , the presence of cystine favours the formation of acid whilst cysteine favours the formation of alcohol. The change from cysteine to cystine is more rapid than the reduction of cystine so that an excess of cystine is soon present which reverses the effect of the cystine originally present. The reversible change  $\text{cysteine} \rightleftharpoons \text{cystine}$  has an important effect on oxidations and reductions in cells, and serious disturbances are produced if this balance is destroyed as in dystrophy and hydrocyanic acid poisoning. The equilibrium between  $\beta$ -hydroxybutyric acid and acetoacetic acid is also influenced by the cysteine-cystine system.

G. W. R.

**The so-called Auto-oxidation of Cysteine.** S. SAKUMA (*Biochem. Z.*, 1923, **142**, 68—78).—Cysteine prepared by the reduction of cystine by the Baumann and Friedmann methods, carefully purified by treatment with barium hydroxide and hydrogen sulphide, and recrystallised as the hydrochloride from ethyl or propyl alcohol, using quartz or porcelain vessels in place of glass, is oxidised 100 to 250 times more slowly at a  $p_H$  7.7 than cysteine preparations previously mentioned in the literature. The author's preparation showed  $[\alpha]_D -228^\circ$ . The auto-oxidation of cysteine is therefore ascribed to a catalytic oxidation caused by an impurity (probably metallic) which, in the case of the author's crude preparations, was iron. By the increased rate of oxidation of a highly purified cysteine traces of iron, not detectable by ordinary analytical methods, may be revealed. The inhibition of cysteine oxidation by cyanides is ascribed to their action on the metallic impurity and not on the cysteine itself. Pyrophosphates have a similar inhibiting influence. J. P.

**$\alpha$ -Vinylcrotonaldehyde and, presumably, Sorbic Aldehyde [ $\Delta^{\gamma}$ -Hexadienaldehyde] from Acetaldehyde.** S. ZEISEL and M. NEUWIRTH (*Annalen*, 1923, **433**, 121—138).—Zeisel and von Bittó (A., 1908, i, 761) obtained two doubly-unsaturated, open-chain aldehydes, having b. p. 55—60°/24—26 mm., and 75—80°/24—26 mm., respectively, by the auto-condensation of acetaldehyde by means of sodium acetate. These are now shown to be  $\alpha$ -vinylcrotonaldehyde and  $\Delta^{\gamma}$ -hexadienaldehyde, respectively, by reducing the product of the reaction by means of fine iron wire and 50% acetic acid containing nickel acetate; the reaction is allowed to proceed for four days at the ordinary temperature, but is finally completed at 100°.  $\alpha$ -Ethylbutaldehyde and  $n$ -hexan- $\alpha$ -ol are produced, together with small quantities of normal, unsaturated 6-carbon alcohols. The aldehyde is recognised by oxidation to  $\alpha$ -ethylbutyric acid, by means of cold, aqueous chromic acid solution. The mixture of hexanol and its unsaturated analogue is further reduced by the action of hydrogen in the presence of a nickel catalyst at 175—230°, and  $n$ -hexan- $\alpha$ -ol, b. p. 150—157°, is isolated from the product; it is recognised by oxidising it to  $n$ -hexoic acid by means of boiling, aqueous chromic acid solution.

The formation of  $\Delta^{\gamma}$ -hexadienaldehyde may occur by the condensation of the methyl group of acetaldehyde with the aldehyde radicle of crotonaldehyde, or, conversely, condensation may occur between the methyl group of crotonaldehyde and the aldehyde group of acetaldehyde; either reaction will be followed by the elimination of water. Or aldol, rather than crotonaldehyde, may react with acetaldehyde, 2 mols. of water being subsequently removed. For production of  $\alpha$ -vinylcrotonaldehyde there is, however, only one feasible explanation; condensation takes place between the aldehyde group of acetaldehyde and the methylene radicle of aldol, 2 mols. of water being then eliminated:



W. S. N.

**Hydrogenation of certain Ketones in Presence of Pure or Impure Platinum Black.** M. FAILLEBIN (*Compt. rend.*, 1923, 177, 1118—1120).—It was previously shown (A., 1923, i, 92) that better yields of alcohols were obtained by the hydrogenation of ketones and aldehydes in presence of platinum black containing iron than in presence of pure platinum black. It is now found that ethyl acetoacetate, on hydrogenation using pure platinum black, gives ethyl butyrate, whereas, if the black contains iron, almost pure ethyl  $\beta$ -hydroxybutyrate results. This ester is not hydrogenated in presence of pure platinum, so that the two different results must be due to two distinct processes.

Aluminium gives results similar to those obtained with iron, in the cases of ethyl acetoacetate and benzaldehyde, whilst with  $\delta$ -*p*-methoxyphenyl- $\beta$ -butanone a 50% conversion into alcohol occurs, whereas in the absence of aluminium platinum black gives no alcohol.

Platinum black containing colloidal silica (obtained by adding a solution of sodium silicate in hydrochloric acid to chloroplatinic acid, etc.) allows of the conversion of ethyl acetoacetate into hydroxy-ester, but in the case of most aldehydes and ketones behaves like pure platinum.

The decisive nature of the results obtained with ethyl acetoacetate could be attributed to the production and reduction of the enolic form of the ester. On the other hand, the pure enolic form could not be hydrogenated, using pure platinum black, to give the hydroxy-ester, although it was shown that the catalyst does not convert the enolic into the ketonic form. Similarly, the use of solvents in which the ester is known to exist mainly as enol led to no better results.

With acetylacetone (which contains 80% of the enolic form), the iron-platinum catalyst gave a mixture of the ketone-alcohol and the dihydroxy-compound, whereas, with a platinum catalyst, methyl *n*-propyl ketone and *n*-pentane were obtained. The effects described may be due to the formation of complex iron or aluminium compounds with enolic forms, but iron and aluminium acetylacetonates and the copper derivative of ethyl acetoacetate are not hydrogenated using pure platinum black. Again, the metal hydroxides may stabilise the enolic form (cf. also, Carothers and Adam, A., 1923, ii, 310).  
E. E. T.

**Galactose Sulphuric Acid.** S. AKAMATSU (*Biochem. Z.*, 1923, 142, 181—183).—By the action of chlorosulphonic acid in chloroform on dry galactose a pasty product was obtained, which, when treated with ice-cold barium hydroxide solution and repeatedly precipitated from aqueous solution by the addition of alcohol, yielded *barium galactose tetrasulphate*,  $C_6H_8O_6(SO_3)_4Ba_2 \cdot 3H_2O$ , as a colourless powder, readily soluble in water, and capable of reducing boiling Fehling's solution. The barium salt was not fermented by yeast or by sulphatase (A., 1923, i, 1148). It began to decompose at 60°. By the action of potassium carbonate solution it was converted to the normal *potassium* salt,  $C_6H_8O_6(SO_3)_4K_4$ , which gave

no precipitate with barium chloride, decomposed at  $200^{\circ}$ , and had  $[\alpha]_D^{20} +41.7^{\circ}$  ( $c=2.443$ ). J. P.

**Position of the Point of Pseudo-transition of Dextrose :**  $S_{aq} \rightleftharpoons S^a + L$  (in Internal Equilibrium). J. GILLIS (*Rec. trav. chim.*, 1923, **42**, 1077—1079).—The author, using figures obtained by Jackson and Silsbee (A., 1922, i, 986) for the solubility of dextrose in water, has plotted the reciprocal of the temperature against  $\log x$ , where  $x = gM^{-1}/(gM^{-1} + 100M_1^{-1})$ ,  $M$  and  $M_1$  being the mol. weights of dextrose and water, respectively, and  $g$  the weight of anhydrous dextrose contained in 100 g. of water at different temperatures. The curve so obtained, however, does not permit of the determination of the temperature of pseudo-transition, as it might be expected to. The author thinks that this temperature is slightly higher than  $50^{\circ}$ , the experimental figure of Jackson and Silsbee. E. E. T.

**The Preparation of Diisopropylidene Glucose.** P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1923, **57**, 317—318).—Using Fischer and Rund's method (A., 1916, i, 363), diisopropylidene glucose may be prepared from dextrose ( $\alpha$ -glucose) and commercial acetone, although the yields are smaller than when  $\beta$ -glucose and dry acetone are employed. An economy of time is effected by using the former method. E. S.

**Benzylidene isoPropylidene Glucose.** P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1923, **57**, 319—322).—When benzylidene isopropylidene glucose is methylated with methyl sulphate and sodium hydroxide, and the product so obtained is hydrolysed with hydrochloric acid, a methyl glucose, m. p.  $156-157^{\circ}$ ,  $[\alpha]_D^{20} +103^{\circ}$  (initial),  $+57^{\circ}$  (final) (in water), is obtained. Oxidation of the methyl glucose with nitric acid yields a methyl saccharolactone. In both cases, the products are identical with those obtained from diisopropylidene glucose (A., 1923, i, 92). Further, benzylation of benzylidene isopropylidene glucose yields a benzoyl isopropylidene glucose identical with that obtained from diisopropylidene glucose. It is concluded that benzylidene isopropylidene glucose and diisopropylidene glucose have analogous structures and that accordingly the former is  $\epsilon\zeta$ -benzylidene  $\alpha\beta$ -isopropylidene glucose. E. S.

**The Allyl Ethers of Various Carbohydrates.** C. G. TOMECKO and R. ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 2698—2701).—Various carbohydrates are treated with allyl bromide in the presence of 10% sodium hydroxide solution; the following allyl ethers are obtained.  *$\alpha$ -Methyltetra-allylglucoside*, a thick, colourless oil, b. p.  $182^{\circ}/1.5$  mm.,  $n_D^{20}$  1.4836,  $d_{20}^{20}$  1.1519,  $[\alpha]_D^{20} +116.5^{\circ}$  (in alcohol). *Penta-allyl sucrose*, a thick, almost colourless oil. *Allyl dextrin*, *allyl inulin*, *allyl potato starch*, and *allyl maize starch* are white amorphous solids, which, when heated, behave respectively as follows: shrinks at  $155-165^{\circ}$  and gradually decomposes at about  $240-250^{\circ}$ ; shrinks at  $150-155^{\circ}$  and decomposes at  $205-210^{\circ}$ ; shrinks at  $160-165^{\circ}$  and decomposes without melting at  $260-$



270°; and becomes brown at 250—265°, but does not shrink or melt. *Allylated cellulose* has been prepared. W. S. N.

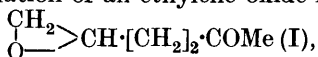
**Some Glucosides and Galactosides of Thiols.** E. POTEL (*Bull. Soc. chim.*, 1923, **33**, [iv], 1459—1465).—The method of preparation in each case consisted in condensation of the sugar with the thiol by means of hydrochloric acid in concentrated solution. The following are described: glucose *n*-propyl mercaptal (cf. Schneider, Sepp, and Stiehler, A., 1918, i, 252); *galactose n-propyl mercaptal*, long, white needles, m. p. 130—131°; *glucose n-butyl mercaptal*, white needles, m. p. 124—125°, slight decomp. at the ordinary temperature; *galactose n-butyl mercaptal*, white needles, m. p. 122—123°; *glucose n-heptyl mercaptal*, a white, crystalline powder, m. p. 116—118°; *galactose n-heptyl mercaptal*, pearly crystals, m. p. 113—115°. The condensation appears to become more difficult with increasing number of carbon atoms in the thiol employed. Galactose combines more readily than glucose. All the above substances are hydrolysed on heating with dilute acids, regenerating thiol and hexose. H. J. E.

**Preparation of  $\alpha$ -Mannose.** P. A. LEVENE (*J. Biol. Chem.*, 1923, **57**, 329—336).— $\alpha$ -Mannose, m. p. (decomp.) 205° after becoming a semi-solid mass at 133° (corr.),  $[\alpha]_D^{20} +30^\circ$  (in water),  $+35^\circ$  (in 80% alcohol), has been prepared from  $\beta$ -mannose, (a) by dissolving in pyridine and precipitating with alcohol, (b) by dissolving in hot water and precipitating with glacial acetic acid at 0°, and (c) by dissolving in concentrated ammonia and precipitating with ether after the addition of alcohol. The first two methods are those used for the preparation of  $\beta$ -glucose and  $\beta$ -galactose; the third method also forms a convenient method for the preparation of these substances. Mannose thus crystallises in the  $\alpha$ -form under conditions in which  $\beta$ -glucose and  $\beta$ -galactose appear. The specific rotation of  $\alpha$ -mannose agrees with that calculated by Hudson and Yanovsky (A., 1917, i, 445), but the sum of the constants  $k_1 + k_2$  in the equation of Hudson (A., 1904, i, 974) and of Lowry (T., 1904, **85**, 1551) has a different value when measured on the  $\alpha$ -form than when obtained from the  $\beta$ -isomeride. It is thus possible that the  $\alpha$ -isomeride contains a third form of mannose. E. S.

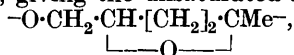
**Action of Chloral on Cellulose.** J. H. ROSS and J. M. PAYNE (*J. Amer. Chem. Soc.*, 1923, **45**, 2363—2366).—When cotton cellulose is treated with chloral hydrate in the presence of an excess of cold, concentrated sulphuric acid, chloral-substituted celluloses or cellulose dextrans are not obtained. Instead, four substances are formed. (a) Triangular or hexagonal plates, m. p. 268° (*monoacetate*, m. p. 198°,  $[\alpha]_D -12^\circ$  in chloroform solution, *methyl ether*, ciliate needles, m. p. about 200°,  $[\alpha]_D -17^\circ$  in acetone-pyridine solution), which is laevorotatory and is evidently identical with Pictet and Reichel's *isodichloralglucose-A* (A., 1923, i, 755). (b) Needles, m. p. 225°,  $[\alpha]_D -15^\circ$  in chloroform solution (*acetate*, thick, rectangular crystals, m. p. 126°,  $[\alpha]_D -21.4^\circ$  in chloroform solution, very soluble *methyl ether*, m. p. about 110°,  $[\alpha]_D -23^\circ$  in

chloroform solution), which is apparently identical with Meunier's dichloralglucose (A., 1896, i, 334). (c) Long needles, m. p. 135—136°,  $[\alpha]_D + 32^\circ$  in benzene,  $+10.5^\circ$  in chloroform solution. (d) A syrup solidifying on cooling, m. p. about 74—75°,  $[\alpha]_D + 14^\circ$  in chloroform solution, which seems to contain some of (b). The substances (c) and (d) are evidently dichloralglucoses; they do not give crystalline acetates or methyl ethers. The same four substances are produced in a similar manner from hydrocellulose, starch, or glucose. In addition to the compounds (a), (b), (c), and (d), parachloralose is formed in every case. Since it is claimed by previous workers (Pictet and Reichel, *loc. cit.*) that this substance is produced by the  $\alpha$ -anhydroglucosidic linking of *d*-glucosan, but not by the  $\beta$ -anhydroglucosidic linking of *l*-glucosan, its formation from cellulose may indicate the presence of one or more  $\alpha$ -linkings in the cellulose molecule. W. S. N.

**Cellulose Chemistry. IV. Properties of  $\gamma\delta$ -Dihydroxycarbonyl Derivatives and their Bearing on the Polymerisation of Polysaccharides.** H. HIBBERT and J. A. TIMM (*J. Amer. Chem. Soc.*, 1923, **45**, 2433—2439).—Methyl  $\gamma\delta$ -dihydroxybutyl ketone,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot[\text{CH}_2]_2\cdot\text{COMe}$ , b. p. 158—160°/7—8 mm. (Traube and Lehmann, A., 1901, i, 501), undergoes dehydration and resinification when heated at 120—130° in the presence of a trace of concentrated sulphuric acid; analysis of the resin, and the direct weighing of the water evolved, show that 1 mol. of water is evolved for every molecule of hydroxy-ketone. This is not due to the primary formation of an ethylene oxide ring,



and subsequent polymerisation, because the substance (I) is known ( $\gamma$ -ketobutylethylene oxide, Kablukow, A., 1888, 1171), and does not undergo polymerisation under the same conditions, although charring occurs after long heating. The explanation favoured is that the elimination of water takes place from the butylene oxide form of the ketone, giving the unsaturated radicle,



which then undergoes polymerisation to give a substance the structure of which is analogous to that advocated for cellulose (*J. Ind. Eng. Chem.*, 1921, **13**, 256, 334). Experiments are in progress which should show whether the ketone contains the butylene oxide, or the alternative amylene oxide, ring. W. S. N.

**Researches on Pectins.** K. SMOLEŃSKI (*Roczniki Chemji*, 1923, **3**, 86—152).—It has already been shown by the author that the pectin of the sugar-beet contains the glycuronic acid residue (A., 1911, ii, 428), and later (*Proceedings of the 2nd Mendeléev Congress*, 1911, 45) it was suggested that glycuronic acid is the intermediate product in the formation of pentoses from hexoses. The work on these substances has now been extended.

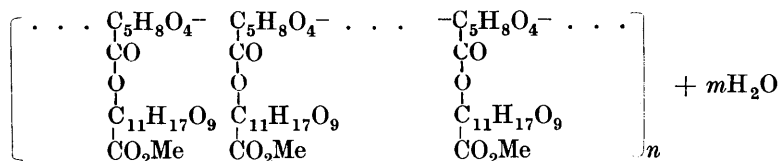
I. [With MME E. SMOLEŃSKA.]—The method of preparation of pectin from sugar-beet residues has been improved. The best

yields are obtained by using dilute mineral acids; the use of alkalis leads to products with a low viscosity in solution, this property being used as a criterion of purity. From the crude material so obtained alcohol precipitates a dry white powder which dissolves in water to give solutions many times more viscous than those of gum arabic; it does not reduce Fehling's solution, gives the naphtha-resorcinol test for glycuronic acid, and a yellow coloration with sodium hydroxide.

The action of 1% sulphuric acid on the purified pectin (previously treated with sodium hydroxide) at 125–130° in an autoclave leads to glycuronic acid which reduces Fehling's solution and gives the naphtha-resorcinol reaction.

II. [With MME A. KOMORNICKA and W. STYPIŃSKI.]—The crude pectin from sugar-beet residues can be divided into two substances by adding alcohol to its aqueous solution; about 60% of the material is insoluble in 75% alcohol. The insoluble portion, or "purified pectin," is found to contain *D*-galacturonic acid in considerable amount, whilst the alcohol-soluble portion is a polysaccharide consisting almost entirely of *L*-arabinose residues; this "araban" is levorotatory and readily undergoes hydrolysis, after which the sign of rotation changes. It is suggested that the original pectin of the sugar-beet is insoluble in water and passes into solution as the result of hydrolysis; this process proceeds rapidly in the presence of 1/200*N*-mineral acid.

The hydrolysis of purified pectin by means of a slight excess of alkali was studied and was found to be complete after two to three hours at 20° or a few minutes at 75°. Methyl alcohol was found in the hydrolysis product (cf. Fellenberg, A., 1917, i, 616; 1918, i, 215). From a consideration of these and other authors' data a possible constitutional formula is suggested:

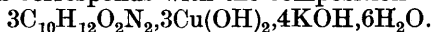


in which galacturonic acid is combined by means of its carboxyl group with the methyl ester of galacto-galacturonic acid. In the original insoluble pectin pentoxide, complexes are also present, in addition to which the existence of gluco-glycuronic complexes is probable. These and the galacto-galacturonic complexes probably form transition stages between hexoside and pentoside complexes; these substances are presumably oxidation products of hexosans such as the starches.

G. A. R. K.

**The Biuret Reaction.** L. HOUGOUNENQ, G. FLORENCE, and E. COUTURE (*Bull. Soc. Chim. biol.*, 1923, 5, 717–721).—On heating in a sealed tube at 180° acetyl glycine and aniline, there was obtained a mixture of acetylglycylanilide, m. p. 196°, and acetyldiglycylanilide, m. p. 246°. The latter gives the ordinary biuret reaction; the

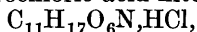
former an emerald-green colour. The green compound was isolated and its analysis corresponds with the composition



Benzoylglycylanilide was the only other compound found to give a green colour with copper sulphate and potassium hydroxide.

C. R. H.

**Reactions of Peptide-like Compounds. II. Derivatives of  $\gamma$ -Amino- $\beta$ -hydroxybutyric Acid.** M. BERGMANN, E. BRAND, and F. WEINMANN (*Z. physiol. Chem.*, 1923, **131**, 1—17).—Potassium cyanide reacts with  $\gamma$ -benzamido- $\beta$ -hydroxypropyl chloride to form  $\gamma$ -benzamido- $\beta$ -hydroxybutyronitrile, long, crossed plates, m. p. 128—129° (corr.). Treatment of this cyanide with alcoholic hydrogen chloride results in the formation of the *imino-ether hydrochloride*, a colourless, crystalline powder, which is readily hydrolysed to *ethyl  $\gamma$ -benzamido- $\beta$ -hydroxybutyrate*, m. p. 99—100°, and from this,  *$\gamma$ -benzamido- $\beta$ -hydroxybutyric acid*, fine needles, m. p. 176—177° (corr.), is easily obtained. By the action of thionyl chloride ring formation occurs, and when the acid chloride m. p. 117—118° (corr. decomp.) formed is decomposed by water, it yields the free acid *2-phenyloxazoline-5-acetic acid*, m. p. 140—141° [*hydrochloride*, m. p. 179° (decomp.)]. The hydrochloride of the cyclic oxazoline compound, when allowed to remain for two hours in aqueous solution, is converted into  *$\gamma$ -amino- $\beta$ -benzoxybutyric acid* [*hydrochloride*, needles, m. p. 215° (decomp.)]. In a similar way, thionyl chloride converts ethyl  $\gamma$ -benzamido- $\beta$ -hydroxybutyrate into *ethyl 2-phenyloxazoline-5-acetate*, a thick oil, b. p. 180°/1.5 mm.,  $n_D^{19.9}$  1.5283 (*hydrochloride*, needles, m. p. 118—119° corr.), whilst this compound is converted by the action of 2*N*-hydrochloric acid into a *compound*,



fine, filamentous, white needles, m. p. 205°, which on treatment with alkali forms a *compound*, m. p. 175°, which is free from chlorine.

From the imino-hydrochloride mentioned above,  *$\gamma$ -benzamido- $\beta$ -hydroxybutyramide*,  $\text{C}_{11}\text{H}_{14}\text{O}_3\text{N}_2 \cdot \text{H}_2\text{O}$ , is obtained by heating at 130° under a pressure of 10 mm. It crystallises from water in the form of prisms, m. p. 130°. This amide on treatment with thionyl chloride forms *2-phenyloxazoline-5-acetamide*, 4—6-sided plates, m. p. 168° (corr.) (*picrate*, citron-yellow crystals, m. p. 156—157° corr.). In acid solution, one nitrogen atom is eliminated from this oxazoline compound, and a strongly reducing substance is formed. The amide may also be conveniently prepared by the action of ammonia on the acid chloride formed from  $\gamma$ -benzamido- $\beta$ -hydroxybutyric acid.  $\gamma$ -Amino- $\beta$ -hydroxybutyric acid is obtained by hydrolysing ethyl  $\gamma$ -benzamido- $\beta$ -hydroxybutyrate with hydrobromic acid (48%), and may be isolated as the *hydrobromide*,  $\text{C}_8\text{H}_9\text{O}_3\text{N} \cdot \text{HBr}$ , long needles, m. p. 78°, whilst the free acid, m. p. 218°, is obtained if the hydrolysis is carried out with sulphuric acid, and the sulphuric acid is removed as barium sulphate. When the acid is heated with zinc dust, the fumes give an intense pyrrole reaction with a pine shaving.  $\gamma$ -Amino- $\beta$ -hydroxybutyric acid has been previously described by Tomita (*A.*, 1923, i, 190).

W. O. K.

**Formaldehyde Compounds of Simple Amino-acids.** M. BERGMANN, M. JACOBSON, and H. SCHOTTE (*Z. physiol. Chem.*, 1923, **131**, 18—28).—By the action of a strong solution of formaldehyde on ethyl glycollate hydrochloride, and subsequent liberation of the base with alkali, a *triformaldehyde-glycine* ester,  $C_3H_6O_2 \cdot N \cdot CH_2 \cdot CO_2Et$ , is obtained. It is a colourless liquid which may be distilled under 1 mm. pressure from a bath at 98—100°. It loses formaldehyde easily on boiling with water, and particularly easily on treatment with acid or alkali. Treatment with barium hydroxide solution results in the formation of the *barium* salt of *methyleneglycine*,  $(CH_2 \cdot N \cdot CH_2 \cdot CO_2)_2Ba \cdot 5H_2O$ , colourless needles or prisms. This compound may also be produced by the action of formaldehyde on glycine in presence of baryta. Treatment of triformaldehydeglycine ester with ammonia yields *triformaldehydeglycinamide*,  $C_3H_6O_2 \cdot N \cdot CH_2 \cdot CO \cdot NH_2$ , glistening leaflets, m. p. 140°. Triformaldehyde- $\gamma$ -amino- $\alpha\beta$ -dihydroxypropane is obtained by the action of formaldehyde on  $\gamma$ -amino- $\alpha\beta$ -dihydroxypropane, and is a syrup, b. p. 120—150°/0.3 mm.; with picric acid, this compound loses formaldehyde and forms a *picrate*,  $C_{10}H_{12}O_9N_4$ , flat, yellow, microscopic needles, m. p. 143—144°, and similarly with oxalic acid an *oxalate* is formed. The hydrochloride of the ethyl ester of serine forms a similar triformaldehyde compound,  $C_9H_{17}O_5N$ , an oil, b. p. 76—78°/0.7 mm.

W. O. K.

**Epichitosamine Penta-acetate.** P. A. LEVENE (*J. Biol. Chem.*, 1923, **57**, 323—327).—Some anomalies are pointed out in connexion with the conclusion of Irvine and Earl (T., 1922, **121**, 2370) that chitosamine has the configuration of dextrose. On the basis of this conclusion, epichitosamine (A., 1919, i, 475) should have the configuration of mannose. On the other hand, from the fact that epichitose is  $\beta$ - $\epsilon$ -anhydrodextrose it would appear that epichitosamine had the configuration of dextrose. Further, when the rotation of the  $\beta$ -carbon atom in the epimeric amino-sugars is calculated from their molecular rotations, it is found to rotate to the left in epichitosamine and to the right in chitosamine; in the corresponding acids, however, the direction of the rotation of the same carbon atom is reversed. This is apparently due to differences produced in the structure of the  $\alpha$ -carbon atom by oxidation.

$\beta$ -*Epichitosamine penta-acetate*,  $C_6H_8O_5N(CH_3 \cdot CO)_5$ , long needles, m. p. 158—159° (corr.),  $[\alpha]_D^{20} - 18^\circ$  (in chloroform), has been prepared by treating epichitosamine hydrochloride with acetic anhydride and pyridine. When heated with zinc chloride in acetic anhydride solution, it is converted into the  $\alpha$ -isomeride. E. S.

**The Two Isomeric Chondrosamine Hydrochlorides and the Rates of their Mutarotation.** P. A. LEVENE (*J. Biol. Chem.*, 1923, **57**, 337—340).—The two isomeric chondrosamine hydrochlorides have been prepared. The  $\beta$ -form had  $[\alpha]_D^{20} + 47^\circ$ , although the extrapolated value obtained from the rate of mutarotation was  $[\alpha]_D^{20} + 44.5^\circ$ ; the  $\alpha$ -form had  $[\alpha]_D^{20} + 121^\circ$ . The difference between

the molecular rotations of the two forms is 16,485 and is thus practically the same as the usual value for other sugars. E. S.

**The Iron-Cyanogen Compounds.** M. KOHN and L. BENCZER (*Monatsh.*, 1923, 44, 97—102).—The solubility of Prussian blue in solutions of the alkali metal oxalates (Kohn, A., 1923, i, 312) is due to the formation of the alkali metal ferrocyanide and the double ferric oxalate, in accordance with the equation  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 8\text{K}_2\text{C}_2\text{O}_4 = 3\text{K}_4\text{Fe}(\text{CN})_6 + 4\text{KFe}(\text{C}_2\text{O}_4)_2$ . Most of the Prussian blue separates again slowly after acidification. Turnbull's blue is also soluble in the normal oxalates, forming potassium ferricyanide and potassium ferrous oxalate, which react to form the ferrocyanide and the double ferric oxalate; addition of acid to the solution precipitates Prussian blue. Ferrous ferrocyanide, obtained as a white precipitate by the addition of ferrous sulphate to potassium ferrocyanide, or to the solution of Prussian blue in the alkali oxalates, dissolves slowly in the oxalate solution with atmospheric oxidation. S. I. L.

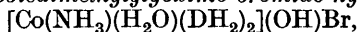
**Reaction between Magnesium and Calcium Salts and Rubidium and Cæsium Salts.** E. MURMANN (*Oesterr. Chem. Ztg.*, 1923, 26, 140—141).—When a very dilute solution containing calcium chloride and potassium ferrocyanide is heated at 50° and mixed with a dilute solution of a rubidium or cæsium salt, a precipitate forms which may be collected and washed with 60% alcohol until free from chlorides. In the case of calcium and cæsium, the precipitate, after being dried at the ordinary temperature, has a composition corresponding approximately with the formula  $\text{Cs}_4\text{Ca}_2\text{Fe}_2(\text{CN})_{12}\cdot\text{H}_2\text{O}$ . Similar compounds are formed when magnesium chloride is used in place of calcium chloride and potassium ferricyanide in place of potassium ferrocyanide. W. P. S.

**Complex Compounds of Cobalt with Dimethylglyoxime.** F. FEIGL and H. RUBINSTEIN (*Annalen*, 1923, 433, 183—190).—Experiments have been made to determine the constitution of the brown compound (Tschugaev, A., 1905, i, 743) formed by the action of dimethylglyoxime on a solution containing cobalt-ions.

The action of dimethylglyoxime on cobaltous chloride in hot, concentrated aqueous-alcoholic solution, or, better, in boiling acetone solution, gives *cobaltobisdimethylglyoxime chloride*,



( $\text{DH}_2$ =dimethylglyoxime), green crystals. This compound is converted by means of fuming hydrobromic acid in alcoholic solution into *cobaltobisdimethylglyoxime bromide*, green crystals. Both the chloride and the bromide have an intensely sweet taste. The bromide undergoes hydrolysis when boiled with water, giving *cobaltobisdimethylglyoxime bromide hydroxide*,  $[\text{Co}(\text{DH}_2)_2](\text{OH})\text{Br}$ , yellowish-brown crystals; the reverse reaction is brought about by the action of concentrated hydrobromic acid. The bromide is converted by the action of aqueous-alcoholic ammonia into *cobaltoaquaoamminobisdimethylglyoxime bromide hydroxide*,



yellowish-brown crystals (blackish-brown, crystalline *periodide*).

The action of dimethylglyoxime on Naumann's compound,  $\text{CoCl}_2 \cdot 2\text{NH}_3$ , in warm acetone solution gives *diamminocobaltobisdimethylglyoxime chloride*,  $[\text{Co}(\text{NH}_3)_2(\text{DH}_2)_2]\text{Cl}_2$ , yellow crystals, together with the compound  $[\text{Co}(\text{DH}_2)_2]\text{Cl}_2$ . Evidently, besides the simple addition of two glyoxime molecules to the complex  $\text{CoCl}_2 \cdot 2\text{NH}_3$ , substitution of the two  $\text{NH}_3$  molecules by one glyoxime molecule, followed by addition of a second oxime molecule, also occurs. This process takes place exclusively when dimethylglyoxime reacts in boiling acetone solution with the compound  $\text{CoCl}_2 \cdot 2\text{NH}_2 \cdot \text{OH}$  (Feldt, A., 1894, ii, 187), the sole product being the compound  $[\text{Co}(\text{NH}_2)_2]\text{Cl}_2$ . The prolonged action of dimethylglyoxime, in boiling solution, on the compound  $\text{CoCl}_2 \cdot 2\text{NH}_3$  leads to the formation of an insoluble, glistening, crystalline, ruby-red compound of unknown constitution. When cobaltous hydroxide and dimethylglyoxime are boiled in alcoholic solution, a brown solution is obtained from which a black compound, possibly cobaltibisdimethylglyoxime hydroxide,  $\text{Co}(\text{OH})_3 \cdot 2\text{DH}_2$ , is isolated.

The action of ammonia on the bromide (above) causes, therefore, an increase from four to six in the co-ordination number of the cobalt atom, which, however, remains bivalent. Tschugaev, on the other hand, obtained complexes containing trivalent cobalt, by the use of strongly basic substances (A., 1906, i, 814). In the experiments described above, however, ammonia is allowed to react with a substance already containing bivalent cobalt, whereas, in Tschugaev's experiments, dimethylglyoxime was caused to react with cobaltammine complexes in which a trivalent cobalt atom was already present. The formation of an additive compound from dimethylglyoxime and the compound  $\text{CoCl}_2 \cdot 2\text{NH}_3$ , whilst with the compound  $\text{CoCl}_2 \cdot 2\text{NH}_2 \cdot \text{OH}$  the simple chloride,  $[\text{Co}(\text{DH}_2)_2]\text{Cl}_2$ , is formed, certainly proves that the cobalt atom is bivalent in the simpler compounds described. W. S. N.

**The Constitution of the so-called  $\beta$ -Dimethylisothiohydantoin.** W. WÜDICH (*Monatsh.*, 1923, **44**, 83–90).—The constitution of the substance obtained by Andreasch (A., 1888, 47) by the action of methyl iodide on the silver compound of isothiohydantoin has been further examined. The silver compound contains two atoms of silver in the molecule, but is too unstable for analysis, decomposing even on long washing. The yield of the dimethyl compound is poor, amounting only to 11% of the theoretical; it has m. p.  $174^\circ$  (not  $114^\circ$  as given by Andreasch), and the formula is not  $\text{C}_5\text{H}_5\text{ON}_2\text{S}$ , but  $\text{C}_5\text{H}_{10}\text{O}_2\text{N}_2\text{S}$ .

By heating with hydrochloric acid in a sealed tube at  $150^\circ$ , and neutralising the product with barium hydroxide, barium methylthiolacetate  $(\text{SMe} \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{Ba}$ , was obtained. The formation of the dimethyl compound is therefore accompanied by disruption of the thiazole ring,  $\text{S} \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{NH}) \end{smallmatrix} \text{NH} \rightarrow \text{SMe} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{OMe}$ , and the silver compound must have the formula  $\text{SAg} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{OAg}$ . This constitution of the dimethyl compound, namely, methyl-

thiolacetyl $\alpha$ -methylcarbamide, was confirmed by Kirpal and Bühn's modification of Zeisel's method for the estimation of methoxyl groups (A., 1914, ii, 497), it being established by a blank determination with synthetic barium methylthiolacetate that the group  $\text{SMe}\cdot$  does not yield methyl iodide under these conditions.

The corresponding *ethyl* compound,  $\text{C}_7\text{H}_{14}\text{O}_2\text{N}_2\text{S}$ , white needles, m. p.  $156^\circ$ , and benzyl compound,  $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_2\text{S}$ , m. p.  $183^\circ$ , were prepared.

By treatment of isothiohydantoin in aqueous solution with ammoniacal lead acetate, a lead salt,  $\text{C}_3\text{H}_4\text{O}_2\text{N}_2\text{SPb}$ , was obtained, thus confirming the formula suggested for the silver compound.

S. I. L.

### Preparation and Detonating Qualities of Cyanuric Triazide.

C. A. TAYLOR and W. H. RINKENBACH (*U.S. Bur. Mines, Repts. Investigations*, 1923, No. 2513).—Cyanuric triazide,  $(\text{CN})_3\text{N}_9$ , white crystals, m. p.  $94^\circ$ , was prepared in 90% yield by the action of an aqueous solution of sodium azide on cyanuric chloride (prepared in 95% yield by James's method); the substance detonates when heated quickly. Small crystals are more sensitive to impact and friction than mercury fulminate; large crystals detonate when broken. In the molten state it is very sensitive to friction. It is non-irritating to the skin, and is non-poisonous in fairly large doses to rats and guinea-pigs, but the materials used in its preparation are irritating and poisonous. CHEMICAL ABSTRACTS.

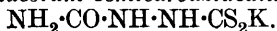
**Ring Closure with Hydrazinedicarbonamides containing Sulphur. IV. The Mechanism of Intramolecular Displacement.** F. ARNDT and F. BIELICH (*Ber.*, 1923, 56, [B], 2276—2283; cf. A., 1921, i, 813; 1922, i, 375; 1923, i, 611).—The author has previously expressed the view that, in the formation of cyclic compounds from hydrazinedicarbonamides containing sulphur, the most basic product (thiodiazole) is formed in an acid medium, whereas the most acidic product (triazole) is produced in the presence of bases. This rule is now found to require modification. The whole investigation points to the conclusion that intramolecular displacements are the result of two reactions consisting of first an elimination (of hydrogen sulphide, mercaptan, ammonia, or aniline) and subsequently a ring closure and that the former is the primary process which controls the direction of the latter. The elimination may occur in two ways. If it can be conceived as occurring solely on one side of the molecule, and without closure of the ring, it yields compounds in which a cyanamide, carbimide, or thio-carbimide group is formed from a hydrazo-nitrogen atom. Since such strongly unsaturated hydrazides have never been isolated, it must be assumed that their tendency towards transformation is so marked that the equilibrium between them and the eliminated molecule on the one hand, and the original material on the other, remains strongly displaced in favour of the latter. It is, however, permanently disturbed when a group attached to a carbon atom at the other side of the molecule can



add itself at the unsaturated group whereby elimination is completed with closure of the ring. The second case is that in which the eliminated molecule can be produced only by simultaneous co-operation of groups attached at the ends of the molecule, so that elimination and ring closure are intimately associated. Elimination of mercaptan then occurs much less readily than in the first case, and is only possible under exceptionally favourable conditions, such as the acidity of the eliminated hydrogen atom.

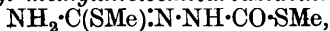
In general, it is found that an acid medium favours the loss of ammonia or amine, whereas elimination of hydrogen sulphide or, particularly, of mercaptan occurs more readily in the presence of alkali. The groups,  $\text{NH}_2$ ,  $\text{NHR}$ ,  $\text{SH}$ , or  $\text{SR}$ , are most readily removed when attached to  $\text{CO}$ , with more difficulty when united to  $\text{C}(\text{:NH})\text{-SR}$ , and with most difficulty from the group  $\text{CS}$ . Since the different factors overlap in the action, elimination frequently occurs in several directions, but each mode of loss in one and the same medium leads to only one ring closure.

The following substances are described. Potassium thiosemicarbazidedithiocarbonate,  $\text{NH}_2\text{CS}\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}_2\text{K}$ , coarse, colourless crystals and the *di-silver* salt,  $\text{C}_2\text{H}_3\text{N}_3\text{S}_3\text{Ag}_2$ . *Methylthiosemicarbazidedithiocarbonate*, small, colourless crystals, m. p.  $153^\circ$ , and the corresponding dimethyl compound,  $\text{NH}_2\text{CS}\cdot\text{NH}\cdot\text{N}\cdot\text{C}(\text{SMe})_2$ , small crystals, m. p.  $106^\circ$  (Busch and Biehler, A., 1916, i, 760, give m. p.  $101\text{--}102^\circ$ ). *Methyl methylthiolsemicarbazidodithiocarbonate*,  $\text{NH}_2\text{C}(\text{SMe})\text{:N}\cdot\text{NH}\cdot\text{CS}_2\text{Me}$ , from thiosemicarbazide-*S*-methyl ether and methyl chlorodithioformate, a crystalline powder, m. p.  $133\text{--}135^\circ$  when heated rapidly, and the corresponding trimethyl compound,  $\text{NH}_2\text{C}(\text{SMe})\text{:N}\cdot\text{N}\cdot\text{C}(\text{SMe})_2$ , m. p.  $58\text{--}59^\circ$  (Busch, *loc. cit.*, gives m. p.  $60^\circ$ ). *Potassium semicarbazidedithiocarbonate*,



*Methyl semicarbazidedithiocarbonate*, m. p.  $193\text{--}194^\circ$  (Busch, *loc. cit.*, gives m. p.  $191\text{--}192^\circ$ ), which is converted by ferric chloride in acid solution into *thiourazole disulphide*,  $\text{C}_3\text{H}_7\text{ON}_3\text{S}_2$ , m. p.  $246^\circ$ , and by heating above its melting point into the com-

ound,  $\text{N:C}(\text{SMe})\text{NH}\text{--CO}\text{>S}$ , small prisms, m. p.  $96^\circ$ . *Dimethyl semicarbazidodithiocarbonate*,  $\text{NH}_2\text{CO}\cdot\text{NH}\cdot\text{N:C}(\text{SMe})_2$ , coarse leaflets, m. p.  $124^\circ$ . *Methyl methylthiolsemicarbazidodithiocarbonate*,



m. p.  $128^\circ$  (decomp.), and the corresponding *trimethyl* compound,  $\text{NH}_2\text{C}(\text{SMe})\text{:N}\cdot\text{NMe}\cdot\text{CO}\cdot\text{SMe}$ , m. p.  $185^\circ$  (decomp.); the latter substance is transformed by sodium hydroxide solution into *N-methylthiourazole methyl ether*, small needles, m. p.  $204^\circ$ .

H. W.

**The Yields of some Grignard Reagents.** H. GILMAN and R. McCracken (*J. Amer. Chem. Soc.*, 1923, 45, 2462—2466).—Using essentially the method of preparation (A., 1923, i, 193) which gives the best yield of magnesium ethyl iodide, and the method of analysis previously employed (A., 1923, ii, 272), the following yields are obtained of Grignard reagent from the halide mentioned.

*n*-Propyl iodide, 79·35, *n*-butyl iodide, 65·23, *n*-amyl iodide, 75·76, *n*-hexyl iodide, 59·50, *n*-heptyl iodide, 64·27, *n*-octyl iodide, 44·22, lauryl bromide, 73·70, *n*-butyl bromide, 91·23, *isobutyl* bromide, 78·23, *sec.*-butyl bromide, 68·26, *tert.*-butyl bromide, 20·62, *n*-butyl chloride, 87·38, bromobenzene, 94·37, iodobenzene, 84·58, *o*-bromotoluene, 86·65, *m*-bromotoluene, 84·75, *p*-bromotoluene, 88·16, benzyl chloride, 94·28,  $\alpha$ -bromonaphthalene, 70·50, bromocyclohexane, 68·32,  $\beta$ -bromostyrene, 47·59% of theory. W. S. N.

**Organo-zinc Compounds.** A. JOB and R. REICH (*Bull. Soc. chim.*, 1923, **33**, [iv], 1414—1433; cf. A., 1922, i, 645).—Details are given of the preparation of zinc ethyl iodide in ethereal solution and in ethyl acetate solution, also of methods of estimating organo-zinc and organo-magnesium compounds. Of the latter, the iodine method when modified by the elimination of various sources of error is stated to be the most accurate and satisfactory. Zinc ethyl iodide reacts with cuprous chloride, bromide, and cyanide yielding cuprous iodide and the corresponding zinc ethyl compound, ethyl acetate being the most suitable medium for the reaction. All three resulting substances with iodine yield ethyl iodide and zinc chloriodide. Sodium acts on zinc ethyl iodide in ethereal solution with formation of sodium ethoxide, ethane, and ethylene, accompanied by liberation of metallic zinc. The equations given are  $2\text{ZnEtI} + 2\text{Na} \rightarrow \text{Zn} + 2\text{NaI} + \text{ZnEt}_2$ ;  $\text{ZnEt}_2 + 2\text{Na} \rightarrow 2\text{NaEt} + \text{Zn}$ ;  $2\text{NaEt} + 2\text{Et}_2\text{O} \rightarrow 2\text{OEtNa} + 2\text{C}_2\text{H}_4 + 2\text{C}_2\text{H}_6$ . Finely divided calcium or magnesium have a similar action. Magnesium ethyl bromide reacts with zinc ethyl iodide with development of heat, but no products that would throw light on the nature of the reaction were isolated. Zinc compounds are stated to have considerable advantage over magnesium compounds for determining hydroxyl groups in organic substances and a detailed description of the method recommended is given together with the means of overcoming certain experimental difficulties. Unlike the corresponding magnesium compounds, the zinc alkyl iodides do not react with the oxygen atom of ketones or ethers, and thus, being without action on ketonic tautomers, afford a means of observing and measuring the rate of transformation from the ketonic to the enolic form.

H. J. E.

**Propylstannonic Acid.** J. G. F. DRUCE (*Chem. News*, 1923, **127**, 306—308).— $\alpha$ -Propylstannonic acid is obtained by shaking propyl bromide with an alkaline solution of potassium hydrogen stannite containing enough alcohol to give a homogeneous mixture, and, after fourteen days, neutralising with hydrochloric acid. It forms a gelatinous precipitate which dries to a white powder. The potassium salt,  $\text{C}_3\text{H}_7\text{SnO}_2\text{K}$ , is deliquescent. The acid also forms a sodium salt and basic calcium and barium salts. When distilled, the acid decomposes, giving a mixture of propane, propyl alcohol, water, and propylene, leaving a residue containing stannous and stannic oxides. When boiled with an excess of 10% potassium or sodium hydroxide,  $\alpha$ -propylstannonic acid is converted into tin dipropyl oxide,  $\text{SnOPr}_2$ , a white powder which decomposes

at high temperatures, leaving a residue of stannic oxide. *Tin propyl trichloride*,  $\text{SnPrCl}_3$ , is obtained by boiling  $\alpha$ -propylstannonic acid with a benzene solution of hydrogen chloride; it forms colourless, deliquescent crystals. *Tin propyl tribromide* is obtained by dissolving  $\alpha$ -propylstannonic acid in concentrated hydrobromic acid.

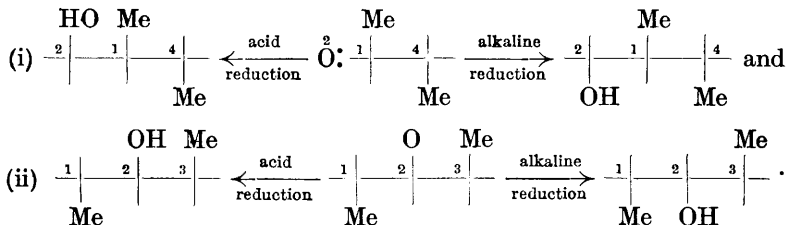
E. H. R.

**Organo-metallic Compounds. I. Introduction. II. Equivalent Conductivity of Tin Trimethyl Chloride in Ethyl Alcohol.** C. A. KRAUS and C. C. CALLIS (*J. Amer. Chem. Soc.*, 1923, **45**, 2624—2632).—The organo-metallic compounds of the types  $\text{M}^n\text{R}_{n+1}\text{X}$  and  $\text{M}^n\text{R}_{n-1}\text{X}$  exhibit electrolytic properties, but only the members of the first type are true electrolytes. The members of the second type exhibit electrolytic properties only under particular conditions. Data are given for the electrical conductivity of tin trimethyl iodide in the pure state and in various solvents, including benzene, ethyl ether, nitrobenzene, nitromethane, benzonitrile, methyl salicylate, ethyl acetate, acetone, amyl alcohol, benzyl alcohol, pyridine, and ethyl alcohol. The pure compound is a poor conductor ( $k=0.3 \times 10^{-5}$ ), whilst solutions of this compound in solvents of the non-basic type are also poor conductors, even although the dielectric constant of the solvent may be high. Solutions in the alcohols and amines are relatively good conductors. The equivalent conductivity of tin trimethyl chloride in absolute alcohol at low concentrations ( $0.1566 \times 10^{-3}$ — $16.5707 \times 10^{-3}N$ ) has been measured at  $25^\circ$ . From these measurements, the value 30.8 is deduced for  $\Lambda_\infty$ . Up to a concentration of  $10^{-3}N$ , the conductivity values conform to the law of mass action within the limits of experimental error. The mass action constant has the value  $0.349 \times 10^{-4}$ . The properties of compounds of the type of tin trimethyl chloride are discussed. It is suggested that the electrolytic properties of solutions of this and similar compounds in the alcohols and amines are due to the formation of a more electropositive group by combination of the tin trimethyl group with the solvent. It is pointed out that the properties of tin trimethyl chloride correspond closely with the properties of methyl iodide and more particularly with those of the halogen acids. The properties of the tin trimethyl group and of its compounds may be accounted for on the basis of the electro-affinity of this group. The analogy which this group bears to hydrogen is pointed out.

J. F. S.

**The Stereochemistry of the Tri-substituted cycloHexanes.** A. SKITA (*Ber.*, 1923, **56**, [B], 2234—2244; cf. Skita and Schenck, A., 1922, i, 240; Skita, A., 1923, i, 460, 671).—Although a considerable amount of information is available with regard to the formation of the theoretically possible, disubstituted *cyclohexanes*, very little work has been done with trisubstituted compounds; the hydrogenation of *m*-4-xylydine and *m*-4-xylenol has, however, been studied to some extent. Reduction of the latter compound occurs in such a manner that the methyl groups occupy the trans-position relatively to one another. The present com-

munication adduces evidence to show that this behaviour is general since 1:4-dimethylcyclohexan-2-one and its oxime are reduced to mixtures of isomeric 1:4-dimethylcyclohexan-2-ols and 1:4-dimethylcyclohexyl-2-amines, whereas 1:3-dimethylcyclohexan-2-one and its oxime yield only a single 1:3-dimethylcyclohexan-2-ol and 1:3-dimethylcyclohexyl-2-amine, independently of the conditions under which reduction occurs. The results are explained in accordance with the schemes :



The fourth and sixth formulæ are identical.

[With L. WINTERHALDER and W. SCHNEIDER.]—*p*-2-Xylenol is converted by hydrogen in acid solution in the presence of colloidal platinum into a mixture of 1<sup>c</sup>:4<sup>t</sup>-dimethylcyclohexane, b. p. 119.5°/atmospheric pressure, and 1<sup>c</sup>:4<sup>t</sup>-dimethylcyclohexan-2<sup>c</sup>-ol, a colourless liquid, b. p. 74°/14 mm., 180°/atmospheric pressure,  $d_4^{20}$  0.9066,  $n_D^{20}$  1.45377 (*phenylurethane*, needles, m. p. 113°). It is oxidised by Beckmann's chromic acid solution to 1<sup>c</sup>:4<sup>t</sup>-dimethylcyclohexan-1-one, b. p. 178° (corr.); the *oxime*, needles, m. p. 111°, and the *semicarbazone*, leaflets, m. p. 173°, are described. Reduction of the ketone in an acid medium leads to the formation of 1<sup>c</sup>:4<sup>t</sup>-dimethylcyclohexan-2<sup>c</sup>-ol (see above), whereas it is transformed by treatment with sodium and moist ether into 1<sup>t</sup>:4<sup>c</sup>-dimethylcyclohexan-2<sup>c</sup>-ol, a liquid with a pleasant odour, b. p. 179° (corr.),  $d_4^{20}$  0.9032,  $n_D^{20}$  1.45297 (*phenylurethane*, crystals, m. p. 117°). Catalytic hydrogenation of 1<sup>c</sup>:4<sup>t</sup>-dimethylcyclohexanoneoxime dissolved in acetic acid (50%) in the presence of colloidal platinum yields 1<sup>c</sup>:4<sup>t</sup>-dimethylcyclohexyl-2<sup>c</sup>-amine, b. p. 166° (corr.),  $d_4^{20}$  0.8502,  $n_D^{20}$  1.45247 (*benzoyl derivative*, m. p. 120°; *hydrochloride*, needles, m. p. 207°; *picrate*, golden-yellow leaflets, m. p. 175°; *phenylthiocarbamide* compound, long needles, m. p. 165°) whereas treatment of it with sodium and alcohol gives the isomeric 1<sup>t</sup>:4<sup>c</sup>-dimethylcyclohexyl-2<sup>c</sup>-amine, b. p. 164° (corr.),  $d_4^{20}$  0.8420,  $n_D^{20}$  1.44976 (*benzoyl derivative*, crystals, m. p. 175°; *hydrochloride*, small needles, m. p. 247°; *picrate*, yellow leaflets, m. p. 198°; *phenylthiocarbamide derivative*, m. p. 222°).

Hydrogenation of *p*-2-xyldine dissolved in a mixture of glacial acetic and concentrated hydrochloric acids in the presence of colloidal platinum yields a mixture of almost equal quantities of the stereoisomeric 2:5-dimethylcyclohexylamines described above, which are separated from one another by fractional crystallisation of the corresponding benzoyl derivatives; the mother-liquors contain relatively very small amounts of a third *benzoyl derivative*,

which is hydrolysed by concentrated hydrochloric acid to 1':4'-dimethylcyclohexyl-2'-amine, b. p. 168° (corr.),  $d_4^{20}$  0.8860.

Hydrogenation of *m*-2-xylenol dissolved in acetic and hydrochloric acids in the presence of colloidal platinum yields a mixture of 1':3'-dimethylcyclohexane, b. p. 118–119°, and 1':3'-dimethylcyclohexan-2'-ol, b. p. 172°,  $d_4^{20}$  0.91618,  $n_D^{20}$  1.46124 (*phenylurethane*, crystals, m. p. 158°). The alcohol is oxidised by Beckmann's chromic acid mixture to 1':3'-dimethylcyclohexanone, b. p. 174° (*oxime*, crystals, m. p. 86°; *semicarbazone*, m. p. 198°). The ketone is converted by catalytic hydrogenation in acid solution or by means of sodium and moist ether into 1':3'-dimethylcyclohexan-2'-ol, which is identical with the product described above. Reduction of the oxime of the ketone, whether in acid or alkaline solution, yields 1':3'-dimethylcyclohexyl-2'-amine, b. p. 73°/29 mm., 167°/atmospheric pressure,  $d_4^{20}$  0.8564,  $n_D^{20}$  1.4549 (*benzoyl derivative*, m. p. 197°; *hydrochloride*, colourless crystals, decomp. 282°; *picrate*, yellow crystals, m. p. 191°; *acetyl compound*, m. p. 198°; *phenylcarbamide derivative*, m. p. 205°; *phenylthiocarbamide compound*).

Catalytic reduction of *m*-2-xylidine in acid solution in the presence of colloidal platinum gives mainly (90%) 1':3'-dimethylcyclohexyl-2'-amine; the crude product of the reaction is benzoylated, and the benzoyl derivatives are fractionally crystallised from glacial acetic acid, whereby in addition to the compound, m. p. 195°, a second *benzoyl derivative*, m. p. 121°, is isolated. The latter compound is hydrolysed to 1':3'-dimethylcyclohexyl-2'-amine, b. p. 168.5,  $d_4^{20}$  0.8625 (*hydrochloride*, m. p. 266° after softening at 263°).  
H. W.

**Identification of Amines.** C. S. MARVEL and F. E. SMITH (*J. Amer. Chem. Soc.*, 1923, **45**, 2696–2698).—*p*-Bromobenzene-sulphonalkylamides, having the m. p. stated, have been prepared from the following amines. Methylamine, m. p. 77°; benzylamine, m. p. 117°; dimethylamine, m. p. 94°; piperidine, m. p. 91°; *o*-toluidine, m. p. 116°; *p*-toluidine, m. p. 98°; *o*-chloroaniline, m. p. 105°; *p*-chloroaniline, m. p. 134°; *p*-bromoaniline, m. p. 145°; *p*-anisidine, m. p. 142°; *p*-phenetidine, m. p. 143°;  $\alpha$ -naphthylamine, m. p. 183.5°;  $\beta$ -naphthylamine, m. p. 129°; methylaniline, m. p. 92°; ethylaniline, m. p. 91°; propylaniline, m. p. 109°; butylaniline, m. p. 87°; *p*-bromoethylaniline, m. p. 118.5°. *p*-Bromoethylaniline, b. p. 143–147°/20 mm., is prepared by brominating ethylaniline in glacial acetic acid solution.

W. S. N.

**Aromatic Sulphonic Acids and Sulphones.** H. MEYER [with, in part, W. SCHMIDT and R. GRIM] (*Annalen*, 1923, **433**, 327–350).—In the preparation of sulphonic acids, it is practicable, and more economical, to use an excess of hydrocarbon, rather than of sulphuric acid; when the mixture is boiled, the water formed in the reaction distils off in the hydrocarbon vapour. In the sulphonation of a non-volatile hydrocarbon, carbon tetrachloride is added. An apparatus is described in which the hydrocarbon or solvent vapour is condensed, and the liquid dried and returned

to the reaction flask; the water formed is run off periodically from the drying apparatus, the quantity collected recording on the progress of the reaction. The conversion of the sulphuric acid, which, moreover, need not be highly concentrated, is practically quantitative; also, an anhydrous product is isolated, merely by distilling off the excess of hydrocarbon. The following sulphonic acids have been prepared by this method. Benzenesulphonic acid,  $+H_2O$ ; toluenesulphonic acid,  $+H_2O$ ; *p*-xylenesulphonic acid,  $+2H_2O$ ; chlorobenzenesulphonic acid,  $+H_2O$ ; naphthalenesulphonic acid (85.3%  $\beta$ -acid and 14.7%  $\alpha$ -acid), and anisolesulphonic acid. Naphthalene or anisole is sulphonated in the presence of carbon tetrachloride. In the sulphonation of toluene, vanadic acid or mercuric sulphate, but not kieselguhr or animal charcoal, acts as a catalyst.

In preparing anhydrides of sulphonic acids (Meyer and Schlegl, A., 1913, i, 608) it is advisable, but not always necessary, to use the pure alkali salt of the acid, and pure thionyl chloride. Toluene-*p*-sulphonic anhydride has now been obtained pure in this way; it forms colourless crystals, m. p.  $125^\circ$ . *m*-Xylenesulphonic anhydride, m. p.  $139^\circ$ , is somewhat readily decomposed by contact with moist air. When *m*-xylenesulphonic acid and thionyl chloride are heated at  $160^\circ$  for three to four hours, the products are 4-chloro-*m*-xylene, b. p.  $186^\circ$ ; 4:6-dichloro-*m*-xylene, m. p.  $68^\circ$ , b. p.  $220-230^\circ$ ; and a crystalline compound, m. p.  $112^\circ$ , perhaps identical with the trichloro-*m*-xylene of Claus and Burstert (A., 1890, 1105).

During the formation of sulphonic acids, traces of sulphones are generally produced; the yield of sulphone is greater if the reaction is continued at a higher temperature (sealed tube), or if the hydrocarbon employed has a high b. p. (e.g., anisole). Simple or mixed sulphones may be conveniently prepared by passing the vapour of a hydrocarbon over a sulphonic acid, heated at, say,  $150^\circ$ ; the issuing vapour is condensed, the water removed, and the dried liquid returned to be used again. Di-*p*-tolylsulphone is oxidised by means of 3% potassium permanganate solution to dicarboxydiphenylsulphone, m. p.  $370^\circ$  (cf. Michael and Adair, A., 1878, 415); *dimethyl* ester, slender, white needles, m. p.  $194^\circ$ ; *diethyl* ester, glistening scales, m. p.  $158^\circ$ ; *dichloride*, needles, *diimide*, glistening scales, m. p.  $384^\circ$ ; *dianilide*, small, faintly rose-coloured leaflets, m. p.  $376^\circ$ . The diamide is converted by Hofmann's method into di-*p*-aminophenylsulphone. The action of concentrated nitric acid on a cold solution of ditolylsulphone in concentrated sulphuric acid gives 3:3'-*dinitroditolylsulphone*, pale yellow plates, m. p.  $160^\circ$ ; 3:5:3':5'-*tetranitroditolylsulphone*, colourless needles, m. p.  $266^\circ$ , is formed at  $100^\circ$ . The reduction of the dinitro-compound by means of boiling glacial acetic acid, concentrated hydrochloric acid, and zinc powder, gives 3:3'-*di-aminoditolylsulphone*, glistening, faintly rose-coloured leaflets, m. p.  $154^\circ$ ; *diacetyl* derivative, colourless leaflets, m. p.  $197^\circ$ . Di-*m*-xylylsulphone, elongated, rhombic prisms, m. p.  $121^\circ$ , is oxidised by means of permanganate to a *tetracarboxylic acid*, monoclinic tablets, m. p.  $294^\circ$  (decomp.); *tetraethyl* ester, microscopic tablets,

m. p. 235° (decomp.). *Dimesitylsulphone* forms slender, colourless needles, m. p. 195°. *Ditetrahydronaphthylsulphone* forms colourless needles, m. p. 135°; it is obtained by the action of the hydrocarbon vapour on concentrated sulphuric acid at 220°, or by the condensation of the hydrocarbon with the sulphonyl chloride in the presence of aluminium chloride. Phenyltolylsulphone is prepared from toluene and benzenesulphonic acid, or from benzene and toluenesulphonic acid, at 135—140°; it is gradually decomposed by the action of chlorine at 130°, giving benzenesulphonyl chloride, and a *chlorophenyltolylsulphone*, long needles, m. p. 126°. *p-Tolyl-m-xylylsulphone*, aggregates of long, slender prisms, m. p. 121°, is prepared from toluene and *m*-xylenesulphonic acid at 170—180°, or from *m*-xylene, toluene-*p*-sulphonyl chloride, and aluminium trichloride. Phenyl- $\psi$ -cumylsulphone, m. p. 160°, from benzene and  $\psi$ -cumenesulphonic acid at 150°. *p-Tolyl- $\psi$ -cumylsulphone*, m. p. 159°. *m-Xylyl- $\psi$ -cumylsulphone*, m. p. 125°. *Phenylmesitylsulphone*, glistening leaflets, m. p. 116°. *Tolylmesitylsulphone*, needles, m. p. 119°, from mesitylene and toluenesulphonyl chloride, or from toluene and mesitylenesulphonyl chloride, in the presence of aluminium chloride. *m-Xylylmesitylsulphone*, long, rectangular plates, m. p. 149°. Phenyl-*p*-chlorophenylsulphone, m. p. 91°. *p-Chlorophenyl-p-tolylsulphone*, rhombic leaflets, m. p. 128°, is converted by the action of chlorine into *p*-chlorobenzoyl chloride and a *dichlorophenyltolylsulphone*, clusters of needles, m. p. 120—121°. *Tolyl- $\beta$ -naphthylsulphone*, small leaflets, m. p. 154°. *m-Xylyl- $\beta$ -naphthylsulphone*, colourless leaflets, m. p. 128°. *p-Chlorophenyl- $\beta$ -naphthylsulphone*, m. p. about 136°. *Tolyltetrahydronaphthylsulphone*, m. p. 112°. *Phenyltetrahydronaphthylsulphone*, needles, m. p. 78°. *m-Xylyltetrahydronaphthylsulphone*, rhombs, m. p. 78°. *p-Xylyltetrahydronaphthylsulphone*, rhombic leaflets, m. p. 115°. *Mesityltetrahydronaphthylsulphone*, slender needles, m. p. 105°. *p-Chlorophenyltetrahydronaphthylsulphone*, colourless needles, m. p. 136°. The action of toluene vapour at 130° on  $\alpha$ -naphthalenesulphonic acid gives naphthalene, toluenesulphonic acid, and ditolylsulphone; benzene has a similar action. *Tolyl- $\alpha$ -naphthylsulphone*, hard, glistening leaflets, m. p. 122°, and *m-xylyl- $\alpha$ -naphthylsulphone*, small, white leaflets, m. p. 119°, can, however, be obtained with the aid of aluminium chloride. Since *p*-dichlorobenzenesulphonic acid behaves like  $\alpha$ -naphthalenesulphonic acid, *p-dichlorophenyl-p-tolylsulphone*, leaflets, m. p. 139°, and *p-dichlorophenyl-m-xylylsulphone*, slender, colourless needles, m. p. 135°, are also prepared by the aluminium chloride method.  $\alpha$ -Chlorotoluene-*p*-sulphonic acid decomposes above 110°, with elimination of hydrogen chloride, and formation of toluenesulphonic acid; consequently, by the action of *m*-xylene vapour or toluene vapour, tolylxylylsulphone or ditolylsulphone, respectively, is produced.

[With L. STEINMETZER.]—When toluene vapour is allowed to act on phenol-*p*-sulphonic acid at 150—160°, the latter decomposes into *di-p-hydroxydiphenylsulphone*, clusters of large needles, m. p. 239° (*dibenzoate*, m. p. 243°), and sulphuric acid; consequently, *di-p-tolylsulphone* also appears in the product, together with

resinous material. With benzene or *m*-xylene, the second sulphone is not formed, owing to excessive resinification. Phenol-*o*-sulphonic acid behaves like the para-derivative, but the action of toluene or xylene at 150° on phenol-2 : 4-disulphonic acid gives di-*p*-tolylsulphone or dixylylsulphone; thus the elimination of the first sulphonic acid radicle proceeds much more rapidly than that of the second. *p*-Cresolsulphonic acid is evidently more stable, since it reacts normally with benzene vapour at 140° or with toluene vapour at 150°, to give, respectively, *phenyl-p-cresolsulphone*, microscopic leaflets, m. p. 195° (decomp.) (violet coloration with ferric chloride), or *tolyl-p-cresolsulphone*, quadratic leaflets, m. p. 58°. 2-Tetrahydronaphthol-3-phenylsulphone, white leaflets, m. p. 197°, is obtained from benzene vapour and tetrahydronaphthol-sulphonic acid at 110–120°. The methyl ether of this acid, +2H<sub>2</sub>O, has m. p. 165°, and not 107°, as generally stated; it cannot be converted into a sulphone.

Methylcyclohexane cannot be used as a solvent in place of carbon tetrachloride, since even at 100° it is dehydrogenated by the action of 96% sulphuric acid, and converted into toluene-*p*-sulphonic acid.

W. S. N.

### The Constitution of the *m*-Xylenedisulphonyl Chlorides.

J. POLLAK and O. LUSTIG (*Annalen*, 1923, 433, 191–201).—Doubt has already been thrown (Pollak and Schädler, A., 1918, i, 497; Pollak and Rudich, A., 1923, i, 27) on the constitutions assigned by Pfannenstill (A., 1892, 1340) to the *m*-xylenedisulphonyl chlorides. The solid isomeride, m. p. 130° (cf. Wischin, A., 1891, 73; also Pfannenstill, *loc. cit.*), is now shown to be *m*-xylene-4 : 6-disulphonyl chloride; the oily dichloride is, perhaps, *m*-xylene-2 : 4-disulphonyl chloride, but further experimental work is required, and is in progress.

The chloride, m. p. 130°, is synthesised by a method which leaves no doubt as to its structure. *m*-Xylene-4-sulphonic acid must have the formula assigned to it, since it gives, on nitration, three isomeric mono-nitro-derivatives, one of which is also obtained by sulphonating 4-nitro-*m*-xylene, and must therefore be 6-nitro-*m*-xylene-4-sulphonic acid (Claus and Schmidt, A., 1886, 708). 6-Nitro-*m*-xylene-4-sulphonic acid, the purity of which is shown by conversion into its chloride, m. p. 98°, is reduced by means of ammonium sulphide to the 6-amino-derivative, which is diazotised, and then treated in neutral solution with potassium xanthate. The product is hydrolysed by means of alkali hydroxide, and oxidised by means of potassium permanganate. The resulting acid is treated with phosphorus pentachloride, with the production of *m*-xylene-4 : 6-disulphonyl chloride, identical with the chloride obtained by Wischin (*loc. cit.*) and by Pfannenstill (*loc. cit.*). Incidentally, the same compound may more conveniently be prepared by heating *m*-xylene or *m*-xylene-4-sulphonic acid (or its sodium salt) with seven times its weight of chlorosulphonic acid at 150–160°.

Pfannenstill's formulæ were based on the production of the solid chloride, not only from *m*-xylene-4-sulphonic acid, but also,



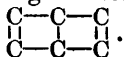
together with an oily isomeride, from the 2-sulphonic acid. Apparently the latter must have been impure; but a more likely explanation is that, during further sulphonation, isomerisation to the 4-sulphonic acid first occurs, this being actually known to occur during the sulphonation of benzene (Behrend and Mertelsmann, A., 1911, i, 189).

The action of cold nitric acid, *d* 1.52, on *m*-xylene-4-sulphonic acid gives 2 : 6-dinitro-*m*-xylene-4-sulphonic acid, which is identified by conversion into its chloride (Limpricht and Gronow, A., 1885, 1232).

The action of chlorosulphonic acid, seven parts, on *p*-xylene at 150–160° gives isomeric disulphonyl chlorides, (a) large crystals, *m. p.* 81°, (b) small crystals, *m. p.* 164°, in the ratio 10 : 1 (cf. Pfannenstill, *loc. cit.*; also Holmes, A., 1891, 1374), the former of which is provisionally designated *p*-xylene-2 : 6-disulphonyl chloride.

W. S. N.

**Stereoisomerism among Derivatives of Diphenyl.** T. M. LOWRY (*Nature*, 1923, 112, 654).—In the use of Dewar's formula for benzene (*e.g.*, Turner, A., 1923, i, 1085; Kenner, *ibid.*), the para-linking should be regarded as indicating only the existence of "free affinities" on the 1 and 4 carbon atoms, or of an electrovalency between them. The length of the carbon-to-carbon bond is constant at about 1.5 Å., but there is no justification for assuming consequent distortion of the hexagon to the quadrilateral



A. A. E.

**Preparation of Hydrogenation Products of Naphthalene and its Derivatives.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRO (D.R.-P. 370974; from *Chem. Zentr.*, 1923, [iv], 539).—Water is allowed to act slowly on a mixture of alkali metals with a solution of naphthalene or its derivatives in an indifferent solvent. For example, by slow addition of water to a mixture of naphthalene and metallic sodium in solvent naphtha at 145°, tetrahydronaphthalene is obtained. When a mixture of aliphatic hydrocarbons of *b. p.* 115–120° is used in place of solvent naphtha, dihydronaphthalene is obtained.  $\alpha$ -Naphthylamine is similarly hydrogenated to tetrahydro- $\alpha$ -naphthylamine, and  $\beta$ -naphthol ethyl ether to tetrahydro- $\beta$ -naphthyl ethyl ether, an oil, *b. p.* 155°/28 mm., having a pleasant odour. It is identical with the product obtained by ethylation of tetrahydro- $\beta$ -naphthol.

G. W. R.

**Stereoisomerism of Decahydronaphthalene and its Derivatives.** W. HÜCKEL (*Nach. K. Ges. Wiss. Göttingen*, 1923, 43–56; from *Chem. Zentr.*, 1923, iii, 766–767).—The author's investigations on decahydro- $\beta$ -naphthol (decalol) render the existence of *cis*- and *trans*-isomerides of decahydronaphthalene probable. The assumption of Mascarelli (A., 1911, i, 964–965) that the two components of decahydro- $\beta$ -naphthol of *m. p.* 75° and 105°, respectively, have the hydroxyls in *cis*- and *trans*-positions is held to be erroneous, since the author has obtained different products on

oxidising them. By oxidation of the decalol of m. p.  $105^{\circ}$ , a decalone is obtained having  $d_4^{20}$  1.005, whilst from the decalol having m. p.  $75^{\circ}$  a decalone having  $d_4^{20}$  0.975 is obtained. Both give the corresponding decalols on reduction. By the further oxidation of both ketones, there is the possibility of the formation of two acids of the composition  $C_{10}H_{16}O_4$ , namely, cyclohexane-1 : 2-diacetic acid,  $C_6H_{10}(CH_2 \cdot CO_2H)_2$  (I) and 2-carboxycyclohexane-1-propionic acid,  $CO_2H \cdot C_6H_{10} \cdot CH_2 \cdot CH_2 \cdot CO_2H$  (II). From the one ketone the *cis*- and from the other ketone the *trans*-form of one or both of these acids should be obtainable. Both forms of I are unknown, but the *cis*- and *trans*-forms of II have been obtained (Windaus and Hüchel, A., 1922, i, 658). The decalol of m. p.  $105^{\circ}$  gives on oxidation with alkaline potassium permanganate a mixture of two acids of m. p.  $101^{\circ}$  and  $159$ — $161^{\circ}$ , respectively, whilst the decalol of m. p.  $75^{\circ}$ , similarly oxidised, gives acids of m. p.  $143^{\circ}$  and  $167^{\circ}$ , respectively. The acids of m. p.  $101^{\circ}$  and  $143^{\circ}$  were identical with the *cis*- and *trans*-forms of II, so that the other acids must be the *cis*- and *trans*-forms of I. The contradictory data obtained for the melting points and densities of decahydronaphthalene are due to the occurrence of mixtures of *cis*- and *trans*-forms. *Cis*- $\beta$ -Decahydronaphthol, m. p.  $105^{\circ}$ , prepared by hydrogenation of *ac*- $\beta$ -tetrahydronaphthol, gives *cis*- $\beta$ -decahydronaphthalone, b. p.  $247^{\circ}/755$  mm.;  $d_4^{21}$  1.0039;  $n_D^{20}$  1.49180; the *semicarbazone* has m. p.  $182$ — $183^{\circ}$ ; the *oxime* is a viscid oil. Hydrogenation of *o*-carboxyphenylpropionic acid gives *cis*-2-carboxycyclohexane-1-propionic acid, m. p.  $109$ — $110^{\circ}$ . The *diethyl* ester has b. p.  $315$ — $320^{\circ}/760$  mm. and  $183^{\circ}/20$  mm.; the *dianilide* has m. p.  $200^{\circ}$  immediately after preparation; after keeping for one month, the m. p. is  $163^{\circ}$ . *trans*- $\beta$ -Decahydronaphthalone gives a *semicarbazone* with m. p.  $192$ — $193^{\circ}$ ; the *oxime* has m. p.  $75^{\circ}$ . *trans*-Decahydronaphthalene has b. p.  $185^{\circ}/753$  mm.;  $d_4^{20}$  0.872;  $n_D^{20}$  1.47009. *cis*-Decahydronaphthalene has b. p.  $193^{\circ}$ ;  $d_4^{20}$  0.898;  $n_D^{20}$  1.48279.

G. W. R.

**Chlorination of Decalin [Decahydronaphthalene].** I. W. BORSCHÉ and E. LANGE (*Annalen*, 1923, **434**, 219—236).—Hüchel (preceding abstract) has shown that decalin is a mixture of *cis*- and *trans*-forms, a fact unknown to Leroux (A., 1904, i, 986), some difficulties connected with the results of the latter author now being removed.

Chlorination of decalin, corresponding with the introduction of one chlorine atom, affords only 25% of 2-chlorodecahydronaphthalene (b. p.  $121$ — $122^{\circ}/18$  mm.) (see below). The latter is, further, a mixture of *cis*- and *trans*-forms. *cis*- $\beta$ -Chlorodecahydronaphthalene from the decahydronaphthol of m. p.  $102$ — $104^{\circ}$ , has b. p.  $110$ — $112^{\circ}/15$  mm. The *trans*-isomeride (from the decahydronaphthol of m. p.  $76^{\circ}$ ) has not been obtained pure. The mixture of chlorodecalins, on heating with aniline, affords a mixture (b. p.  $76$ — $80^{\circ}/15$  mm.) of  $\Delta^1$ - and  $\Delta^2$ -octahydronaphthalenes (octalins), the former in larger quantity; this is proved by the results of oxidation, when (besides oxalic acid, and an acid,  $C_{10}H_{16}O_5$  or  $C_{10}H_{18}O_5$ ,

leaflets, m. p. 116—118° [indef.], *o*-carboxycyclohexanepropionic acid, and a smaller quantity of cyclohexane-1:2-diacetic acid (mixture of *cis*- and *trans*-forms, m. p. 152—153°) are formed.

The calcium salt of *o*-carboxycyclohexanepropionic acid, on heating, gives the hexahydro- $\alpha$ -hydrindone described by Windaus, Hüchel, and Reverej (A., 1923, i, 220).

The above mixture of *cis*- and *trans*-cyclohexane-1:2-diacetic acids cannot be separated by distilling (b. p. 170—180°/10 mm.) or by repeated fractional crystallisation; nor can an artificial mixture (m. p. 152—153°) of the individual acids be separated (the *cis*-acid, m. p. 158—160°, being obtained by oxidising *cis*-2-octahydronaphthalene; the *trans*-acid [Leroux] having m. p. 167°). Similarly, on conversion into derivatives, mixtures of *cis*- and *trans*-forms of these acids are obtained, with the following constants: *diamide*, m. p. 274—275°; *dianilide*, m. p. 295—300° (decomp.); *anhydride*, resin, b. p. 180°/10 mm.; *ethyl ester*, b. p. 147°/7 mm. Again, *hexahydro-2-hydrindone*, obtained from the mixture of acids by (1) distilling with acetic anhydride, (2) heating with concentrated hydrochloric acid at 180—200°, (3) heating the calcium salts, or (4) the action of sodium on the ester (followed by hydrolysis, etc.), is a mixture. The latter gives a 2-nitro-4-cyanophenylhydrazone, orange-red needles, m. p. 190—192°, and a *semi-carbazone*, white leaflets, m. p. (decomp.) 235° or 240° (with slow or rapid heating, respectively), regenerating the mixture of hydrindones (b. p. 108—112°/15 mm.) when treated with oxalic acid.

Since the cyclohexanediactic acid (m. p. 167°) obtained by Leroux is now shown to be the *trans*-form, his 2:3-decahydronaphthalene glycols and his dibromodecahydronaphthalene (m. p. 85°) must also have been derivatives of *trans*-decalin.

A Grignard reagent prepared from the above mixture of 2-chlorodecalins, on treating with carbon dioxide, etc., gives a mixture of the *cis*- and *trans*-decahydronaphthalene-2-carboxylic acids, which may be separated through the *amides* (m. p. 165—166° and 195°, respectively). The *cis*-acid is a resin, b. p. 150°/15 mm. (*anilide*, needles, m. p. 128—130°), the *trans*-acid having m. p. 103° (*anilide*, needles, m. p. 155—158°).

The above mixture of octahydronaphthalenes, gives, as isolable products, a dibromide, m. p. 170°, together with some hexahydronaphthalenetetrabromide (m. p. 184°), owing to the presence of dichlorodecahydronaphthalenes in the original chlorodecalin mixture.

Pure *cis*-2-octahydronaphthalene (b. p. 72—73°/15 mm.; from *cis*-2-chlorodecalin) gives a *dibromide*, m. p. 170°, which, however, cannot be converted into the corresponding dihydroxy-compound and so oxidised to acids of known configuration.

The original decalin chlorination mixture contains dichlorodecahydronaphthalenes (b. p. 148—150°/18 mm.), converted by aniline into hexahydronaphthalenes (b. p. 75—85°/15 mm.). The latter, with bromine, give a mixture of *hexahydronaphthalenetetrabromides* (m. p. 184° and 200°, respectively) and 2-octahydronaphthalene-dibromide (m. p. 170°) and, on oxidation with permanganate affords

a mixture of oxalic acid, cyclohexane-1:2-diacetic acid, and a hexahydrophthalic acid (methyl ester, b. p. 175—180°/15 mm.).

E. E. T.

***m*-Chloroaniline and *m*-Chlorophenol.** I. J. RINKES (*Rec. trav. chim.*, 1923, **42**, 1092).—Seekles (A., 1923, i, 237) has overlooked data published by Holleman and Rinkes (A., 1911, i, 535). The m. p. of *m*-chloroaniline has been re-determined by Blanksma, and the figure  $-10.4^{\circ}$  confirmed.

E. E. T.

**The Catalytic Reduction of the Multiple Carbon-Nitrogen Linking.** K. W. ROSENMUND and E. PFANKUCH (*Ber.*, 1923, **56**, [B], 2258—2262).—An account of partly completed work induced by the recent publications of Taipale (A., 1923, i, 547, 905; Lochte and Bailey, A., 1922, i, 329; 1923, i, 26, 906).

It is shown that the catalytic reduction of oxime acetates may proceed in a manner differing from that of the oximes themselves, since gallaldoxime gives digallylamine, whereas its acetate yields gallylamine. Similarly, benzaldoxime acetate and benzophenone-oxime acetate give better yields of the corresponding primary amines than those obtained from the oximes.

The catalytic reduction of nitriles in glacial acetic acid solution in the presence of palladium leads to the production of primary amines, whereas Paal and Gerum (A., 1909, i, 381) and Rupe and Glenz (A., 1923, i, 100) have obtained mainly secondary amines by working in the presence of aqueous alcohol or a neutral solvent. The reaction is facilitated by the addition of hydrogen chloride or concentrated sulphuric acid. Phenylacetoneitrile yields  $\beta$ -phenylethylamine; *o*-chlorobenzonitrile gives *o*-chlorobenzylamine in the presence of concentrated sulphuric acid, and benzylamine in the presence of sodium acetate. *p*-Hydroxyphenylacetoneitrile, on the other hand, forms di- $\beta$ -*p*-hydroxyphenylethylamine, which does not appear to be accompanied by the primary base. The production of the secondary base is attributed to the elimination of ammonia from the primary amine in the immediate vicinity of the catalyst, and thus resembles the catalytic formation of ethers during the reduction of aldehydes. The change can be inhibited to some extent by the addition of quinoline, which causes the production of appreciable quantities of  $\beta$ -*p*-hydroxyphenylethylamine in addition to the secondary base.

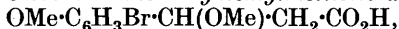
Helianthin is smoothly reduced to *p*-aminodimethylaniline and sulphanic acid. Somewhat unexpectedly, particularly when considered in the light of Taipale's experiences with aliphatic azines (*loc. cit.*), it is found that benzyldeneazine and *o*-hydroxybenzyldeneazine yield the corresponding primary amines. Benzyldeneaniline and benzophenoneanil yield aniline and (?) toluene or diphenylmethane, respectively. The formation of intermediate products such as benzyaniline appears to be excluded, since they are not further reducible.

The following observations are incidentally recorded. Benzophenoneoxime acetate has m. p. 69—70° instead of 55° as recorded in the literature. Benzhydrylamine hydrochloride,  $C_{13}H_{14}NCl$ , has

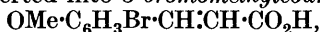
m. p. 270°. *Di-β-p-hydroxyphenylethylamine* crystallises in hexagonal platelets, m. p. about 190° (*hydrochloride*, m. p. 221—223°).  
H. W.

**Preparation of Highly Chlorinated Hydroaromatic Products containing Nitrogen.** SOCIÉTÉ ANONYME ANCIEN. DURAND, HUGUENIN ET CIE (Brit. Pat. 193843).—The hydrochlorides of aromatic amines are chlorinated with gaseous chlorine in dry inert solvents, such as benzene or chlorobenzene to yield highly chlorinated hydroaromatic compounds containing nitrogen. Aniline dissolved in chlorobenzene, on saturation with hydrogen chloride and treatment with chlorine at 100° for two hours yields *1-chloroimino-2:2:3:4:4:5:6:6-octachlorocyclohexane*, m. p. 151°. If benzene is used as solvent and chlorine led in at a lower temperature and its introduction stopped as soon as dissolution is complete, *4-chloroimino-1:3:3:5:5:6-hexachlorocyclohexene* or *3-chloroimino-2:4:4:5:6:6-hexachlorocyclohexene* (the constitution doubtful), m. p. 125°, is produced. Both these substances are stable, decomposition first occurring at 170°.  $\alpha$ -Naphthylaminehydrochloride suspended in chlorobenzene and treated with chlorine at 100° yields *1-chloroimino-2:2:3:4:4-pentachlorotetrahydronaphthalene*, m. p. 122°;  $\beta$ -naphthylamine hydrochloride reacts even more readily, and treated in benzene at the ordinary temperature gives *2-chloroimino-1:1:3:3:4-pentachlorotetrahydronaphthalene*, m. p. 118.5°. The aminoanthraquinones behave similarly to the naphthylamines; from the  $\alpha$ -compound, *1-chloroimino-2:2:3:4:4-pentachlorotetrahydroanthraquinone*, m. p. 190°, and from the  $\beta$ -compound, *2-chloroimino-1:1:3:3:4-pentachlorotetrahydroanthraquinone*, m. p. 210°, are produced.  
T. S. W.

**The Action of Hypobromous Acid on Phenol and some Phenol Derivatives.** E. BIILMANN and E. RIMBERT (*Bull. Soc. chim.*, 1923, 33, [iv], 1473—1481).—2:4:6-Tribromophenol, 2:4:6-tribromo-*m*-cresol, 2:6-dibromo-*p*-nitrophenol, 4:6-dibromo-*o*-nitrophenol, 3:5-dibromosalicylic acid, and 3-bromoanisic acid were obtained by the action of hypobromous acid on the corresponding phenols, nitrophenols, and acids. Hypobromous acid reacts with  $\beta$ -methoxymethylmelilotic acid (cf. Biilmann and Starcke, A., 1912, i, 461), yielding *5-bromo-2-methoxymethylmelilotic acid*,



white needles, m. p. 126.5—127°, which on treatment with hydrochloric acid is converted into *5-bromomethylcoumaric acid*,



white needles, m. p. 222—223°. The latter, on treatment with permanganate, is oxidised to 5-bromo-2-methoxybenzoic acid, whilst the action of a solution of bromine in carbon disulphide results in the formation of  $\alpha\beta$ -5-tribromomethylmelilotic acid. This has m. p. 201°, not 197° as stated by Biilmann and Lund (A., 1923, i, 219).  $\beta$ -Methoxymethylmelilotic acid on treatment with hydrochloric acid yields methylcoumaric acid, which is also obtained from the same reagent and the mercuric compound of methoxymethylmelilotic acid.  
H. J. E.

**The Kinetic Behaviour of Mixtures of Isomeric Nitrophenols in the Reduction with Stannous Chloride.** A. KLEMENC [with A. KLEIN] (*Annalen*, 1923, **433**, 351—357).—The velocity constants (bimolecular) for the reduction by means of hydrochloric acid and stannous chloride of *o*-nitrophenol, *m*-nitrophenol, and *p*-nitrophenol have been measured, and Goldschmidt and Sunde's figures (*A.*, 1906, i, 734) for the ortho- and meta-compounds and their calculated value for the para-derivative are confirmed. Measurements have also been made of the velocity of reduction of mixtures of *o*- and *p*-nitrophenols, and of *m*- and *p*-nitrophenols. The mixture behaves as though only one compound were present, in a concentration equal to the total concentration of the two isomerides, a bimolecular velocity constant being thus attained; in other words, the reduction of each individual does not proceed independently, as was found by van't Hoff ("Études," 1884, 96) for the isomeric dibromosuccinic acids. It follows that the relative concentrations of isomeric nitrophenols cannot be determined in this way, although this might be possible by the use of a different reducing agent. W. S. N.

**The Influence of Substitution in the Components of Binary Solution Equilibria. XLII. The Binary Systems of Succinimide with Phenols.** R. KREMANN and K. DIETRICH (*Monatsh.*, 1923, **44**, 151—162).—The freezing-point curves of mixtures of various phenols with succinimide have been plotted. With phenol, the curve indicates a compound between equal molecular proportions. A similar compound is formed with  $\beta$ -naphthol, but in agreement with the generally smaller tendency of  $\alpha$ -naphthol to form additive compounds, the curve for the latter is a simple eutectic, with no indication at all of combination. With pyrogallol and the three dihydroxybenzenes, simple molecular compounds are formed in each case in the molecular proportion 1 : 1. The introduction of nitro-groups diminishes the tendency to form additive compounds; *p*-nitrophenol, in which the nitro-group is farthest away from the hydroxyl group, forms an additive compound (1 : 1), but no compounds are formed with *o*- or *m*-nitrophenol, or with 2 : 4-dinitrophenol or picric acid. S. I. L.

**The Temperature of Explosion for Endothermic Substances. II. Trinitro-*m*-cresolates and their Explosion Temperatures.** R. L. DATTA, L. MISRA, and J. C. BARDHAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2430—2433; cf. Datta and Chatterjee, *T.*, 1919, **115**, 1006).—The temperature of explosion may be determined by the method previously used with an accuracy, apparently, of 1°; it is quite characteristic, and, if a melting- or boiling-point cannot be taken, should be of value in characterising, or ascertaining the purity of, endothermic substances.

A series of additive compounds of trinitro-*m*-cresol has been examined. In the following, "T" stands for  $\text{OH}\cdot\text{C}_6\text{HMe}(\text{NO}_2)_3$ , and "E.p." for the explosion temperature; the names of the second constituent of the trinitrocresolates are given, the formula of the additive complex, and its properties. *Acenaphthene*,  $\text{C}_{12}\text{H}_{10}\cdot 2\text{T}$ ,

yellow feathers, m. p.  $120^{\circ}$ , E.p.  $451^{\circ}$ ; *fluorene*,  $C_{13}H_{10}$ , T, deep yellow needles, m. p.  $109^{\circ}$ , E.p.  $421^{\circ}$ ; *allylamine*,  $3C_3H_7N$ , T, lustrous yellow (? crystals), m. p.  $165^{\circ}$ , E.p.  $265^{\circ}$ ; *benzylamine*,  $C_7H_9N$ , T, golden-yellow needles, m. p.  $185^{\circ}$ , E.p.  $406^{\circ}$ ; *camphylamine*,  $C_{10}H_{19}N$ , 2T, lemon-yellow needles, m. p.  $183^{\circ}$ , E.p.  $391^{\circ}$ ; *menthylamine*,  $C_{10}H_{21}N$ , 2T, lemon-yellow needles, m. p.  $200^{\circ}$  (decomp.), E.p.  $410^{\circ}$ ; *piperazine*,  $2C_4H_{10}N_2$ , T, lemon-yellow needles, m. p.  $220-225^{\circ}$  (decomp.), E.p.  $359^{\circ}$ ;  $\alpha$ -*naphthylamine*,  $C_{10}H_9N$ , T, dirty-yellow needles, m. p.  $165-170^{\circ}$  (decomp.), E.p.  $470^{\circ}$ ; *p-chloroaniline*,  $C_6H_6NCl$ , 2T, lemon-yellow needles, m. p.  $170-172^{\circ}$ , E.p.  $449^{\circ}$ ; *p-bromoaniline*,  $C_6H_6NBr$ , 2T, lemon-yellow granules, m. p.  $172.5^{\circ}$ , E.p.  $441^{\circ}$ ; *p-iodoaniline*,  $C_6H_6NI$ , 2T, bright yellow needles, m. p.  $152^{\circ}$ , E.p.  $466^{\circ}$ ; *o-anisidine*,  $OMe \cdot C_6H_4 \cdot NH_2$ , T, pale-yellow needles, m. p.  $178^{\circ}$  (decomp.), E.p.  $349^{\circ}$ ; *o-phenetidine*,  $OEt \cdot C_6H_4 \cdot NH_2$ , T, bright yellow needles, m. p.  $165^{\circ}$ , E.p.  $385^{\circ}$ ; *hexamethylenetetramine*,  $C_6H_{12}N_4$ , T, m. p.  $175^{\circ}$ ; E.p.  $325^{\circ}$ ;  $\psi$ -*cumidine*,  $C_6H_2Me_3 \cdot NH_2$ , 2T, velvety-yellow needles, m. p.  $183^{\circ}$  (decomp.), E.p.  $477^{\circ}$ ; *triphenylguanidine*,  $NPh \cdot C(NHPh)_2$ , T, brilliant yellow, prismatic needles, m. p.  $182^{\circ}$ , E.p.  $454^{\circ}$ ;  $\alpha$ -*naphthyl dimethylamine*,  $C_{10}H_7 \cdot NMe_2$ , T, hard, brilliant plates, m. p.  $154^{\circ}$ , E.p.  $358^{\circ}$ ;  $\alpha$ -*naphthol*,  $C_{10}H_7 \cdot OH$ , T, orange-yellow, silky needles, m. p.  $159^{\circ}$ , E.p.  $472^{\circ}$ ;  $\beta$ -*naphthol*,  $C_{10}H_7 \cdot OH$ , T, orange needles, m. p.  $124^{\circ}$ , E.p.  $452^{\circ}$ .

W. S. N.

**Esterification of Naphthols in Presence of Catalysts.** (MISS) M. ALOE (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1921, [iii], 27, 75—80).—The reactions of  $\alpha$ - and  $\beta$ -naphthols with acetic, phenylcinnamic and benzoic anhydrides either alone or in presence of a catalyst have been investigated, the results obtained being similar to those described by Bakunin and Giordani (A., 1920, i, 543). These reactions are catalysed by ferric chloride, fuming sulphuric acid, phosphoric oxide, iodine, chlorine, and hydrochloric and hydrobromic acids.

$\alpha$ -*Naphthyl phenylcinnamate*,  $C_{14}H_{11} \cdot CO_2 \cdot C_{10}H_7$ , forms slender, flesh-coloured needles, m. p.  $119^{\circ}$ , the  $\beta$ -*naphthyl* compound, being a white, pulverulent compound, beginning to become pasty at  $115^{\circ}$ , m. p.  $130-145^{\circ}$ .

T. H. P.

**The Mode of Action of Auxochromes.** H. KAUFFMANN (*Annalen*, 1923, 433, 237—241).—Whereas *o*-hydroxystilbene is colourless, its potassium salt is yellow. The latter can only possess a quinonoid structure if the potassium atom is attached to carbon; the alternative, and more probable, formula, in which the metal is bound to oxygen, is benzenoid. These facts constitute a further demonstration (cf. A., 1906, i, 577) of the incorrectness of the view that the action of auxochromes in conferring colour on benzene derivatives is to be ascribed to a quinonoid form.

[With ELISABETH LAEMLE.]—*o*-Hydroxystilbene is conveniently prepared by heating *o*-hydroxyphenylbenzylcarbinol at  $180-200^{\circ}$ , or, better, by boiling it with acetic anhydride; the carbinol is readily obtained by the interaction of salicylaldehyde and magnesium benzyl chloride in cold ethereal solution. *o*-Hydroxystilbene is converted by means of methyl sulphate into *o*-methoxystilbene.

The absorption curves for the phenol and its methyl ether are very similar, and only show selective absorption in the ultra-violet. The curve for the potassium salt, however, has two peaks, and shows absorption in the visible spectrum.

W. S. N.

**Preparation of Dihydroxyperylene.** H. PEREIRA (Brit. Pat. 191363).— $\beta\beta$ -Dinaphthol is intimately mixed with anhydrous aluminium chloride and a basic substance such as one of the oxides or hydroxides or carbonates of the alkalis or alkaline earths, and the mixture is heated for thirty minutes at  $170^\circ$ . The residue is boiled with dilute hydrochloric acid and well washed. 1 : 12-Dihydroxyperylene remains in satisfactory yield.

T. S. W.

**Ethylene and Trimethylene Ethers of Quinol.** M. KOHN and L. BENCZER (*Annalen*, 1923, **433**, 305—313; cf. Kohn and Wilhelm, A., 1923, i, 558; Kohn and Safrin, *ibid*, i, 559).—Phenyl *p*-hydroxyphenyl ethylene ether,  $\text{OPh}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , almost colourless crystals, m. p.  $152\text{--}154^\circ$ , is formed by boiling quinol with  $\beta$ -bromophenetole in concentrated aqueous solution, a concentrated solution of potassium hydroxide being gradually added. It gives a *benzoate*, leaflets, m. p.  $126^\circ$ , and, by the use of methyl sulphate, a *methyl ether*, m. p.  $103\text{--}104^\circ$ , which is also obtained when quinol methyl ether and  $\beta$ -bromophenetole are boiled with sodium ethoxide in alcoholic solution. Phenyl *p*-hydroxyphenyl ethylene ether reacts with a further molecule of  $\beta$ -bromophenetole in boiling, alcoholic sodium ethoxide solution, to give *quinol bisphenoxyethyl ether*, leaflets, m. p.  $180^\circ$ , which is also produced in small amount in the preparation of the original phenolic ether. The action of ethylene bromide on phenyl *p*-hydroxyphenyl ethylene ether in boiling, alcoholic sodium ethoxide solution gives *bis- $\beta$ -phenoxy-*p*-ethoxyphenyl ethylene ether*, microscopic needles, m. p.  $217^\circ$ , which is also obtained by the action of diquinol ethylene ether (1 mol.) on  $\beta$ -bromophenetole (2 mols.) under similar conditions; the use of trimethylene bromide leads to the formation of *bis- $\beta$ -phenoxy-*p*-ethoxyphenyl trimethylene ether*, leaflets, m. p.  $174\text{--}175^\circ$ , which is likewise obtained from diquinol trimethylene ether and  $\beta$ -bromophenetole. Quinol and phenyl  $\gamma$ -bromopropyl ether react in a boiling, aqueous solution containing potassium hydroxide to give *phenyl p-hydroxyphenyl trimethylene ether*, microscopic needles, m. p.  $63^\circ$ , *benzoate*, tablets, m. p.  $88\text{--}90^\circ$ , *methyl ether*, leaflets, m. p.  $44\text{--}46^\circ$ ; the methoxy-derivative is also obtained by the action of quinol methyl ether and phenyl  $\gamma$ -bromopropyl ether in the presence of sodium ethoxide. Phenyl *p*-hydroxyphenyl trimethylene ether reacts with a second molecule of phenyl  $\gamma$ -bromopropyl ether in the presence of sodium ethoxide to give *quinol bisphenoxypropyl ether*, small, flat rods, m. p.  $120^\circ$ ; if  $\beta$ -bromophenetole is used, the product is *quinol  $\beta$ -phenoxyethyl  $\gamma$ -phenoxypropyl ether*, leaflets, m. p.  $114\text{--}115^\circ$ , which is also prepared from phenyl *p*-hydroxyphenyl ethylene ether and phenyl  $\gamma$ -bromopropyl ether. Phenyl *p*-hydroxyphenyl trimethylene ether and ethylene bromide, or diquinol ethylene ether and phenyl  $\gamma$ -bromopropyl ether, react in boiling, alcoholic sodium ethoxide solution to give *bis- $\gamma$ -phenoxy-*



*p*-propoxyphenyl ethylene ether, leaflets, m. p. 149°; under similar conditions, *p*-hydroxyphenyl trimethylene ether and trimethylene bromide, or diquinol trimethylene ether and phenyl  $\gamma$ -bromopropyl ether, gives *bis*- $\gamma$ -phenoxy-*p*-propoxyphenyl trimethylene ether, needles, m. p. 147°.

W. S. N.

**Preparation of Diphenylene Sulphide by the Action of Sodamide on Diphenyl Sulphoxide.** A. SCHÖNBERG (*Ber.*, 1923, 56, [B], 2275).—Diphenyl sulphoxide, m. p. 70—71°, is readily prepared by the action of aluminium chloride on a mixture of benzene and thionyl chloride. It is transformed into diphenylene sulphide,  $S < \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}$ , needles, m. p. 97—98°, when its solution in

boiling toluene is subjected to protracted treatment with finely divided sodamide.

H. W.

**Derivatives of Dithioethylene and Dithioacetylene.** E. FROMM and H. LANDMANN (*Ber.*, 1923, 56, [B], 2290—2294).—A continuation of the work of Fromm, Benzinger, and Schäfer (*A.*, 1913, i, 174) and Fromm and Siebert (*A.*, 1922, i, 542).

Attempts to prepare dithioethylene were unsuccessful, since dichloroethylene could not be caused to react with an alcoholic solution of sodium sulphide or sodium hydrogen sulphide, even under increased pressure. With sodium ethoxide, an explosion results owing to the evolution of chloroacetylene.

*s*-Diethylthiolacetylene is converted by a mixture of glacial acetic and 50% sulphuric acids into *ethylthiolacetaldehyde ethylmercaptan*,  $SEt \cdot CH_2 \cdot CH(SEt)_2$ , a heavy, unstable liquid which is oxidised by hydrogen peroxide to *triethylsulphone-ethane*,  $SO_2Et \cdot CH_2 \cdot CH(SO_2Et)_2$ , colourless needles, m. p. 144°; the reaction consists primarily in the addition of the elements of water with formation of the product  $SEt \cdot CH_2 \cdot CH(OH) \cdot SEt$ , which becomes decomposed into ethyl mercaptan and the substituted aldehyde,  $SEt \cdot CH_2 \cdot CHO$ ; the products then react with one another to give the mercaptal, the yield of which can therefore be considerably improved by initial addition of a molecular proportion of ethyl mercaptan. Similarly, dibenzylthioethylene is converted into the unstable *benzylmercaptan* of *benzylthiolacetaldehyde*, which is oxidised by potassium permanganate to  $\alpha\beta$ -*dibenzylsulphone- $\alpha$ -benzylthioethane*,  $CH_2Ph \cdot SO_2 \cdot CH(S \cdot CH_2Ph) \cdot SO_2 \cdot CH_2Ph$ , m. p. 142°, and by hydrogen peroxide (30%) to *tribenzylsulphone-ethane*,  $CH_2Ph \cdot SO_2 \cdot CH_2 \cdot CH(SO_2 \cdot CH_2Ph)_2$ , lustrous leaflets, m. p. 261°. The sulphone-sulphide is reduced by zinc dust and glacial acetic acid to *dibenzylsulphone-ethane*, m. p. 304°, which is also obtained (together with benzyl mercaptan) from the trisulphone.

*Diethylsulphone-ethylene*,  $SO_2Et \cdot CH : CH \cdot SO_2Et$ , slender needles, m. p. 88°, is prepared by the oxidation of diethylthioethylene with hydrogen peroxide; it is reduced by zinc dust and acetic acid to diethylsulphone-ethane, m. p. 137°. Dibenzylthioethylene is oxidised by potassium permanganate to  $\alpha$ -*benzylthiol- $\beta$ -benzylsulphone-ethylene*,  $CH_2Ph \cdot S \cdot CH : CH \cdot SO_2 \cdot CH_2Ph$ , lustrous needles, m. p. 127°, which is not affected by zinc dust and acetic acid, and

by hydrogen peroxide to *dibenzylsulphone-ethylene*, colourless needles, m. p.  $167^{\circ}$ , which is reduced to *dibenzylsulphone-ethane*, m. p.  $304^{\circ}$ .

The presence of the conjugated double bonds in *dibenzylsulphone-ethylene* causes it to react with phenylhydrazine, with the ultimate production of the *phenylhydrazone* of *benzylsulphonacetaldehyde*,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$ , pale yellow crystals, m. p.  $139$ — $140^{\circ}$ , and the *phenylhydrazine* salt of *benzylsulphinic acid*, lustrous leaflets, m. p.  $181^{\circ}$ .

Although *dibenzylsulphone-ethylene* readily unites with hydrogen, it does not appear possible to add the elements of water. On the other hand,  $\alpha$ -benzylthiol- $\beta$ -benzylsulphone-ethylene, which cannot be reduced, readily combines with water to form the *benzylmercaptal* of *benzylsulphonacetaldehyde*,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}(\text{SO}_2\cdot\text{CH}_2\text{Ph})_2$ , slender needles, m. p.  $81^{\circ}$ , which is oxidised by hydrogen peroxide to *tribenzylsulphone-ethane*, m. p.  $261^{\circ}$ .

*Dibenzylthiolacetylene* is oxidised by hydrogen peroxide at the atmospheric temperature to *dibenzylsulphone-acetylene*,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{C}\equiv\text{C}\cdot\text{SO}_2\cdot\text{CH}_2\text{Ph}$ , lustrous leaflets, m. p.  $212^{\circ}$ ; on account of the instability of the material, it has not been found possible to add the elements of water.

*s*-Tetrachloroethane and sodium benzylmercaptide give *tetra-benzylthiolethane*, crystals, m. p.  $63^{\circ}$ , which is oxidised by hydrogen peroxide in the presence of glacial acetic acid to *tetrabenzylsulphone-ethane*, lustrous leaflets, m. p.  $203^{\circ}$ .  
H. W.

**Catalytic Dehydration of Hydroaromatic Alcohols.** J. B. SENDERENS (*Compt. rend.*, 1923, **177**, 1183—1186).—*cyclo*Hexanol, when distilled with 3% of its weight of sulphuric acid trihydrate, gives a 92% yield of *cyclo*hexene, the production of which depends on its steady removal from the reaction mixture; practically none is formed simply by heating under reflux. *cyclo*Hexane-1 : 2-diol is very little affected by sulphuric acid trihydrate, about 20% being converted into condensed hydrocarbons. Concentrated sulphuric acid at  $110^{\circ}$  affords a resin and a little  $\Delta^{1:3}$ -*cyclo*hexadiene. *cyclo*Hexane-1 : 3-diol is readily converted by the trihydrate at  $130$ — $145^{\circ}$  into  $\Delta^{1:3}$ - and  $\Delta^{1:4}$ -*cyclo*hexadienes, *cyclo*hexane-1 : 4-diol, under similar conditions, affording  $\Delta^{1:3}$ -*cyclo*hexadiene.  
E. E. T.

**Halochromic Phenomena with Phenylethinylcarbinols.** W. WELTZIEN, F. MICHEEL, and K. HESS (*Annalen*, 1923, **433**, 247—267).—It has already been shown that certain arylethinylcarbinols, a quinonoid rearrangement of which is highly improbable, are, as regards halochromy, in every way similar to carbinols, including radicles of the triphenylmethyl type containing so-called tervalent carbon (Hess and Weltzien, A., 1922, i, 35). Trianisylethinylcarbinol, and phenylethinyl dianisylethinylcarbinol have now been prepared by the method previously employed, and shown to behave in the same way. This confirms the previous conclusion, that in derivatives of triphenylmethane exhibiting halochromy, this property is not destroyed by replacing the phenyl groups by "gap-linkings."

A better method for preparing *p*-methoxyphenylacetylene than

that given by Manchot (A., 1912, i, 230) is as follows. Anisaldehyde and ethyl acetate are condensed by means of sodium to ethyl *p*-methoxycinnamate, the dibromide of which is hydrolysed by boiling for four hours with alcoholic potassium hydroxide solution, to give *p*-methoxyphenylpropionic acid, the copper salt of which is decomposed by the action of steam to give the required product.

The action of thionyl chloride on sodium *p*-methoxyphenylpropionate in ethereal suspension at  $-20^{\circ}$  gives *p*-methoxyphenylpropionyl chloride, small, slightly yellow needles, m. p.  $43^{\circ}$ , which is treated in ethyl chloride solution at  $-20^{\circ}$  with two equivalents of magnesium *p*-methoxyphenylethynyl bromide, prepared in ethereal solution from ethyl bromide and *p*-methoxyphenylacetylene; the product is trianisylethynylcarbinol,  $\text{OH}\cdot\text{C}(\text{C}:\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_3$ , an amorphous, slightly brown powder, which darkens on keeping, and sinters and melts at  $55\text{--}60^{\circ}$ . It is reduced in absolute alcoholic solution by means of platinum black and hydrogen, to give trianisylethylcarbinol, small, fragile, snow-white needles, m. p.  $74^{\circ}$ .

Phenylethynyldianisylethynylcarbinol,  $\text{OH}\cdot\text{C}(\text{C}:\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2\cdot\text{C}:\text{CPh}$ , a brown powder, is obtained by the interaction of phenylpropionyl chloride (1 mol.) and magnesium *p*-methoxyphenylethynyl bromide (4 mols.) in ethereal solution at  $-20^{\circ}$ .

The halochromy of these and other carbinols is investigated at  $-78^{\circ}$  in solutions in various inert solvents. Trianisylethynylcarbinol gives a *perchlorate*,  $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}:\text{C})_3\text{C}\cdot\text{ClO}_4\ldots\text{HClO}_4$ , an explosive powder having a green lustre, which is deep blue in solution, but the perchlorates of diphenylphenylethynylcarbinol and triphenylethynylcarbinol are too soluble to be isolated. Trianisylethynylcarbinol gives an insoluble, dark blue *sulphate*, and a deep blue *hydrochloride*, which has a green lustre, and decomposes at the ordinary temperature with evolution of hydrogen chloride. With sulphuric acid or hydrochloric acid, phenylethynyldianisylethynylcarbinol and phenyldianisylethynylcarbinol give, respectively, blue and orange-red colorations. Additive compounds with *stannic chloride* are as follows: triphenylcarbinol, orange-yellow,  $\text{CPh}_3\cdot\text{OH}\ldots 2\text{SnCl}_4$ , which gradually loses hydrogen chloride and stannic chloride when kept at the ordinary temperature in a vacuum; trianisylcarbinol, phenyldianisylcarbinol, or diphenylphenylethynylcarbinol, orange-red; triphenylethynylcarbinol, dark violet, and trianisylethynylcarbinol, bluish-violet, which pass, when kept in a vacuum, to substances of the composition  $\text{C}(\text{C}:\text{C}\cdot\text{R})_3\cdot\text{O}\cdot\text{SnCl}_3$ . Trianisylethynylcarbinol, phenyldianisylethynylcarbinol, triphenylethynylcarbinol, phenyldiphenylethynylcarbinol, and diphenylphenylethynylcarbinol do not give coloured solutions in trichloroacetic acid or liquid sulphur dioxide, but the first gives a dark blue, and the second a blue, solution in nitric acid.

Diphenylphenylethynylcarbinol may be recovered quantitatively from its dark orange-red solution in concentrated sulphuric acid by neutralising by means of ammonia; but if the solution is kept until it is yellow, phenyl phenylstyryl ketone is obtained. Triphenylethynylcarbinol may also be recovered from its solution in sulphuric acid, but not trianisylethynylcarbinol, which evidently

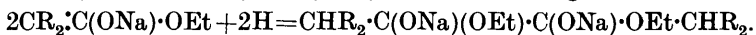
undergoes transformation very readily; but the first experiment shows that the halochromic phenomena are given by the untransformed material. Moreover, both the last-mentioned compounds, and also triphenylcarbinol, may be recovered by decomposing the double tin salts at  $-78^{\circ}$  by the gradual addition of moist acetone to its solution in chloroform and ethyl chloride.

Straus and Dützmann (A., 1922, i, 148) have found that the addition of groups to derivatives of chlorodiphenylmethane influence the intensity but not the depth of the colour. The same conclusion is now drawn with regard to the carbinols investigated, any of which, with different solvents, gives either a colourless solution, or solutions having the same shade of colour, although of varying intensity.

Objection is taken to the view of Skraup and Freundlich (A., 1923, i, 667), that the halochromy of unsaturated ketones with acids or metallic halides is a reaction of the ethylene linking, because exactly the same type of additive compound with stannic chloride,  $2X \dots SnCl_4$ , is formed by a great number of alcohols and ketones, quite irrespective of whether they are saturated or not, or of the extent to which they are unsaturated.

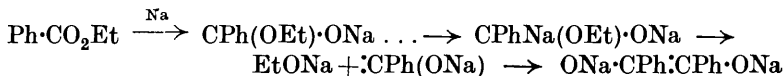
W. S. N.

**Formation of  $\alpha\beta$ -Ketone-alcohols (Acyloins) and  $\alpha\beta$ -Diketones by the Action of Alkali Metals on Aliphatic Esters.** H. SCHEIBLER and F. EMDEN (*Annalen*, 1923, 434, 265—284).—(1) *Mechanism of the Reaction during the Synthesis of Acyloins*.—The mechanism suggested by Bouveault and Locquin (A., 1906, i, 782) is difficult to reconcile with the mechanism of ethyl acetoacetate formation. It is now shown that the same compound,  $CH_2:C(ONa) \cdot OEt$ , may be initially formed in both syntheses. In the ethyl acetoacetate synthesis, each molecule of the initial compound at once reacts with ethyl acetate (present in excess), but in presence of a solvent and with deficiency of ethyl acetate, this second process is delayed, hydrogenation occurring instead:



The latter compound then reacts with the excess of sodium present, as follows:  $CHR_2:C(ONa)(OEt) \cdot C(ONa)(OEt)CHR_2 + 2Na = 2H + 2EtONa + CR_2:C(ONa) \cdot C(ONa):CR_2$   $CR_2:C(ONa) \cdot C(ONa):CR_2 + 2H = CHR_2:C(ONa):C(ONa)CHR_2$ , the product being the disodium derivative of acyloin in the case of ethyl acetate. In some cases (cf. Scheibler, Ziegner, and Pfeffer, A., 1923, i, 82) hydrogenation is more profound.

Ethyl  $\alpha\alpha$ -dimethylpropionate and benzoate, which are incapable of affording enolic derivatives, are very slowly converted by sodium, in ethereal solution, into  $\alpha\beta$ -ketone alcohols, unaccompanied, however, by  $\alpha\beta$ -diketones. Metal ketyls are probably the intermediaries in such processes:



(2) *Autoxidation of Endiolates*.—The disodium (or dipotassium) derivatives of the type,  $CHR_2:C(ONa):C(ONa)CHR_2$ , on decom-

position with water, afford acyloins, but if the experiment is carried out without excluding oxygen, autoxidation of the metal derivative (for which the name *endiolate* is proposed) occurs, an  $\alpha\beta$ -diketone resulting. Occasionally, a benzil-benzilic acid change also occurs, *e.g.*, with the potassium derivative from ethyl *isobutyrate*, when  $\alpha$ -hydroxy- $\beta$ -methyl- $\alpha$ -isopropylbutyric acid results. The endiولات, which are highly coloured, react with ethyl bromide (*cf.* Bouveault and Locquin, *loc. cit.*) to give the corresponding *O*-ethers. The di-potassium derivative of pyrocatechol may be regarded as an endiolate, when its autoxidation falls into line with that of the compounds under discussion.

Ethyl dibenzylacetate (1 mol.) when left in ethereal solution over powdered sodium (2 atoms), in absence of air, affords a yellow product which, on decomposition with water, gives (83% yield) *tetrabenzylacetoin* ( $\gamma$ -hydroxy- $\alpha\alpha\delta\delta$ -*tetrabenzylbutane*- $\beta$ -one), colourless leaflets, m. p. 148—149°, together with a little  $\alpha\alpha\delta\delta$ -*tetrabenzylbutane*- $\beta\gamma$ -dione, yellow needles, m. p. 121—122°. The former substance does not react with hydroxylamine or with phenylhydrazine. When potassium is substituted for sodium in the above preparation, a red reaction mixture is obtained (affording the same decomposition products as before) and this, on treating with ethyl bromide, gives  $\beta\gamma$ -diethoxy- $\alpha\alpha\delta\delta$ -*tetrabenzyl*- $\Delta^{\beta}$ -butene (m. p. 158°), which does not respond to bromine or permanganate tests for unsaturation, and is unaffected by prolonged heating with aqueous hydrobromic acid or alcoholic potassium hydroxide. A mixture of hydriodic acid and phenol effects the conversion of the diethoxy-into the dihydroxy-compound.

The above diketone is readily obtained (1) by aërating the reaction mixture (affording otherwise the acetoin), or (2) by the action of nitric acid on the acetoin. The diketone does not react with hydroxylamine, phenylhydrazine, or *m*-tolylenediamine. Hydrogen peroxide converts it, quantitatively, into dibenzylacetic acid, whilst on fusion with alkali it is partly converted into the acetoin. The moist ethereal solution is rapidly decolorised in sunlight, with formation of the acetoin, the original colour reappearing on excluding light. A yellow oil probably containing an aldehyde, b. p. 160—200°, is formed in this process.

Sodamide converts ethyl dibenzylacetate into a mixture of dibenzylacetamide and *tetrabenzylldiacetamide* (m. p. 172—173°).

By the action of sodium or potassium on various esters, with or without admission of air, various acyloins, etc., have been obtained in an impure state:  $\delta$ -hydroxy- $\alpha\eta$ -diphenyl- $\alpha\eta$ -dimethylhexane- $\gamma$ -one (from ethyl  $\beta$ -phenyl- $\alpha$ -methylpropionate) has b. p. 225—235°/25 mm.;  $\delta$ -hydroxy- $\alpha\eta$ -diphenylhexane- $\gamma$ -one (from ethyl  $\beta$ -phenylpropionate) has b. p. 240—265°/38 mm.; and  $\alpha\eta$ -diphenyl- $\alpha\eta$ -dimethylhexane- $\gamma\delta$ -dione has b. p. 225—230°/27 mm. E. E. T.

**The Action of Nitric Acid on Naphthalic Anhydride.** M. A. MIHĂILESCU and A. STEOPOE (*Bull. Acad. Sci. Roumaine*, 1923, 8, 102—110).—Contrary to statements in the literature, naphthalic anhydride can be nitrated by nitric acid, the progress of the reaction

depending on the concentration of acid, duration of boiling, and the amount of nitrous acid present. Some oxidation may also occur. The best results are obtained by boiling naphthalic anhydride with fuming nitric acid ( $d$  1.47), when there is obtained a mixture of 3-nitronaphthalic anhydride, m. p. 251—252° (other authors give 247—249°) and a dinitronaphthalic anhydride, yellow needles, m. p. 207—208°. There is also obtained a small quantity of an unknown substance, m. p. 175° (decomp.), giving a red coloration with alkali; some resin is also formed. Naphthalic anhydride, or its nitro-compounds, should not be recrystallised from nitric acid, as recommended by others, but from acetic acid. E. H. R.

**Action of "Aspirin" on Urethane.** E. COMANDUCCI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1921, [iii], 27, 48—52).—At the ordinary temperature, urethane and *o*-acetoxybenzoic acid do not react, but when heated together they give rise to products varying with the proportions of the compounds taken. The reaction commences at about 90°, ethyl acetate and salicylurethane being formed,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{OAc} + \text{NH}_2\cdot\text{CO}\cdot\text{OEt} = \text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{NH}_2 + \text{CH}_3\cdot\text{CO}_2\text{Et}$ . At a temperature exceeding 130°, the mass turns yellow, with formation of acetic acid and a little ethyl acetate, whilst at 180—182° carbon dioxide and ammonia are produced and at about 200° phenol, salicylamide, the nitrile of salicylic acid, and carbonylsalicylamide.

*Salicylurethane* forms white crystals, m. p. 113°; *salicylamide*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$ , forms yellow leaflets, m. p. 133°, and in aqueous or alcoholic solution gives an intense violet coloration with ferric chloride; the nitrile of *salicylic acid*,  $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CN})_x$ , is a yellow compound, m. p. 280°. *Carbonylsalicylamide* (annexed formula), forms straw-yellow laminae, m. p. 221°, and in alcoholic solution gives a pink coloration with ferric chloride. T. H. P.

**Addition to Compounds with Marked Conjugation. II. Addition of Hydrogen and Bromine to Cinnamylidene Derivatives.** K. VON AUWERS and W. MÜLLER (*Annalen*, 1923, 434, 165—184).—Cinnamylidene derivatives are studied in a similar manner to that used in the case of analogous aliphatic acids (this vol., i, 8). Cinnamylideneacetic acid gives an  $\alpha\beta$ -dibromide, crotonylidene- and cinnamylidene-malonic esters giving  $\gamma\delta$ -dibromides.

Reduction of cinnamylidenemalonic acid (cf. Thiele and Meisenheimer, A., 1899, i, 603) gives, besides the  $\alpha\delta$ -dihydro-acid (*anilide*, m. p. 83—85°),  $\delta$ -phenyl- $\gamma$ -valerolactone- $\alpha$ -carboxylic acid, yellow crystals, m. p. 123—124° (with loss of carbon dioxide). The latter acid on heating, gives  $\delta$ -phenyl- $\gamma$ -valerolactone, whilst the lactonic acid is also formed by treating the above  $\alpha\delta$ -dihydro-acid successively with hydrogen bromide and water.

Cinnamylideneacetic acid and bromine afford a mixture of *cis*- $\alpha$ -bromocinnamylideneacetic acid (m. p. 182—183°; methyl ester, m. p. 60—61°), and  $\beta$ -bromo- $\gamma$ -benzylidenebutyric acid, m. p. 135—136°. The latter, on ozonolysis, affords benzaldehyde, and on treatment with sodium carbonate gives a mixture of cinnamylideneacetic acid

and phenylbutadiene. The above *cis*-acid is best obtained from the cinnamylideneacetic acid-bromine mixture by the action of sodium acetate.

The last-mentioned mixture, which at the outset contains little but  $\alpha\beta$ -dibromo- $\gamma$ -benzylidenebutyric acid, on ozonolysis (before secondary reactions set in) and subsequent treatment of the product with semicarbazide, gives a mixture of the semicarbazones of benzaldehyde and of bromofumaric (*maleic*?) semialdehyde (m. p. 247°), together with a small quantity of a substance (m. p. 248—250°) which is probably  $\beta$ -bromoacraldehyde semicarbazone.  $\alpha$ -Bromoacraldehyde semicarbazone, prepared for comparison, decomposes at 160°.

Methyl cinnamylideneacetate with bromine affords methyl  $\alpha\beta$ -dibromo- $\gamma$ -benzylidenebutyrate (m. p. 80—81°), which with cold sodium hydroxide, followed by the hot alcoholic reagent, is converted into trans- $\alpha$ -bromocinnamylideneacetic acid (m. p. 194°), this being convertible into the methyl ester, and obtainable again therefrom without change of configuration. Ozonolysis of the ester of m. p. 80—81° gives, after treating the product with semicarbazide, a mixture of benzoic acid, benzaldehyde semicarbazone, the above semicarbazone melting at 247°, and the corresponding methyl ester,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{CBr}\cdot\text{CO}_2\text{Me}$ , m. p. 214—215°. The dibromo-ester (m. p. 80—81°), with bromine in sunlight, gives  $\alpha\beta\gamma\delta$ -tetrabromo- $\delta$ -phenylbutyric acid.

The  $\gamma\delta$ -dibromide of methyl cinnamylidenemalonate, on treatment with potassium acetate, gives methyl  $\gamma$ -bromocinnamylidenemalonate (m. p. 86.5—88.5°), which on ozonolysis affords benzoic, oxalic, and mesoxalic acids, the latter being identified as the *p*-nitrophenylhydrazone, m. p. 202°.

$\gamma$ -Bromo- $\beta$ -hydroxy- $\gamma$ -benzylidenebutyric acid (from malonic acid,  $\alpha$ -bromocinnamaldehyde, and pyridine) has m. p. 113—114°, and is converted by hydrochloric acid into  $\gamma$ -bromocinnamylideneacetic acid, m. p. 137.5—138.5°, which forms methyl and ethyl esters melting, respectively, at 59—60° and 56—57°, and with bromine affords  $\alpha\beta\gamma$ -tribromo- $\gamma$ -benzylidenebutyric acid (m. p. 146—147°). The latter acid, on ozonolysis, gives benzaldehyde as the only recognisable product.

E. E. T.

**Molecular Rearrangements of the Camphor Series. XIV. Structure of isoCampholactone.** P. K. PORTER and W. A. NOYES (*J. Amer. Chem. Soc.*, 1923, 45, 2366—2373).—The following proof is offered that isocampholactone (Noyes, A., 1895, i, 295, 552) is the lactone of 3-hydroxy-1:2:3-trimethylcyclopentane-1-carboxylic acid.

When it is oxidised by means of nitric acid, there are formed nitroisocampholactone and a lactonic acid,  $\begin{array}{c} \text{O} \\ | \\ \text{CO} \end{array} > \text{C}_7\text{H}_{11}\cdot\text{CO}_2\text{H}$  (Noyes and Homberger, A., 1911, i, 110). The latter is converted successively into the disodium and the *disilver* salts of the hydroxydicarboxylic acid; the disilver salt is transformed by means of ethereal methyl iodide into the *dimethyl* ester, b. p. 156—160°/25

mm., which is only very slightly attacked by the action of Beckmann's chromic acid mixture, even after keeping for twelve hours. Hence the hydroxyl group is tertiary. The lactonic acid is converted by heating with phosphorus pentachloride into the acid chloride, which is not isolated, but is treated in dry ethereal solution with cold concentrated ammonia solution ( $d$  0.9), whereby an *amide*, m. p. 162—163°, is obtained. The action of cold sodium hypobromite solution on the amide gives an oily *keto-acid* (*barium* salt,  $+2\text{H}_2\text{O}$ ), from which it follows that the amide and hydroxyl radicles are attached to the same carbon atom. This keto-acid reacts in ethereal solution with magnesium methyl iodide to give *isocampholactone*, and a small quantity of an *acid*, m. p. 96—97°,  $[\alpha]_D^{25} -37.5^\circ$  (in alcohol), probably the *trans*-hydroxydicarboxylic acid. These reactions can only be explained if *isocampholactone* has the structure suggested, whilst the lactonic acid formed from it by oxidation is the lactone of 3-hydroxy-1 : 2-dimethylcyclopentane-1 : 2-dicarboxylic acid. The amide is then the 3-amide of this acid, and the keto-acid is 1 : 2-dimethylcyclopentan-3-one-1-carboxylic acid.

It is considered probable that the 2-methyl group in *isocampholactone* is in the *trans*-position with respect to the other two methyl groups, whilst in *campholactone* all three lie in the same plane.

Nitro*isocampholactone*, which presumably has the nitro-group in the position 2, is converted almost quantitatively, on treatment with warm 2*N*-sodium hydroxide solution, into acetone and 2-nitro-1-methylcyclobutane-1-carboxylic acid, m. p. 70—72°,  $[\alpha]_{435}^{25} -246.81^\circ$ ,  $[\alpha]_{546.1}^{25} -119.3^\circ$ ,  $[\alpha]_{578}^{25} -101.51^\circ$ ,  $[\alpha]_D^{25} -87.31^\circ$ , *barium* salt, needles, *silver* salt, *methyl* ester, b. p. 120—125°/5 mm. (slight decomp.),  $[\alpha]_{546.1}^{25} -93.2^\circ$ ,  $[\alpha]_{578.7}^{25} -80.2^\circ$ ,  $d^{20}$  1.16907,  $n$  1.4416. The *amide*, m. p. 94—95°, is obtained by decomposing nitro*isocampholactone* by means of concentrated ammonia solution. The acid, its amide, or its methyl ester gives a blue coloration with nitrous acid, which demonstrates the presence of a secondary nitro-group and a cyclobutane ring, rather than a tertiary nitro-group and a cyclopropane ring. This conclusion is supported by the fact that the amide gives a *sodium* salt, which is hydrolysed to the cyclobutane acid by means of dilute sulphuric acid or of sodium hydroxide solution; with the latter reagent, a blue coloration is produced, and nitrous oxide is evolved. Similarly, the methyl ester gives a *sodium* salt, which gives a blue solution when hydrolysed by means of dilute sulphuric acid, nitrous oxide being generated. W. S. N.

**Preparation of Mixed Esters of Phthalic Acid.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 371046; from *Chem. Zentr.*, 1923, iv, 538).—Basic mixed esters of phthalic acid of the general formula,  $\text{Aryl} \cdot (\text{CO}_2\text{R})^1 \cdot (\text{CO}_2\text{R}')^2$ , where aryl denotes phenyl or substituted phenyl,  $\text{R} = \text{alkyl}$ , and  $\text{R}' = \text{an alkylamine group}$  such as  $-\text{CH}_2 \cdot \text{CH}_2 \cdot \text{N}(\text{Alkyl})_2$ , are prepared by the action of a phthalic ester chloride on an alkylamine, or of a hydrogen phthalate on a halogenalkyldialkylamine. *Methyl diethylaminoethyl*



*phthalate*,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot[\text{CH}_2]_2\cdot\text{NEt}_2$ , is prepared from methyl phthalate chloride and diethylaminoethanol; it is a yellow oil; the *hydrochloride* has m. p.  $114^\circ$ . *Benzyl diethylaminoethyl phthalate*, from benzyl hydrogen phthalate and chloroethyl diethylamine, is a light yellow oil. *Ethyl diethylaminoethyl 3 : 6-dichlorophthalate*,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{CO}_2\cdot[\text{CH}_2]_2\cdot\text{NEt}_2$ , from chloroethyldiethylamine and ethyl hydrogen 3 : 6-dichlorophthalate, is a light yellow oil; the *hydrochloride* has m. p.  $165^\circ$ . *Methyl dimethylaminoethyl phthalate* is a yellow oil; the *hydrochloride* has m. p.  $103^\circ$ .  
G. W. R.

**Some Derivatives of Deoxycholic Acid.** J. PASCUAL VILA (*Anal. Fis. Quím.*, 1923, **21**, 397—400).—*Methyl deoxycholate* prepared by esterification of deoxycholic acid, forms needles, m. p.  $75$ — $78^\circ$ . By the action on it of gaseous carbonyl chloride, a *chloroformate*,  $\text{OH}\cdot\text{C}_{23}\text{H}_{37}(\text{O}\cdot\text{COCl})\cdot\text{CO}_2\text{Me}$ , crystals, m. p.  $138$ — $139^\circ$ , is obtained. By heating this at  $140^\circ$ , *methyl chlorohydroxycholanate*,  $\text{OH}\cdot\text{C}_{23}\text{H}_{37}\text{Cl}\cdot\text{CO}_2\text{Me}$ , needles, m. p.  $121$ — $122^\circ$ , is obtained.  
G. W. R.

**Preparation of an isoDeoxycholic Acid.** J. PASCUAL VILA (*Anal. Fis. Quím.*, 1923, **21**, 390—396; cf. Boedecker and Volk, A., 1922, i, 1027).—An *isodeoxycholic acid* was prepared by the author by the following method. Methyl cholate is treated with a current of carbonyl chloride, whereby a chloroformic ester, having the composition  $\text{C}_{23}\text{H}_{36}(\text{OH})_2(\text{O}\cdot\text{COCl})\cdot\text{CO}_2\text{Me}$  is obtained. It is crystalline and has m. p.  $140$ — $141^\circ$  (decomp.). This compound is heated above its melting point and the product treated with sodium ethoxide in ethyl-alcoholic solution, whereby *chlorodihydroxycholanolic acid*,  $\text{C}_{23}\text{H}_{36}\text{Cl}(\text{OH})_2\cdot\text{CO}_2\text{H}$ , is obtained, having m. p.  $196$ — $197^\circ$ . Treatment of this compound with sodium amyl-oxide yields *dihydroxycholenic acid*,  $\text{C}_{23}\text{H}_{35}(\text{OH})_2\cdot\text{CO}_2\text{H}$ , which is obtained in two forms, namely, large prisms or needles, m. p.  $216$ — $217^\circ$ , and needles, m. p.  $181^\circ$ . Hydrogenation of the product having m. p.  $216$ — $217^\circ$  in the presence of palladium yields  $\beta$ -*isodeoxycholic acid*,  $\text{C}_{23}\text{H}_{37}(\text{OH})_2\cdot\text{CO}_2\text{H}$ , m. p.  $226$ — $227^\circ$ . The constitution of these compounds is discussed.  
G. W. R.

**Hyoglycodeoxycholic Acid and Hyodeoxycholic Acid.** A. WINDAUS and A. BOHNE (*Annalen*, 1923, **433**, 278—287).—A preliminary account of this work has already appeared (A., 1923, i, 922).

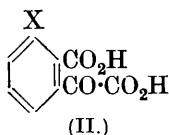
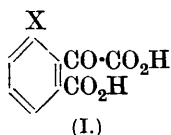
Hyodeoxycholic acid, small, four-sided leaflets, m. p.  $196$ — $197^\circ$  (potassium salt, slender needles), is obtained by the action of 15% potassium hydroxide solution at  $135^\circ$  on the sodium salt of hyoglycodeoxycholic acid, hexagonal leaflets, m. p.  $215$ — $216^\circ$  (from glacial acetic acid or ethyl acetate), or m. p.  $150$ — $151^\circ$  (from aqueous alcohol), *methyl ester*, small, elongated leaflets, m. p.  $215$ — $216^\circ$ . It is oxidised by means of chromic anhydride in cold glacial acetic acid—concentrated sulphuric acid solution, to *dehydro-*

*hyodeoxycholic acid*,  $C_{24}H_{36}O_4 \cdot 2H_2O$ , m. p. 203—204°,  $+H_2O$ , four-sided leaflets, m. p. 161.5—162° (*disemicarbazone*, indefinite crystals, *methyl ester*, small leaflets, m. p. 139°, *ethyl ester*, spangles, m. p. 140°). This diketo-acid is reduced by means of zinc amalgam in boiling, glacial acetic acid—concentrated hydrochloric acid solution to *hyocholanic acid*, leaflets, m. p. 162°, which is identical with the acid,  $C_{24}H_{40}O_2$ , obtained by Windaus and Neukirchen (A., 1920, i, 41) from cholestan, and gives the following esters: *methyl*, small prisms or leaflets, m. p. 90—91°; *ethyl*, glistening leaflets, m. p. 84°; *propyl*, slender needles, m. p. 101°; *n-butyl*, fan-shaped aggregates, m. p. 87°. *Propyl cholanate*, prisms, has m. p. 56—57°; *butyl cholanate*, prisms, has m. p. 53°. When hyodeoxycholic acid is heated at 320—340° under 15 mm. pressure, 2 mols. of water are eliminated, with formation of *hyocholadienic acid*,  $C_{24}H_{36}O_2$ , rosettes of small, slender needles, sinters at 135°, m. p. 142°. The reduction of this unsaturated acid in glacial acetic acid solution by means of palladium black and hydrogen gives a mixture, m. p. 142° (indefinite), of cholanic and hyocholanic acids, in contrast with the behaviour of the diketo-acid (above), which gives exclusively hyocholanic acid. Evidently the asymmetry of the carbon atom 5 (cf. A., 1923, i, 922) is lost in the unsaturated acid, which can only mean that there is a double bond between the atoms 5 and 4, or 5 and 6. Hence one of the two hydroxyl groups in hyodeoxycholic acid is attacked in the position 4 or 6. W. S. N.

**Syntheses of Dibasic Acids derived from Ethers.** M. GODCHOT (*Compt. rend.*, 1923, 177, 1224—1226).—*Ethyl  $\alpha$ -diphenyldiglycollate*,  $CO_2Et \cdot CHPh \cdot O \cdot CHPh \cdot CO_2Et$  (from the sodium derivative of ethyl phenylglycollate and ethyl  $\alpha$ -bromophenylacetate), on hydrolysis affords the corresponding *acid*, needles, decomposing without melting at 300°. *Ethyl  $\alpha$ -phenyl- $\alpha'$ -methyl-diglycollate* (from the sodium derivative of ethyl phenylglycollate and ethyl  $\alpha$ -bromopropionate), has b. p. 180—190°/15 mm. (with some decomposition), the *acid* (needles) having m. p. 188°. *Ethyl  $\alpha$ -phenyldiglycollate* (from the sodium derivative of ethyl phenylglycollate and ethyl chloroacetate) has b. p. 182—184°/10 mm.,  $d_{20}^{21}$  1.127,  $n_D^{20}$  1.4925. The corresponding *acid* is a syrup, b. p. 203°/15 mm. (slight decomposition). The *diamide* (from the ester and ammonia) melts at 159—160°. E. E. T.

**Benzo-polymethylene Compounds. X. Oxidative Degradation of Tetrahydronaphthalene and Substituted Tetrahydronaphthalenes to Phthalonic Acid and Phthalic Acids.** J. VON BRAUN [with O. BRAUNSDORF, P. ENGELBERTZ, E. HAHN, G. HAHN, O. HAINBACH, W. KREDEL, and K. LARBIG] (*Ber.*, 1923, 56, [B], 2332—2343).—Phthalonic acid may be prepared by the oxidation of naphthalene by alkaline permanganate, but the process suffers from the drawbacks that it can only be applied with very dilute solutions, and the product is contaminated with phthalic acid. Tetrahydronaphthalene, on the other hand, can be almost quantitatively oxidised to phthalonic acid in the presence of very

small volumes of liquid. *ar*-Substituted tetrahydronaphthalenes



can be similarly converted into mixtures of the two possible phthalonic acids (cf. annexed formulæ, I and II), the separation of which from one another is scarcely possible when the substituent is in the

$\beta$ -position, but much easier when it is in the  $\alpha$ -position; in the latter case, the isomerides are frequently formed in very unequal amount and, also, an acid of type I is converted by alcohol and hydrogen chloride into the normal ester, whereas a compound of type II yields the hydrogen ester under these conditions. All substituted phthalonic acids resemble the parent acid in their ready oxidisability by permanganate in acid solution. Since the isomerides I and II yield the same phthalic acids, the preparation of the latter can be effected far more advantageously by two successive actions from substituted tetrahydronaphthalenes than from substituted naphthalenes.

Phthalonic acid is readily prepared by the addition of the requisite quantity of finely-divided permanganate to a hot mixture of 1 : 2 : 3 : 4-tetrahydronaphthalene and water. If the reagents are mixed in the reverse order, the oxidation almost invariably proceeds too far, with the production of phthalic acid. The latter substance is very easily prepared by the oxidation of tetrahydronaphthalene in alkaline solution, removal of the manganese dioxide, acidification of the solution, and further oxidation by permanganate.

6-Nitro-1 : 2 : 3 : 4-tetrahydronaphthalene is converted successively into a mixture of nitrophthalonic acids and 4-nitrophthalic acid, m. p.  $160^{\circ}$ . 5-Nitro-1 : 2 : 3 : 4-tetrahydronaphthalene yields 2-nitro-6-carboxyphenylglyoxylic acid mixed with smaller quantities of 3-nitro-2-carboxyphenylglyoxylic acid and traces of 3-nitrophthalic acid. The acid first named is conveniently purified through its sparingly soluble barium salt ( $+5\text{H}_2\text{O}$ ). It has m. p.  $185^{\circ}$ ; the *hemihydrate* is also described. The *ammonium* salt ( $+8\text{H}_2\text{O}$ ), the *sodium* salt ( $+2\text{H}_2\text{O}$ ), and the *diethyl* ester, m. p.  $65-66^{\circ}$ , are prepared. The isomeric 3-nitro-2-carboxyphenylglyoxylic acid ( $+ \text{H}_2\text{O}$ ) has m. p.  $191^{\circ}$ . The mixture of 5- and 6-nitro-1 : 2 : 3 : 4-tetrahydronaphthalenes (obtained by the mono-nitration of the hydrocarbon) is transformed by successive oxidation in alkaline and acid solution into a mixture of nitrophthalic acids which, when esterified, gives a mixture of ethyl 4-nitrophthalate, m. p.  $35^{\circ}$ , b. p.  $213^{\circ}/17 \text{ mm.}$ , and ethyl hydrogen 3-nitrophthalate, m. p.  $111^{\circ}$ . Hydrolysis of the ester gives the two nitrophthalic acids in the homogeneous condition.

5-Chloro-1 : 2 : 3 : 4-tetrahydronaphthalene, a colourless liquid, b. p.  $115-116^{\circ}/12 \text{ mm.}$ , is prepared in somewhat unsatisfactory yield from the corresponding amine. It is converted by permanganate in alkaline solution into a mixture of acids which are separated by the esterification method. The hydrogen esters are hydrolysed to 3-chlorophthalic acid and 3-chloro-2-carboxyphenylglyoxylic acid, which is isolated in the form of its condensation

product with phenylhydrazine,  $\text{C}_6\text{H}_5\text{Cl} < \begin{smallmatrix} \text{C}(\text{CO}_2\text{H})\cdot\text{N} \\ \text{CO} \text{---} \text{NPh} \end{smallmatrix}$ , m. p. 155°.

The neutral ester is *ethyl 2-chloro-6-carbethoxyphenylglyoxylate*, b. p. 195—197°/13 mm.; it is hydrolysed to 2-chloro-6-carboxyphenylglyoxylic acid, which is analysed as the phenylhydrazine compound, m. p. 215°. The mixture of 5- and 6-chloro-1 : 2 : 3 : 4-tetrahydronaphthalenes, b. p. 117—130°/17 mm., obtained by the chlorination of the hydrocarbon at 10° in the presence of iodine, gives a mixture of chlorophthalic acids in about 70% yield. Separation is effected by esterification. *Ethyl 4-chlorophthalate* is a colourless liquid, b. p. 173—174°/16 mm., which is hydrolysed to 4-chlorophthalic acid, m. p. 157°. *Ethyl hydrogen 3-chlorophthalate* crystallises in coarse prisms, m. p. 118—119°, and gives 3-chlorophthalic acid, m. p. 186—187°; the *imide*, m. p. 233°, and the *chloride*, b. p. 169—171°/16 mm., of the latter are described.

5 : 6 : 7 : 8-Tetrachloro-1 : 2 : 3 : 4-tetrahydronaphthalene, m. p. 172°, b. p. 180°/26 mm., is readily prepared by exhaustive chlorination of tetrahydronaphthalene in diffuse daylight. It is converted by bromine in the presence of boiling carbon disulphide into a *dibromide* (presumably an  $\alpha\beta$ -disubstituted compound), m. p. 142°, which is transformed by sodium ethoxide into tetrachloronaphthalene, m. p. 198°.

5-Bromo-1 : 2 : 3 : 4-tetrahydronaphthalene (cf. Smith, T., 1904, 85, 728) is similarly oxidised to a mixture of 3-bromophthalic acid, 2-bromo-6-carboxyphenylglyoxylic acid, and 3-bromo-2-carboxyphenylglyoxylic acid. The substituted glyoxylic acids could not be isolated in a homogeneous condition. *Ethyl 2-bromo-6-carboxyphenylglyoxylate* has b. p. 202—206°/13 mm. Successive oxidation of the mixture of  $\alpha$ - and  $\beta$ -bromotetrahydronaphthalenes in alkaline and acid solution gives 4-bromophthalic acid, m. p. 171—172° (*ethyl ester*, b. p. 190—191°/16 mm.), and 3-bromophthalic acid, m. p. 188° (*ethyl hydrogen ester*, needles, m. p. 127—128°).

5-Sulphonamido-1 : 2 : 3 : 4-tetrahydronaphthalene is readily converted into 2-sulphonamido-4-carboxyphenylglyoxylic acid, lustrous leaflets, m. p. 181°, which is smoothly converted into the corresponding *anhydride*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3 < \begin{smallmatrix} \text{SO}_2\cdot\text{NH} \\ \text{CO} \text{---} \text{CO} \end{smallmatrix}$ , colourless crystals,

m. p. 261°. Either compound is converted by phenylhydrazine into the *phenylhydrazone*, m. p. 244°. *Ethyl 2-sulphonamido-6-carbethoxyphenylglyoxylate* has m. p. 107—108° after slight previous softening. The phthalonic acid is smoothly oxidised further to 3-sulphamidophthalic acid, m. p. 165°, which is also readily prepared from 5-sulphonamidotetrahydronaphthalene in two stages. 6-Sulphonamidotetrahydronaphthalene gives a mixture of the possible substituted phthalonic acids, which is smoothly oxidised in acid solution to 4-sulphonamidophthalic acid, m. p. 198—200° (*ethyl ester*, slender needles, decomp. 90° after softening at 80°).

6-Thiol-1 : 2 : 3 : 4-tetrahydronaphthalene (cf. Schroeter, A., 1922, i, 126) is easily transformed into the corresponding *benzoyl* derivative, m. p. 98°, and the *disulphide*, m. p. 66°. It is converted by alkali and methyl iodide into 6-methylthiol-1 : 2 : 3 : 4-tetrahydronaphthal-

*ene*, a colourless, almost odourless liquid, b. p. 158—159°/10 mm. 5-Thiol-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 141—143°/11 mm., is prepared from tetrahydronaphthalene-5-sulphonyl chloride; it is transformed by methyl sulphate or methyl iodide into 5-methylthiol-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p. 158—160°/12 mm. Oxidation of the 6-methylthiol in alkaline solution gives a mixture of ketonic acids which can scarcely be caused to crystallise; if, however, the oxidation is continued in acid solution, 4-methylsulphonylphthalic acid, m. p. 191° (decomp.), is readily obtained. The acid passes when heated into the corresponding *anhydride*, m. p. 183—184°, from which the *imide*, m. p. 263° (the *potassium* salt is described), is prepared by the action of ammonia at 200—210°. Ethyl 4-methylsulphonylphthalate has b. p. about 250°/11 mm. If the anhydride is treated with benzene and aluminium chloride at 80°, it is transformed into the acid,  $\text{SOMe}_2 \cdot \text{C}_6\text{H}_3\text{Bz} \cdot \text{CO}_2\text{H}$ , m. p. about 230°, which is converted by sulphuric acid containing 5% of anhydride at 100° into 2-methylsulphonylanthraquinone (cf. Gattermann, A., 1912, i, 998). 5-Methylthioltetrahydronaphthalene is converted by oxidation in alkaline solution into 2-methylsulphonyl-6-carboxyphenylglyoxylic acid, colourless, crystalline granules, decomp. 250°, which is conveniently purified through its *barium* salt, lustrous leaflets ( $+3\text{H}_2\text{O}$ ). Ethyl 2-methylsulphonyl-6-carboethoxyphenylglyoxylate is a very viscous liquid, b. p. 230°/12 mm. The oxidation of the phthalonic acid in acid solution proceeds with unexpected slowness and leads to the production of 3-methylsulphonylphthalic acid, m. p. 187° (decomp.) in only moderate yield. The new acid is easily transformed into the *anhydride*, b. p. 240°/11 mm., m. p. 182—183°, and thence into the *imide*, colourless leaflets, m. p. 264—266° (the *potassium* salt is described).

H. W.

**Simplification of the Gattermann Synthesis of Hydroxy-aldehydes.** R. ADAMS and I. LEVINE (*J. Amer. Chem. Soc.*, 1923, 45, 2373—2377).—The use of anhydrous hydrogen cyanide in the Gattermann synthesis of hydroxy-aldehydes is avoided by using zinc cyanide instead, in the proportion of 1.5 mols. for 1 mol. of phenol. Somewhat more ether is also recommended, about 150 or 200 c.c. to every 20 g. of phenol; the quantity of coloured by-products is thus reduced. The dry ether may be replaced by dry chloroform, but in this solvent a more highly coloured product is obtained. Using dry ether, and passing in anhydrous hydrogen chloride rapidly for one and a half hours, and then more slowly for thirty minutes, the following yields of hydroxy-aldehyde are obtained from the phenols mentioned: resorcinol, 95%; orcinol, 85%;  $\beta$ -naphthol, 85%;  $\alpha$ -naphthol, 72%; pyrogallol, 45%. The imide hydrochloride which actually separates is decomposed by boiling with water or dilute alcohol. Anhydrous zinc cyanide for this reaction is produced by treating aqueous sodium cyanide with magnesium chloride to precipitate any carbonate or hydroxide present, filtering, and adding alcoholic zinc chloride to the filtrate. Since, when zinc cyanide is used, zinc chloride is formed during

the reaction, the addition of the latter reagent is rendered in all cases unnecessary.

W. S. N.

**The Influence of Substitution in the Components of Binary Solution Equilibria. XLIII. The Binary Systems of *m*-Hydroxybenzaldehyde with Phenols and Nitro-compounds.**

R. KREMANN and K. POGANTSCH (*Monatsh.*, 1923, **44**, 163—174).—No indications of combination are shown by the freezing-point curves of *m*-hydroxybenzaldehyde and phenol, the two naphthols, the three dihydroxybenzenes, and pyrogallol; the meta-compound thus differs from *p*-hydroxybenzaldehyde, and resembles *m*-nitrobenzaldehyde. The introduction of one nitro-group into the phenol does not affect the nature of the curves with *m*-hydroxybenzaldehyde, but with 2:4-dinitrophenol and picric acid the curves become horizontal over considerable distances, indicating formation of highly dissociated compounds, due to the increased total affinity between the two components; the three dinitrobenzenes, 2:4-dinitrotoluene, and trinitrotoluene give simple eutectic curves, as do benzoic and salicylic acids.

S. I. L.

**Catalytic Reduction of Aldehyde Acetals.** T. KARIYONE and Y. KIMURA (*J. Pharm. Soc. Japan*, 1923, No. **500**, 746—753).—When benzaldehyde diethyl acetal is reduced in glacial acetic acid solution with hydrogen in the presence of palladised barium sulphate, toluene is easily produced in almost quantitative yield:  $C_6H_5 \cdot CH(OEt)_2 + 2H_2 = C_6H_5Me + 2EtOH$ . In the same way, *p*-methoxybenzaldehyde and *p*-tolualdehyde diethyl acetals gave *p*-methoxycresol and *p*-xylene, respectively. The *p*-tolualdehyde diethyl acetal is a colourless liquid, b. p. 116—119°/12 mm.,  $d^{22}_4$  1.006, and  $n^{22}_D$  1.47603. The acetals of cinnamaldehyde and isovaleraldehyde and acetophenone and triethyl orthobenzoate do not give corresponding hydrocarbons. Furfuraldehyde diethyl acetal seems to be reduced to a tetrahydro-compound. The authors therefore conclude that only when the aldehyde acetal group is attached directly to the benzene nucleus is the ethoxyl group easily reduced to the methyl group.

K. K.

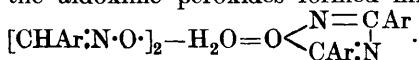
**Peroxides of Monoximes. II.** R. CIUSA and E. PARISI (*Gazzetta*, 1923, **53**, 667—671; cf. A., 1923, i, 579).—Oxidation of benzaldoxime by means of iodine and sodium carbonate yields results similar to those obtained by Bougault and Robin (A., 1919, i, 489), excepting that the two isomeric dibenzenyloxoazoximes, m. p. 135° and 63°, respectively (A., 1923, i, 1018), are formed.

Oxidation of benzaldoxime by means of nitrous anhydride gives: (1) benzoylbenzaldoxime, (2) benzoic acid, (3) a small proportion of a crystalline compound, m. p. 158°, (4) diphenylglyoxime peroxide, and (5) benzenylazoxime.

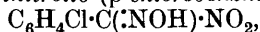
Treatment of *m*-nitrobenzaldoxime with iodine and sodium carbonate results in the formation of: *m*-nitrobenzoyl-*m*-nitrobenzaldoxime,  $C_{14}H_9O_6N_3$ , which crystallises in small, colourless needles, m. p. 180°, *m*-nitrobenzoic acid, and the nitrogen-free compound, m. p. 124°, previously obtained (A., 1923, i, 579), but not yet identified.

T. H. P.

**Aromatic Nitrolic Acids.** G. RUGGERI (*Gazzetta*, 1923, 53, 691—698).—Certain arylnitrolic acids may be obtained by treating the aryl aldoximes with nitrogen peroxide (0.5 mol.), which has been used hitherto for the conversion of aldoximes into the corresponding peroxides or the primary dinitro-hydrocarbons. The results obtained by Ponzio (A., 1906, i, 593, 735), Behrend and Tryller (A., 1895, i, 201), and the author indicate that the initial products of the action of nitrogen peroxide on arylaldoximes are always nitrolic acids. Some of the latter are stable, and may be isolated, whereas others are readily oxidised to dinitro-derivatives of hydrocarbons by excess of the reagent, and others again, by elimination of the nitro-group and union of the residues of two molecules, are transformed into peroxides of the aldoximes. For the latter reaction to occur, the nitrolic acids must exhibit the structure of nitrites,  $\text{CHAr}\cdot\text{N}\cdot\text{O}\cdot\text{NO}_2$ , or of *N*-nitro-derivatives,  $\text{CHAr}\cdot\text{N}(\text{NO}_2)\cdot\text{O}$ ; the former gives for the peroxides the formula  $[\text{CHAr}\cdot\text{N}\cdot\text{O}\cdot]_2$  and the latter the formula  $[\text{CHAr}\cdot\text{N}(\text{O})\cdot]_2$ , which is in accord with the nitronic structure,  $\text{CHAr}\cdot\text{NH}\cdot\text{O}$ , proposed by Staudinger and Miescher (A., 1919, i, 584) for the aldoximes and demonstrated experimentally for many of their derivatives. *p*-Chlorophenylmethylnitrolic and *m*-nitrophenylmethylnitrolic acids are stable in the air if pure and resemble phenylmethylnitrolic acid in being transformable into the peroxides of the corresponding dioximes, but differ from it by being capable of benzylation and of conversion into 1:2:4-oxadiazoles. The latter are possibly derived, not directly from the nitrolic acids by simultaneous elimination of a molecule of nitric and one of nitrous acid, but from the aldoxime peroxides formed initially from the nitrolic acids:



*p*-Chlorophenylmethylnitrolic (*p*-chlorobenznitrolic) acid,



obtained by the action of nitrogen peroxide on *p*-chlorobenzaldoxime in anhydrous ethereal solution, crystallises in pale straw-coloured, slender, silky needles, m. p. 78—79° (decomp.), and dissolves with an intense red coloration in solutions of the alkali carbonates or hydroxides, in the latter case without immediate change but with ultimate decolorisation and separation of a mixture of di-*p*-chlorobenzenylazoxime and di-*p*-chlorobenzildioxime. The same two compounds are formed when the nitrolic acid is heated with various organic solvents. The benzoyl derivative of *p*-chlorophenylmethylnitrolic acid,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{C}(\text{NOAc})\cdot\text{NO}_2$ , crystallises in long, lustrous needles, m. p. 115°.

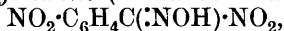
3:5-Di-*p*-chlorophenyl-1:2:4-oxadiazole,  $\begin{array}{c} \text{N}\cdot\text{C}(\text{C}_6\text{H}_4\text{Cl}) \\ \text{O}\cdot\text{C}(\text{C}_6\text{H}_4\text{Cl}) \end{array} \gg \text{N}$ , forms long, flattened, lustrous needles, m. p. 180—181°.

Di-*p*-chlorobenzildioxime peroxide,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{C}_2\text{N}_2\text{O}_2\cdot\text{C}_6\text{H}_4\text{Cl}$ , forms long, white laminae, m. p. 193—194°.

*p*-Chlorophenyldinitromethane,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}(\text{NO}_2)_2$ , obtained by the action of nitrogen peroxide on *p*-chlorobenzaldoxime, crystallises in white needles, m. p. 55° (decomp.). Its potassium derivative,

$C_6H_4Cl \cdot CK(NO_2)_2$ , forms large, orange-yellow prisms and is highly stable in the air but explodes when heated. The *p*-chlorophenyl-dinitromethane is accompanied by a small proportion of *p*-chlorobenzaldehyde, the *phenylhydrazone* of which,  $C_{13}H_{11}N_2Cl$ , crystallises in small, straw-yellow needles, m. p.  $132^\circ$ .

*m*-Nitrophenylmethylnitrolic (*m*-nitrobenznitrolic) acid,

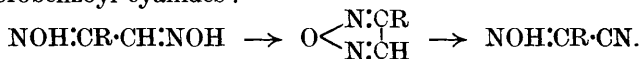


separates in pale straw-coloured, flattened needles, m. p.  $89^\circ$  (decomp.), and behaves like *p*-chlorophenylmethylnitrolic acid towards alkali hydroxide solutions. Its solution in sodium carbonate solution gradually yields a mixture of 3:5-di-*m*-nitrophenyl-1:2:4-oxadiazole and di-*m*-nitrobenzildioxime peroxide. Its *benzoyl* derivative,  $NO_2 \cdot C_6H_4 \cdot C(:NOBz) \cdot NO_2$ , crystallises in pale yellow prisms, m. p.  $145^\circ$ , and softens a few degrees below its melting point.

T. H. P.

**Dioximes. XIII.** L. AVOGADRO (*Gazzetta*, 1923, **53**, 698—707; *Atti R. Accad. Sci. Torino*, 1923, **58**, 269—282).—The results obtained with phenylglyoxime (A., 1923, i, 472) rendered it probable that its derivatives substituted in the nucleus, such as *p*-tolylglyoxime, *p*-chloro- and *p*-bromo-phenylglyoximes, etc., are capable of existing in two forms. The author has now prepared these derivatives by various methods and finds that the modifications described by Söderbaum (Beilstein, III, 92, 95) and Collet (A., 1902, i, 625) are actually mixtures of two individual compounds, inter-related in the same way as the two phenylglyoximes. As  $\alpha$ -modifications are designated those which give green nickel salts soluble in cold dilute acetic acid, the  $\beta$ -varieties yielding reddish-brown nickel salts insoluble even in hot dilute acetic acid. The  $\beta$ -forms melt at the higher temperatures, are the more stable, and may be obtained from the  $\alpha$ -isomerides by fusion or by heating with dilute acetic acid. The nickel salts of the  $\beta$ -forms are derived by replacement of two oximinic hydrogen atoms, one from each of two molecules of the glyoxime, whereas those of the  $\alpha$ -forms are not obtainable pure but are probably formed by the substitution of one atom of the metal for the two oximinic hydrogen atoms of a single molecule. Only the  $\beta$ -compounds are able, in aqueous solution, to attack compact nickel and cobalt, forming the corresponding complex salts.

Owing to the isomerisation of the  $\alpha$ - into the  $\beta$ -form under the action of acetic anhydride, the two phenylglyoximes yield but one diacetyl derivative, but the *p*-tolyl- or *p*-chlorophenyl-glyoximes give two distinct diacetyl compounds. Further, the  $\alpha$ -forms of *p*-tolyl- and *p*-chlorophenyl-glyoximes, like that of phenylglyoxime, cannot be benzoylated on account of the ease with which they undergo anhydridisation into the corresponding furazans, these being capable of isomerisation into the oximes of *p*-toluoyl and *p*-chlorobenzoyl cyanides:





The same behaviour is probably exhibited by the two *p*-bromophenylglyoximes, but the author has not investigated the derivatives of these.

As regards the nature of the isomerism of the new glyoximes, the action on the latter of nitrogen tetroxide has not yet been studied, but exclusion of geometrical isomerism is demonstrated by the observation that in the  $\beta$ -forms, but not in the  $\alpha$ -forms, the two oximino-groups are equivalent.

$\alpha$ -*p*-Tolylglyoxime,  $C_6H_4Me \cdot C(NOH) \cdot CH : NOH$ , crystallises in white prisms, m. p. 170—171°. The nickel salt,  $C_6H_4O_2N_2Ni$ , forms a greenish-yellow precipitate or a brownish-yellow, amorphous powder which remains unmelted at 300°. The diacetyl derivative,  $C_{13}H_{14}O_4N_2$ , crystallises in white prisms, m. p. 115°, and dissolves in 20% sodium hydroxide solution with formation of *p*-tolylfuran and the oxime of *p*-toluoyl cyanide. Treatment of the glyoxime in sodium hydroxide solution with benzoyl chloride yields the benzoyl derivative of *p*-toluoyl cyanide oxime,  $C_6H_4Me \cdot C(CN) : NOBz$ , which separates in white needles, m. p. 147—148°.

$\beta$ -*p*-Tolylglyoxime forms pale straw-yellow laminæ, m. p. 192—193°. Its nickel salt,  $(C_6H_4O_2N_2)_2Ni$ , is obtained as a blood-red, crystalline powder which becomes brown, without melting, at 300°; it is readily decomposed by dilute mineral acids but resists the action of hot acetic acid. The cobaltous salt forms a coffee-coloured powder. The diacetyl derivative crystallises in white needles, m. p. 73—74°, and is dissolved slowly by 20% sodium hydroxide solution with formation of the original glyoxime.

*p*-Tolylfuran,  $O \begin{smallmatrix} N : C \cdot C_6H_4Me \\ N : CH \end{smallmatrix}$ , crystallises in prisms of characteristic odour, m. p. 52°, is not affected by concentrated sulphuric, hydrochloric, or nitric acid, but is converted by either boiling water or the hydroxides of the alkali metals into

*p*-Toluoyl cyanide oxime,  $C_6H_4Me \cdot C(CN) : NOH$ , which crystallises in lustrous laminæ, m. p. 117°, and may be prepared also by the action of sodium and amyl nitrite on the nitrile of *p*-tolylacetic acid.

*p*-Chloro-oximinoacetophenone,  $C_6H_4Cl \cdot CO \cdot CH : NOH$ , obtained by treating *p*-chloroacetophenone with sodium ethoxide and amyl nitrite, crystallises in straw-coloured needles, m. p. 170°.

$\alpha$ -*p*-Chlorophenylglyoxime,  $C_6H_4Cl \cdot C(NOH) \cdot CH : NOH$ , forms white prisms, m. p. 165°, and its diacetyl derivative, microscopic laminæ, m. p. 123—124°. The benzoyl derivative of *p*-chloro-oximino-phenylacetone nitrile has m. p. 117—118°; Zimmermann (A., 1903, i, 92) gave 115—116°.

$\beta$ -*p*-Chlorophenylglyoxime crystallises in pale straw-yellow needles or prisms, m. p. 188°. Its nickel salt,  $(C_6H_4O_2N_2Cl)_2Ni$ , forms orange-red prisms which begin to turn brown, without melting, at about 305°. Its diacetyl derivative crystallises in white prisms, m. p. 128—129° (decomp.), and its dibenzoyl compound in lustrous needles, m. p. 159°.

*p*-Chlorophenylfurazan,  $O < \begin{smallmatrix} N:C\cdot C_6H_4Cl \\ N:CH \end{smallmatrix}$ , forms white needles, m. p. 103—104°, has a characteristic odour, is not affected by concentrated sulphuric, hydrochloric, or nitric acid, and is converted by alkali hydroxide or by boiling water into oximino-*p*-chlorobenzyl cyanide.  
T. H. P.

**Dioximes. XIV.** G. PONZIO and G. RUGGERI (*Gazzetta*, 1923, **53**, 708—713).—According to Behrend and Schmitz (A., 1904, i, 108), the action of sodium carbonate or hydroxide on methylchloroglyoxime yields a dibasic acid which was, however, not obtained pure. The authors find that gradual addition of dilute aqueous sodium carbonate to a dilute ethereal solution of a chloroglyoxime results in the elimination of two molecules of hydrogen chloride from two molecules of the oxime, the residues then giving dioximes of diacylglyoxime peroxides.

The *dioxime of diacetylglyoxime peroxide*,  $C_2O_2N_2(CMe:N\cdot OH)_2$ , obtained from methylchloroglyoxime, crystallises in large prisms or white laminæ, m. p. 145°, and forms a *hydrochloride* which separates in white laminæ; its *dibenzoyl* derivative,  $C_{20}H_{16}O_6N_4$ , forms white needles, m. p. 160°. This dioxime greatly resembles and is possibly identical with the compound obtained by Behrend and Tryller (A., 1895, i, 201) by the action of hydroxylamine hydrochloride on the oil formed by heating at 80—90° the product of the interaction of acetone and nitric acid (cf. Steffens, A., 1900, i, 74).

The *dioxime of dibenzoylglyoxime peroxide*,  $C_2O_2N_2(CPh:N\cdot OH)_2$ , prepared from chlorophenylglyoxime (cf. A., 1923, i, 473), crystallises in white needles with straw-yellow reflection, m. p. 156°, and its *dibenzoyl* compound,  $C_{30}H_{20}O_6N_4$ , in white prisms, m. p. 148°.

*Diphenyltetraketone tetra-oxime*,  $C_6H_5\cdot [C:NOH]_4\cdot C_6H_5$ , prepared by reducing the preceding dioxime by means of zinc dust and glacial acetic acid, forms a white, microcrystalline powder, turning yellow at about 230°, m. p. 255—256° (decomp.). Its *tetrabenzoyl* derivative,  $C_{44}H_{30}O_8N_4$ , crystallises in lustrous, white needles, m. p. 257° (decomp.).

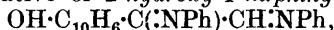
According to Claisen and Manasse (A., 1893, i, 464), the action of sodium hydroxide on chloro-oximinoacetophenone yields sodium benzoate, whilst that of sodium carbonate gives an oil which, on protracted heating, passes into solution. It is now found that treatment of chloro-oximinoacetophenone in ethereal solution with aqueous sodium carbonate solution gives a good yield of dibenzoylglyoxime peroxide.  
T. H. P.

**Dioximes. XV.** G. PONZIO (*Gazzetta*, 1923, **53**, 713—715).—Isomerisation of the  $\alpha$ - into the  $\beta$ -forms of glyoximes may be effected to some extent by simple fusion, but decomposition occurs before the change reaches completion. Contrary to the statement made by Auwers and Meyer (A., 1889, 403), if benzildioxime, m. p. 207°, is heated to its melting point and then immediately cooled, it is

found to have undergone partial conversion into the isomeride with m. p. 237°. Hence, in this case, as in others, the stable form of the glyoxime is that with the highest melting point, and the prefixes  $\alpha$ - and  $\beta$ - require to be interchanged. T. H. P.

**Action of Phenylcarbylamine on  $\beta$ -Naphthol.** M. PASSERINI (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 165—168).—The reaction occurring when phenylcarbylamine and  $\beta$ -naphthol are boiled in alcoholic solution under a reflux condenser differs from any reaction previously observed with the isonitriles (A., 1921, i, 743, 895; 1922, i, 731; 1923, i, 63).

The dianil derivative of 2-hydroxy-1-naphthylglyoxal,



thus obtained, forms lustrous, silky, pink needles, m. p. 169—170°. It yields a benzoyl derivative and, when it is boiled with alcoholic potassium hydroxide solution and the liquid subsequently acidified, the lactone,  $\text{C}_{10}\text{H}_6\langle\text{CO}\rangle\text{CO}$ , is formed. When heated, the lactone loses carbon monoxide and dioxide, giving a neutral compound,  $\text{C}_{20}\text{H}_{12}\text{O}_2$  (? 1 : 2-dioxydinaphthylene,  $\text{C}_{10}\text{H}_6\text{:O}_2\text{:C}_{10}\text{H}_6$ ), together with a little  $\beta$ -naphthol, whilst, when treated in acetic acid solution with hydrogen peroxide, it loses carbon dioxide and yields 2-hydroxy-1-naphthoic acid; the lactone forms a yellow, crystalline, *phenylhydrazone*, m. p. 224—225°. Free 2-hydroxy-1-naphthylglyoxal has not been obtained but the corresponding *diphenylhydrazone*, which forms yellow crystals, m. p. 240°, is formed when the above dianil derivative is treated when hot with phenylhydrazine.

T. H. P.

**The Aminoacetophenones as Colour Intermediates.** G. T. MORGAN and J. E. MOSS (*J. Soc. Chem. Ind.*, 1923, 42, 461—463r).—Nitration of acetophenone below  $-11^\circ$  gives a mixture of 56 to 65% of *m*-nitro- and 31 to 22% of *o*-nitro-acetophenone. At higher temperatures the proportion of the ortho-derivative increases; at  $15^\circ$  there is obtained 35.6% of *o*-nitro-, 32.5% of *m*-nitro-acetophenone, and 20.6% of *m*-nitrobenzoic acid. *o*-Nitroacetophenone is best reduced to *o*-aminoacetophenone with tin and concentrated hydrochloric acid; when dilute acid is used, the product appears to be *o*-acetyl- $\beta$ -phenylhydroxylamine. *m*-Nitroacetophenone can be reduced quantitatively to the amine by iron filings and water acidified with acetic acid.

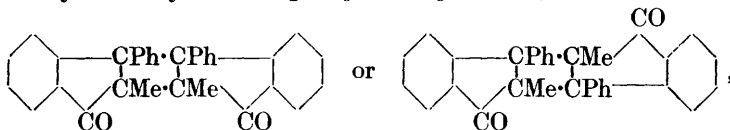
With diazo-compounds *m*-aminoacetophenone does not couple to give aminoazo-derivatives, but forms diazoamines. With *p*-nitrodiazobenzene, it gives *p*-nitrobenzenediazo-3-aminoacetophenone, pale yellow plates, m. p. 188°. It follows that *m*-aminoacetophenone cannot be used, as can *m*-toluidine, as a middle component for azo dyes; but the aminoacetophenones can be diazotised and used as primary components for such dyes. The dyes obtained from *o*-aminoacetophenone diazotised and coupled with  $\beta$ -naphthol or its sulphonic acids have no definite mordanting properties. This negative result may be taken to support the hydrazone formul-

ation for azo-colours from *o*-aminoacetophenone. *Acetophenone-m-azo-β-naphthol* forms rosettes of glistening, brownish-red, flattened needles with green reflex, m. p. 155°; with concentrated sulphuric acid, it gives an intense, carmine-red coloration, whilst the corresponding dyes from *o*- and *p*-aminoacetophenones give violet and deep purple colorations, respectively. With *β*-naphthol-6-sulphonic acid, diazotised *o*-, *m*-, and *p*-aminoacetophenones give brick-red to brownish-red dyes, which give, respectively, vermilion, reddish-orange, and carmine colorations with sulphuric acid. They give brick-red shades on wool, the ortho-compound giving the yellowest and the para-compound the darkest shade. E. H. R.

**Indones. V. Conversion of 3-Phenyl-2-methylindone into Diphenyldimethyltruxones by the Action of Ultra-violet Rays.**

REMO DE FAZI (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 227—230).—It has been shown that 3-phenyl-2-methylindone may be obtained from ethyl *β*-hydroxy-*ββ*-diphenyl-*α*-methylpropionate (A., 1916, i, 151), whereas, under similar conditions, ethyl *β*-hydroxy-*ββ*-diphenylpropionate yields 3-phenylindone and two isomeric diphenyltruxones (A., 1920, i, 316). When treated with concentrated sulphuric acid, however, 3-phenyl-2-methylindone does not yield a truxone, but gives an emerald-green solution, and when this is poured on to ice the original indone is obtained; consequently diphenyldimethyltruxones cannot be synthesised by this method.

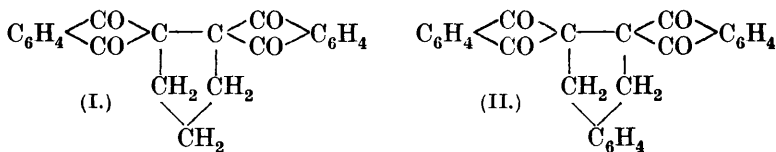
It seems, however, that indones may be transformed into truxones by the action of ultra-violet rays. Under this agency, 3-phenyl-2-methylindone yields a *diphenyldimethyltruxone*,



which forms white crystals, m. p. 307—308°, and in benzene solution gradually yields a small proportion of pale yellow crystals, m. p. 259—260°, possibly of another diphenyldimethyltruxone. After repeated crystallisation from alcohol, the compound, m. p. 307—308°, gives with concentrated sulphuric acid an emerald-green solution, which yields the original 3-phenyl-2-methylindone when poured on to ice. T. H. P.

**Spirans. XI. Synthesis of Dispirans.** D. RADULESCU (*Bull. Soc. Ştiinţe Cluj*, 1922, 1, 335—336; from *Chem. Zentr.*, 1923, iii, 140; cf. A., 1923, i, 1197, 1211, 1240).—The author has synthesised dispirans from bisdiketohydrindene (Gabriel and Leupold, A., 1898, i, 481) by a method by means of which tri- and penta-spirans also may possibly be obtained. By the action of trimethylene bromide on the dipotassium salt of bisdiketohydrindene in anisole solution at 140°, cyclopentanbis-1:2-diketohydrindene-1:2:2:2-dispiran, C<sub>21</sub>H<sub>14</sub>O<sub>4</sub> (I) is obtained as light pink, strongly refracting prisms, m. p. 254°; it sublimes above 350°.

1 : 2 : 3 : 4 - *Tetrahydronaphthalenebis* - 1 : 2 - *diketohydrindene* - 2 : 2 : 3 : 2 - *dispiran* (II) is obtained by a similar reaction, using *o*-xylylene bromide; it forms pink, strongly refracting prisms with m. p. 265°, subliming above 350°. Bisdiketohydrindene and ethyl bromoacetate yield *ethyl bisdiketohydrindene* - 2 : 2 - *diacetate*,  $C_{26}H_{22}O_8$ , needles, m. p. 174°.



G. W. R.

### Anthraquinonylurethanes ; Anthraquinonylcarbamides.

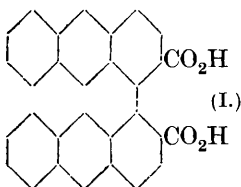
M. BATTEGAY and J. BERNHARDT (*Bull. Soc. chim.*, 1923, **33**, [iv], 1510—1536).—A more detailed description of work previously published (*A.*, 1922, i, 1041). The following substances are described. *Anthraquinonyl-1-urethane*, yellow spangles, m. p. 215°, prepared by the action of ethyl chloroformate on 1-aminoanthraquinone in nitrobenzene. *4-Nitroanthraquinonyl-1-urethane*, brown crystals, m. p. 245°, from 4-nitro-1-aminoanthraquinone. *4-Hydroxyanthraquinonyl-1-urethane*, red crystals, m. p. 225°, from 1-amino-4-hydroxyanthraquinone, with which ethyl chloroformate appears to react only as regards the amino-group. *4-Methoxyanthraquinonyl-1-urethane*, red needles with a yellow lustre, m. p. 230°, from 1-amino-4-methoxyanthraquinone. *4-Benzamidoanthraquinonyl-1-urethane*, red needles, m. p. 248°, from 4-nitro-1-aminoanthraquinone by benzylation, reduction with sodium sulphide, and subsequent treatment of the resulting 4-benzamido-1-aminoanthraquinone with ethyl chloroformate. *Anthraquinonyl-1-carbamyl chloride*, a yellow solid, decomp. 120°, prepared by the action of dry carbonyl chloride on a nitrobenzene solution of 1-aminoanthraquinone. *Anthraquinonyl-2-carbamyl chloride*, a grey solid turning yellow on exposure to air, decomp. 230°, similarly prepared, considerably more stable than its isomeride. 1 : 1' - *Dianthraquinonylcarbamide*, yellow crystals, m. p. 340—350°, by the action of carbonyl chloride on 1-aminoanthraquinone in nitrobenzene in presence of anhydrous sodium acetate, distinguished from the 2 : 2' - isomeride (cf. *A.*, 1911, i, 655) by the production of an orange as distinct from a yellow precipitate on diluting its solution in concentrated sulphuric acid. 1 : 2' - *Dianthraquinonylcarbamide*, a yellow solid, m. p. above 360° with sublimation, prepared by condensing 1-aminoanthraquinone with anthraquinonyl-2-carbamyl chloride in nitrobenzene solution; an attempt to use 2-aminoanthraquinone and anthraquinonyl-1-carbamyl chloride resulted only in the formation of a mixture of  $\alpha$ - and  $\beta$ -aminoanthraquinone. 4 : 4' - *Dinitro-1 : 1' - dianthraquinonylcarbamide*, dark yellow crystals, m. p. above 360° with sublimation, by the action of carbonyl chloride on 4-nitro-1-aminoanthraquinone in nitrobenzene in presence of sodium acetate.

4 : 4'-*Dihydroxy*-1 : 1'-*dianthraquinonylcarbamide*, violet-black crystals, m. p. above 360°, from 4-hydroxy-1-aminoanthraquinone. 4 : 4'-*Dimethoxy*-1 : 1'-*dianthraquinonylcarbamide*, a brown, crystalline powder, m. p. above 350°, subliming at 320°, from 4-methoxy-1-aminoanthraquinone. 4 : 4'-*Dibenzamido*-1 : 1'-*dianthraquinonylcarbamide*, red crystals, m. p. above 350°, from 1-amino-4-benzamidoanthraquinone. 4-*Nitro*-1 : 2'-*dianthraquinonylcarbamide*, yellow crystals, m. p. above 350°, by heating anthraquinonyl-2-carbamyl chloride with 4-nitro-1-aminoanthraquinone. 4-*Hydroxy*-1 : 2'-*dianthraquinonylcarbamide*, reddish-brown crystals, m. p. above 350°, from the acid chloride and 4-hydroxy-1-aminoanthraquinone. 4-*Methoxy*-1 : 2'-*dianthraquinonylcarbamide*, a yellowish-brown, crystalline powder, m. p. 350°, from the corresponding methoxyl compound. 4-*Benzamido*-1 : 2'-*dianthraquinonylcarbamide*, a reddish-brown solid, m. p. above 350°, from 4-benzamido-1-aminoanthraquinone. *Anthraquinonyl-2-carbamide*, small, yellow crystals, m. p. 360°, by passing dry ammonia into a toluene solution of anthraquinonyl-2-carbamyl chloride; the isomeric acid chloride, treated similarly, yields 1-aminoanthraquinone. *Phenyl-2-anthraquinonylcarbamide*, yellow crystals, m. p. 300°, but decomposition with liberation of aniline starts at 240—250°; prepared by heating aniline with anthraquinonyl-2-carbamyl chloride. *Phenylmethyl-2-anthraquinonylcarbamide*, deep yellow crystals, m. p. 300°, from methyl-aniline and the acid chloride. *p-Nitrophenyl-2-anthraquinonylcarbamide*, yellow crystals, m. p. 360°, from *p*-nitroaniline. The authors give an account of the behaviour of each of the above substances on solution in concentrated sulphuric acid with subsequent dilution and on solution in aqueous sodium hydroxide together with some indication of the tinctorial possibilities in most cases.

H. J. E.

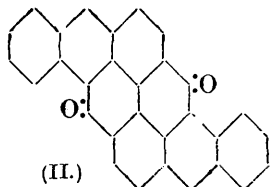
### *amphi-iso*Pyranthrone and its Relation to Pyranthrone.

R. SCHOLL and C. TÄNZER (*Annalen*, 1923, 433, 163—182).—A better yield of 1 : 1'-*dianthraquinonyl-2 : 2'*-dicarboxylic acid (Scholl, A., 1907, i, 540) is obtained by increasing the quantities of glacial acetic acid and chromic anhydride used in the oxidation of 2 : 2'-dimethyl-1 : 1'-*dianthraquinonyl*; instead of the latter, pyranthrone may be used. The diketo-acid is reduced by means of zinc dust in boiling, 24% ammoniacal solution in an atmosphere of nitrogen



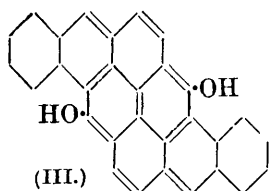
to 1 : 1'-*dianthryl-2 : 2'*-dicarboxylic acid (I), pale greenish-yellow needles or rhombohedral leaflets, which chars at about 183°, and melts indefinitely at 273—275° (m. p. 298°, if heated rapidly). It dissolves in cold, concentrated sulphuric acid with a yellowish-green coloration, changing gradually to greyish-black, or, at 70—75°, to dark violet. It gives a *diacid chloride*, compact, brownish-yellow crystals, decomp. 215°, a *diethyl ester*, slender, lemon-yellow needles, sinters 187°, m. p. 201—203° (decomp.), and a *diamide*, thin, colourless needles. When the acid is heated at 275°, or with

zinc chloride at 180—210°, it is partly converted into *amphi-isopyranthrone* (II); the condensation is more conveniently effected by heating the acid with phosphoric oxide at 180—190°, or by treating the acid chloride with aluminium chloride in cold nitrobenzene solution. *amphi-isopyranthrone* forms slender, lustrous, greyish-violet needles; it does not melt at 360°, but sublimes with partial

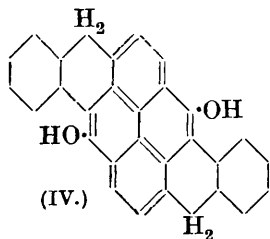


decomposition at higher temperatures. It dissolves in concentrated sulphuric acid with a reddish-violet coloration, changing to dirty green on the addition of a little water. Its solution in neutral solvents is magenta red.

In its chemical behaviour, *amphi-isopyranthrone* resembles anthraquinone rather than benzoquinone or naphthaquinone. It does not react with aqueous hydriodic acid or aqueous sulphurous acid at 100°, with phenylhydrazine at 200°, or with guaiacum resin or hæmatoxylin in boiling, alcoholic solution. It is even more stable towards stannous chloride and hydrochloric acid than anthanthrone, being only reduced in boiling solution to a hydro-



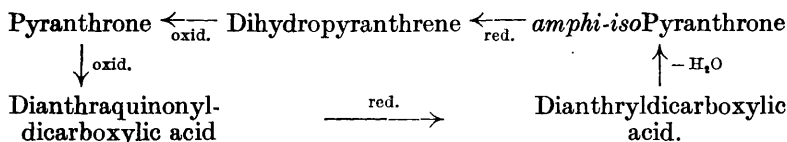
compound, which gives a blue, readily oxidised solution in sodium hydroxide. *amphi-isopyranthrone* reacts with alkaline sodium hyposulphite solution at 30—35° to give a blue vat, from which, in contact with air, the original material separates. The blue vat contains *amphidihydroxydihydropyranthrone* (III), which is isolated as the *di-p-bromobenzoate*, lustrous, copper-coloured needles (cf. Scholl, A., 1910, i, 271); it dissolves in boiling, 30% methyl-alcoholic potassium hydroxide, giving a blue solution. If the reduction is effected at 80—90°, a green vat is obtained, which contains *amphi-*



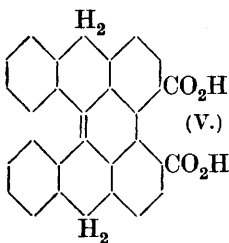
*dihydroxydihydropyranthrone* (IV), which is also isolated as the *di-p-bromobenzoate*, a yellow powder. This benzoate is dehydrogenated when boiled with a solvent of high b. p., giving the pyranthrone derivative; with boiling 30% methyl-alcoholic potassium hydroxide it gives, however, a green solution, which gradually turns blue in contact with the air. This change is not observed with the green, aqueous vat itself; *amphi-isopyranthrone* is gradually precipitated, without the appearance of a blue coloration.

*amphi-isopyranthrone* is reduced, by heating at 180° with hydriodic acid (b. p. 127°) and red phosphorus, to dihydropyranthrone (Scholl, A., 1910, i, 271). A change in the nomenclature of these compounds is introduced, whereby the system formerly described as "pyranthrone" is now designated "dihydropyranthrone." Dihydropyranthrone is oxidised, by means of chromic anhydride in boiling glacial acetic acid solution, to pyranthrone, or, if an

excess of the reagent is used (see above), to 1 : 1'-dianthraquinonyl-2 : 2'-dicarboxylic acid. The following cycle of operations, connecting pyranthrone and *amphi-isopyranthrone*, has therefore been accomplished :



At first it seemed possible that the dianthryldicarboxylic acid (I) was really the isomeric acid (V), since 1 : 1'-dianthraquinonyl and its derivatives are readily reduced to *meso*-benzodianthrone and its derivatives (Scholl and Mansfeld, A., 1910, i, 494). Actually it is found that 2 : 2'-dimethyl-1 : 1'-dianthraquinonyl is converted by the action of copper powder and concentrated sulphuric acid at 40—50° into 2 : 2'-dimethyl*meso*benzodianthrone, yellowish-brown, microscopic prisms, decomp. above 300° (cf. Ullmann and Bincer, A., 1916, i, 483). The blue solution of this



compound in concentrated sulphuric acid is stable in the dark, but in sunlight it quickly becomes magenta, with a brownish-red fluorescence, presumably with formation of 2 : 2'-dimethyl*meso*-naphthodianthrone. 2 : 2'-Dimethyl*meso*benzodianthrone gives a green vat with alkaline hyposulphite solution, which dyes vegetable fibres yellow. It is probable that the reaction by which this compound is formed is a general one, and that the product when 1 : 1'-dianthraquinonyl-2 : 2'-dicarboxylic acid is used is *mesobenzodianthrone-2 : 2'-dicarboxylic acid* (V), a dark orange-yellow substance. Its dirty-green solution in concentrated sulphuric acid does not change in the dark, but becomes brownish-red when exposed to light, presumably with formation of *meso*naphthodianthrone-2 : 2'-dicarboxylic acid. The same change of colour occurs on the addition of a little potassium dichromate. Apparently a change to the same acid also takes place when a solution of the sodium salt, but not the ammonium salt, is boiled. *meso*Benzodianthrone-dicarboxylic acid only gives a green vat with hyposulphite in the presence of cold, very dilute alkali hydroxide, and this vat is rapidly destroyed on warming. A similar vat is obtained by reducing the acid by means of zinc dust and ammonia, but a reduction product cannot be isolated. It is evident that a *meso*naphthodianthrone structure for the acid (I) is to be excluded. W. S. N.

**The Formation of Borneols from Turpentine Oil. I.** Y. MURAYAMA and KEIZO ABE (*J. Pharm. Soc. Japan*, 1923, No. 498, 637—644).—American turpentine oil, b. p. 158—161°,  $d^{15}_4$  0.8644, mainly composed of pinene, was heated with various organic acids at 115—150° during fifteen to twenty hours in a reflux apparatus. Trichloroacetic acid gave a maximum amount of borneol (yield



21%); other acids used were oxalic acid (15%), monochloroacetic acid (14%), phthalic anhydride (3.5%), tartaric acid (0.5%) and citric acid (trace). In the case of oxalic acid, part of the pinene is changed into  $\alpha$ -terpinene (nitrosite, m. p. 152°, and nitrolpiperidine, m. p. 153—155°), but not into dipentene. The products from monochloroacetic acid and phthalic anhydride were lævoratory.

K. K.

**The Influence of Substitution in the Components of Binary Solution Equilibria. XLIV. The Binary Equilibria of Fenchone with Phenols.** R. KREMANN and K. DIETRICH (*Monatsh.*, 1923, **44**, 175—181).—The freezing-point curve for the system fenchone- $\alpha$ -naphthol shows a maximum at 60.5° for equimolecular proportions; the eutectic of the compound with fenchone lies at 1° and 93% fenchone, with  $\alpha$ -naphthol at 55° and 38% fenchone. With  $\beta$ -naphthol an equimolecular compound is indicated by a break at 23°, but the compound only separates with excess of fenchone at the eutectic (10° and 81% fenchone); the m. p. given by Tardy (Beilstein Erg. Bd. 376) corresponds with the complete melting of the solid  $\beta$ -naphthol separated from the compound. The curves for fenchone with phenol, resorcinol, pyrocatechol, pyrogallol, and *o*- and *p*-nitrophenols cannot be completed, as the highly viscous complexes obtained do not crystallise throughout the complete range. With introduction of nitro-groups, the curves may be more nearly completed, picric acid and 2 : 4-dinitrophenol giving complete curves, showing simple eutectics.

S. I. L.

**Cathodic Reduction of Ketones, e.g., of Menthone.** C. SCHALL and W. KIRST (*Z. Elektrochem.*, 1923, **29**, 537—546).—The authors find that the electrolytic reduction of *l*-menthone in acid solution, employing a cathode of pure lead, mercury, or cadmium, exhibits no depolarisation effect at any stage of the reduction, a result differing from that obtained by Tafel in the case of caffeine and succinimide (A., 1905, ii, 224). As the electrolysis proceeds, the cathode potential increases to a maximum, more slowly in the case of a cadmium cathode than with one of lead or mercury, and then decreases. Employing in the electrolysis a lead cathode prepared as described by Tafel (A., 1900, ii, 588) the authors find that the product of the electrolysis consists principally of *l*-menthol, and the current-efficiency of the process is about 31%. When a roughened bright lead cathode is used, a considerable proportion of menthane results from the reduction, whilst if no diaphragm be employed there is considerable production of pinacol. When a cadmium cathode is employed in the electrolytic reduction of an acid solution of *l*-menthone, the product consists very largely of hexahydrocymene, and the process of reduction is an efficient one. The electrolytic reduction process employing a mercury cathode is described and a process for the production of mercury dimethyl detailed, likewise an efficient process for the production of menthane, employing a cadmium cathode. Effects observed with platinum and palladium electrodes are briefly referred to. The mechanism

of the reduction process is discussed on the basis of the production of unstable metallic menthyls.

J. S. G. T.

**The Camphor and Camphenilone Series.** L. RUZICKA (*Annalen*, 1923, 434, 217—218).—A question of priority. Nametkin (A., 1923, i, 934) has overlooked a paper by Ruzicka (A., 1918, i, 398).

E. E. T.

**The Hydrocarbon  $C_{10}H_{16}$  and its Isomerides.** A. GAWALOWSKI (*Pharm. Monatsh.*, 1922, 4, 68—69; from *Chem. Zentr.*, 1923, iii, 846). Oil of turpentine when treated with hydrogen chloride combines, with one or two molecules respectively, according to whether it contains more pinene or camphene, and according to whether a simple or supersaturated product is obtained. Camphene as well as pinene gives additive products with hydrogen chloride. Whilst pinene can give the camphor  $C_{10}H_{16}O$  directly with oxygen, this is not possible in the case of camphene. From the compound,  $C_{10}H_{17}Cl$ , obtained by the action of hydrogen chloride on pinene, a compound,  $C_{10}H_{18}O$ , may be derived. It yields camphene on dissociation. The compound  $C_{10}H_{17}Cl$  is probably bornyl chloride.

G. W. R.

**The Essential Oil of *Ocimum viride* (Willd.) from Grasse and from New Caledonia: Characterisation of  $\alpha$ - and  $\gamma$ -Terpinenes.** L. S. GLICHITCH (*Bull. Soc. chim.*, 1923, 33, [iv], 1536—1539; cf. Goulding and Pelly, P., 1908, 63).—Details are given of the results of examination of two samples of the oil. That from Grasse appears to contain  $\alpha$ - and  $\gamma$ -terpinene together with *d*-limonene and possibly some dipentene, whilst that from New Caledonia, although too small in quantity to furnish trustworthy results, contains an unusually small proportion of thymol [cf. B., Jan.].

H. J. E.

**The Volatile Oil of Manchurian Peppermint.** MANZO NAKAO and CHUZO SHIBUE (*J. Pharm. Soc. Japan*, 1923, No. 499, 725—738).—Manchurian peppermint, transplanted from Japan, yielded 2.2% of oil, which did not give crystals on being cooled with a mixture of ice and common salt. The constants are as follows:  $d^{17}$  0.914,  $d^{15}$  0.916; acid value 0.535, ester value 139.96, and  $[\alpha]_D^{25}$  —54.59°. The oil contains 28.65% of free menthol and 39.16% of combined menthol, chiefly as menthyl acetate, but also as (*iso*?)valerate. Menthone and limonene were also detected. The Korean product gave the following constants:  $d^{15}$  0.911, acid value 1.0, ester value 34.92,  $[\alpha]_D^{25}$  —37.83°; free menthol 58.17%; menthol as menthyl esters 9.73%.

K. K.

**Substitution and Addition of Chlorine to the Caoutchouc Molecule.** J. MCGAVACK (*Ind. Eng. Chem.*, 1923, 15, 961—962).—When chlorine is passed into a solution of caoutchouc in chloroform, without temperature control, during the first part of the reaction substitution takes place practically to the exclusion of addition. As the reaction proceeds, substitution diminishes and addition increases. In the final product, there are three atoms of substituted chlorine and four atoms of added chlorine, the total

percentage of chlorine being about 65. The apparatus used was provided with flow-meters, by which the flow of ingoing and outgoing gases could be measured; in this way, a continuous record of the progress of the reaction was obtained. E. H. R.

**Phytochemistry. I. Betulin.** O. DISCHENDORFER (*Monatsh.*, 1923, **44**, 123—140).—Betulin is best obtained from the bark of birch trees of moderate age (15—25 c.c. diameter stem), the bark being removed in spring and summer, when the tissues are softest. After washing, it is extracted by means of alcohol, the crude product purified by crystallisation from dilute alcoholic potassium hydroxide, and obtained by crystallisation from benzene and then from alcohol in snow-white needles, m. p. 251—252°. The yield of crude product is 23% by weight of the bark. The crystals contain one molecule of alcohol, and effloresce in air. Analysis is very difficult, so that the formula is uncertain; Schulze and Pieroh, whose melting-point figure agrees with that now found, suggested  $C_{32}H_{52}O_2$  or  $C_{33}H_{54}O_2$  (A., 1922, i, 1045), but the mean of several concordant analyses indicates  $C_{30}H_{50}O_2$  or  $C_{30}H_{52}O_2$ . The molecular weight by the micro-method of Rast (A., 1922, ii, 421) was 432, and by the freezing-point method with naphthalene 448 (mean).

Betulin diacetate, m. p. 214° (Schulze and Pieroh give 216—217°), crystallises in rhombic bisphenoids,  $[a : b : c = 0.99165 : 1 : 0.79830]$ . *Monobromobetulin diacetate*,  $C_{30}H_{49}O_2Br(OAc)_2$ , has m. p. 193°. *Betulin dibenzoate*, m. p. 181°, forms monoclinic-prismatic needles, with pseudo-hexagonal habit;  $[a : b : c = 1.0298 : 1 : 0.6458]$ ;  $\beta = 82^\circ 56'$ ; *betulin di-p-bromobenzoate* is obtained as sheaves of needles, m. p. 221—222°.

*alloBetulin* identical with the product obtained by Schulze and Pieroh is also obtained by the action of hydrogen bromide on betulin in chloroform solution; the crystals are triclinic-pedial,  $[a : b : c = 0.60666 : 1 : 1.03745]$ ;  $\alpha = 90^\circ 11'$ ,  $\beta = 95^\circ 6'$ ,  $\gamma = 90^\circ 7'$ ; the suggestion that this substance is isomeric with betulin is supported, and its acetate and formate are prepared; analyses of all these support the formula  $C_{30}H_{50}O_2$  for betulin and allobetulin.

S. I. L.

**Strophanthin. II. The Oxidation of Strophanthidin.** W. A. JACOBS (*J. Biol. Chem.*, 1923, **57**, 553—567; cf. A., 1923, i, 123).—By oxidation of strophanthidin with permanganate in acetone solution an acid,  $C_{23}H_{30}O_7 \cdot \frac{1}{2}H_2O$ , stout plates or leaflets, m. p. 185—190° (with effervescence) after sintering above 175°,  $[\alpha]_D^{20} + 54.8^\circ$  in methyl alcohol, has been obtained. It gives with concentrated sulphuric acid a yellow coloration which rapidly changes through orange to red and purple, and forms a *silver* salt,  $C_{23}H_{29}O_7Ag \cdot 2H_2O$ , small plates and prisms, a *dimethyl* ester,  $C_{24}H_{32}O_7 \cdot H_2O$ , six-sided tablets, m. p. about 160—163° (with frothing) after softening above 150°,  $[\alpha]_D^{20} + 57.6^\circ$  in methyl alcohol, and a *benzoate*,  $C_{31}H_{36}O_8$ , minute prisms, m. p. 243—244° (corr.),  $[\alpha]_D^{20} + 61.0^\circ$  in acetone. The dimethyl ester gives with sulphuric acid a yellow coloration which deepens to orange-red with a purple fluorescence. The acid still contains a lactone group; the product

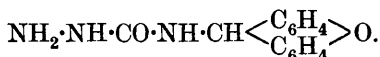
of hydrolysis, however, is reconverted into the same, and not an isomeric, acid on acidification. When the lactone group of the new acid is hydrolysed with alkali and the reaction product oxidised with permanganate in alkaline solution, the secondary alcohol group which is liberated is oxidised to a carbonyl group with the formation of an *acid*,  $C_{23}H_{30}O_8$  (isomeric with strophanthic acid),  $[\alpha]_D^{28} + 28^\circ$  in pyridine, which crystallises either in the anhydrous form, m. p.  $276-278^\circ$  (effervescence) after sintering, or with two molecules of water of crystallisation, m. p.  $268-270^\circ$  after sintering and darkening, according to the conditions of crystallisation, and gives a yellow colour with sulphuric acid which changes through orange to red with a green fluorescence. It forms a *barium* salt,  $C_{23}H_{28}O_8Ba \cdot 6H_2O$ , silky needles, and a *dimethyl* ester,  $C_{25}H_{34}O_8$ , platelets and prisms, m. p.  $251-252^\circ$  (effervescence) after sintering at  $246^\circ$ ,  $[\alpha]_D^{22} - 12.0^\circ$  in acetone. The latter yields a *benzoate*,  $C_{32}H_{38}O_9$ , thin platelets, m. p.  $249-251^\circ$  (decomp.),  $[\alpha]_D^{20} + 7.5^\circ$  in acetone, a *phenylhydrazone*,  $C_{31}H_{40}O_7N_2$ , lustrous platelets, m. p.  $265-266^\circ$  (decomp.), and an *oxime*,  $C_{25}H_{35}O_8N$ , flat needles, m. p.  $272-274^\circ$  (decomp.) after darkening and sintering. Although the acid does not appear to be a lactone, yet when heated with 2% sodium hydroxide the reaction mixture yields, on acidification, a third *acid*,  $C_{23}H_{32}O_9 \cdot 2\frac{1}{2}H_2O$ , glistening needles, m. p.  $185-187^\circ$  (effervescence),  $[\alpha]_D^{28} - 37.0^\circ$  in pyridine, which gives a yellow colour with sulphuric acid, changing to red with a green fluorescence. The analytical figures for this acid, as well as for some of its derivatives, were not entirely satisfactory, but no other formula appears possible. The following derivatives were prepared: *dimethyl* ester,  $C_{25}H_{36}O_9$ , prisms, m. p.  $205-206^\circ$ , no appreciable rotation; *benzoate* of dimethyl ester,  $C_{32}H_{40}O_{10}$ , microscopic plates and prisms, m. p.  $172-174^\circ$ ; *oxime* of dimethyl ester,  $C_{25}H_{37}O_9N \cdot H_2O$ , rhombic prisms, m. p.  $158-160^\circ$  (frothing) after preliminary sintering.

An improved method for the preparation of strophanthic acid is described and the following revised constants are given: m. p. about  $270^\circ$  (effervescence),  $[\alpha]_D^{28} - 22.0^\circ$  in methyl alcohol. With sulphuric acid, it gives a yellow colour changing through orange to red. Contrary to the statement of Feist, strophanthic acid is a lactone; after hydrolysis with alkali, the original acid may be recovered almost quantitatively by acidification, thus differing from strophanthidin, which, under these conditions, yields *isostrophanthidin*. This suggests that strophanthic acid is an oxidation product of the latter substance. Strophanthic acid does not contain a carbonyl group but still retains an alcoholic hydroxyl group as shown by the formation of a *benzoate* of the dimethyl ester,  $C_{32}H_{38}O_9$ , glistening prisms, m. p.  $233-235^\circ$ ,  $[\alpha]_D^{20} - 7.0^\circ$  in acetone. The dimethyl ester of strophanthic acid melts at  $251-253^\circ$ , and not at  $214^\circ$  as stated by Windaus and Hermanns (A., 1915, i, 704). The view of the latter authors, that strophanthic acid is formed from strophanthidin by oxidation of a methyl group, appears to be untenable; it is concluded from the above results that the attack takes place at the carbonyl group both in the formation of this acid and of the acid  $C_{23}H_{30}O_7$  described above. E. S.

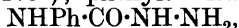
**Strophanthin. III. Crystalline Kombe Strophanthin.**

W. A. JACOBS (*J. Biol. Chem.*, 1923, **57**, 569—572; cf. preceding abstract).—The author considers that strophanthin has one of the following formulæ:  $C_{32}H_{48}O_{12}$  or  $C_{31}H_{46}O_{11}$ . It crystallises with  $3H_2O$  and contains one methoxyl group. The sugar will accordingly have the formula  $C_9H_{18}O_7$  or  $C_8H_{16}O_6$  and probably contains the methoxyl group. Attempts to isolate it in a crystalline form have been unsuccessful. From the fact, however, that strophanthin gives with acetic acid, ferrous sulphate, and a few drops of sulphuric acid a deep purple colour which changes through blue to green on the addition of water (a colour reaction which resembles that given by digitoxin and cymarose), it appears probable that the sugar is a deoxy-compound of the same type as these substances. E. S.

**Action of Xanthydrol on Semicarbazide, Substituted Semicarbazides, Semicarbazones, and Benzoylhydrazine.** A. DOUCET (*Compt. rend.*, 1923, **177**, 1120—1123).—In presence of not more than one molecular proportion of xanthydrol, semicarbazide affords a monoxanthyl derivative (already known); in presence of not less than 2 mols. of xanthydrol, a *dixanthyl* derivative (m. p. 184—185°) results. To determine the constitution of these products, the interaction of xanthydrol and substituted semicarbazides, semicarbazones, and benzoylhydrazine has been studied. Xanthydrol and benzaldehyde semicarbazone give a *monoxanthyl* derivative (m. p. 227—228°), also obtainable from monoxanthylsemicarbazide and benzaldehyde. Xanthydrol and acetone semicarbazone give a *monoxanthyl* derivative (m. p. 213—214°), also obtained by the interaction of acetone and monoxanthylsemicarbazide. Hence, monoxanthylsemicarbazide must have the formula :



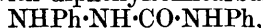
Again, benzoylhydrazine with xanthydrol gives a *monoxanthyl* derivative (m. p. 178—179°); phenylsemicarbazide,



gives a *monoxanthyl* derivative (m. p. 210—211°); whilst diphenylsemicarbazide,  $NPh_2 \cdot CO \cdot NH \cdot NH_2$ , also gives a *monoxanthyl* derivative (m. p. 153—154°). Hence the above dixanthylsemicarbazide (m. p. 184—185°) must have the formula :



Phenylsemicarbazide,  $NHPh \cdot NH \cdot CO \cdot NH_2$ , gave a *monoxanthyl* derivative (m. p. 160—161°) and a *dixanthyl* derivative (m. p. 184—185°), whereas with diphenylsemicarbazide,



only a *monoxanthyl* derivative (m. p. 171—172°) was obtained.

E. E. T.

**Aryl-1 : 3-benzodioxans (Arylmethylenesaligenins).** R. ADAMS, A. W. SLOAN, and B. S. TAYLOR (*J. Amer. Chem. Soc.*, 1923, **45**, 2417—2420).—It is shown that the reaction between

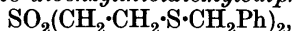
saligenin and benzaldehyde to give 2-phenyl-1:3-benzodioxan (Adams, Fogler, and Kreger, A., 1922, i, 660) is a general one. Derivatives of the reagents mentioned usually react at 100° within from five to thirty minutes, although sometimes nearly two hours may be required. The addition of benzoic acid is seldom necessary. Cinnamaldehyde, but not formaldehyde, acetaldehyde, or but-aldehyde, also undergoes condensation. Definite products are not obtained from nitrosaligenin.

The 2-aryl-1:3-benzodioxans,  $C_6H_4 \begin{smallmatrix} CH_2 \cdot O \\ O - CHR \end{smallmatrix}$ , derived from saligenin and *p*-chlorobenzaldehyde, *p*-bromobenzaldehyde, or *m*-nitrobenzaldehyde have m. p., respectively, 107—107·5°, 117—117·5°, and 88—89·5°. Bromosaligenin,  $C_6H_3Br^{(5)} \cdot OH^{(2)} \cdot CH_2 \cdot OH^{(1)}$ , condenses with the following aldehydes to give the corresponding *bromobenzodioxans*, the m. p. of which are quoted: benzaldehyde, m. p. 85°, *p*-chlorobenzaldehyde, m. p. 147—148°, *p*-bromobenzaldehyde, m. p. 143—144°, cinnamaldehyde, m. p. 118—120°. Methylsaligenin,  $C_6H_3Me^{(6)} \cdot OH^{(2)} \cdot CH_2 \cdot OH^{(1)}$ , is satisfactorily prepared by the reduction of *p*-methylsalicylaldehyde in alcoholic solution by means of hydrogen, platinum oxide, and ferrous chloride (cf. Carothers and Adams, A., 1923, ii, 310). It is condensed with benzaldehyde, and with *p*-bromobenzaldehyde, to give *methylbenzodioxans* having m. p., respectively, 90° and 130°. W. S. N.

**Derivatives of Thiodiglycol, Diethylene Disulphide, and Thioxan.** E. FROMM and B. UNGAR (*Ber.*, 1923, 56, [B], 2286—2289).—Thiodiglycol [ $\beta\beta$ -dihydroxyethyl sulphide] is converted when distilled with potassium hydrogen sulphate into water, 1:4-thioxan,  $O \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} S$  (cf. Clarke, T., 1912, 101, 1788), and diethylene disulphide,  $S \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} S$ . The latter compound is oxidised by hydrogen peroxide (two equivalents) in glacial acetic acid solution to *diethylenedisulphoxide*,  $OS \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} SO$ ; by three equivalents to *diethylenesulphoxidesulphone*,  $OS \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} SO_2$ , m. p. 278—279°, and by four equivalents to the *disulphone*, m. p. above 300°. The sulphoxide-sulphone is converted by boiling, concentrated hydriodic acid into *diethylenesulphonesulphide*, m. p. 200°.

Thioxan, b. p. 147°, is converted by iodine in hot glacial acetic acid solution into the corresponding *di-iodide*,  $O \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} SI_2$ , m. p. 66—67°, and by bromine in the presence of anhydrous ether into the *dibromide*, m. p. 75—80° (decomp.); with boiling ethyl iodide, it gives the *sulphonium iodide*,  $O(CH_2 \cdot CH_2)_2 S \cdot EtI$ , slender, yellow crystals, m. p. 85°. Oxidation of thioxan with regulated amounts of hydrogen peroxide gives successively the corresponding *oxide*,  $O \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} SO$ , colourless plates, which is too hygroscopic to permit analysis, and the *sulphone*,  $C_4H_8O_3S$ , long, colourless

needles, m. p.  $130^{\circ}$ . Boiling concentrated hydriodic acid transforms the compound last mentioned into  $\beta\beta'$ -*di-iodoethylsulphone*, colourless needles, m. p.  $203^{\circ}$ , which is converted by benzylmercaptan and sodium hydroxide into *dibenzylthioldiethylsulphone*,



colourless, lustrous leaflets, m. p.  $100^{\circ}$ ; hydrogen peroxide oxidises the latter substance to the *trisulphone*,  $\text{SO}_2(\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{CH}_2\text{Ph})_2$ , large leaflets, m. p. above  $300^{\circ}$ .  
H. W.

**The Anhalonium Alkaloids. VI. Anhalonine and Lophophorine.** E. SPÄTH and J. GANGL (*Monatsh.*, 1923, **44**, 103—114).—Contrary to the statement of Heffter (A., 1896, i, 267), the relation between these two alkaloids isolated from *Anhalonium Lewinii* is the simplest possible, lophophorine being now found to be identical with *N*-methylanhalonine. The quaternary methyl iodide compound, which is laevorotatory, has m. p.  $223^{\circ}$ , then changing into the racemic form of m. p.  $242$ — $243^{\circ}$ . Only about 1 g. of each substance was available, but the Weber-Tollens reaction having indicated the presence of a methylenedioxy-group, the constitutions were elucidated by syntheses of the two alternatives, viz., for anhalonine (a) 8-methoxy-6 : 7-methylenedioxy-1-methyltetrahydroisoquinoline, and (b) 6-methoxy-7 : 8-methylenedioxy-1-methyltetrahydroisoquinoline, lophophorine being the corresponding *N*-methyl compound. The *N*-methyl derivative of the compound of constitution (a) was synthesised by the action of magnesium methyl iodide on cotarnine iodide, yielding  $\alpha$ -methyl dihydrocotarnine, corresponding with formula (a). The second synthesis was carried out from myristicine by ozonisation to the aldehyde, condensation of this with nitromethane and reduction to homomyristicylamine, the acetyl compound of which condenses to a dihydroisoquinoline compound in presence of phosphoric oxide; reduction finally gave the compound (b) required, the quaternary iodide of which was found to be identical with the racemic form of lophophorine methyl iodide.

Attempts were made to resolve the racemic synthetic anhalonine into the optically active forms by means of tartaric acid and of bromocamphorsulphonic acid, but were unsuccessful. The presence of the optically active alkaloids anhalonine and lophophorine with the inactive anhalonidine and pellotine in the same plant is probably due to the mobility of the asymmetric carbon atoms in the latter.

The following compounds are described: the *picrate* of the quaternary base from lophophorine,  $\text{C}_{20}\text{H}_{22}\text{O}_{10}\text{N}_4$ , m. p.  $211$ — $212^{\circ}$ ; the *picrate* of 8-methoxy-6 : 7-dioxymethylene-1 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, m. p.  $176$ — $177^{\circ}$ ; the *methiodide* of  $\alpha$ -methyl dihydrocotarnine, m. p.  $225^{\circ}$ ;  $\omega$ -nitro-3-methoxy-4 : 5-methylenedioxy-styrene,  $\text{C}_{10}\text{H}_9\text{O}_5\text{N}$ , prepared from myristicine aldehyde by condensation with nitromethane, yellow needles, m. p.  $212$ — $213^{\circ}$ ; *N*-acetylhomomyristicylamine, m. p.  $130^{\circ}$ ; 6-methoxy-7 : 8-dioxymethylene-1-methyl dihydroisoquinoline, m. p.  $60$ — $62^{\circ}$ , and its *picrate*, m. p.  $206$ — $208^{\circ}$ ; the *hydrochloride* of (synthetic) racemic

anhalonine, and the *trinitro-m-cresolate* of the quaternary base from lophophorine,  $C_{21}H_4O_{10}N_4$ , m. p. 171—172°. S. I. L.

**The Action of Penetrating Radium Rays on Caffeine.** A. KAILAN (*Annalen*, 1923, **433**, 272—277).—When a 1.2% aqueous solution of caffeine was exposed in the dark at 6—11° for sixty-two days to the radiation from 110.4 mg. of radium chloride, it became alkaline to the extent of 0.0018*N* and the specific conductivity was increased by  $170 \times 10^{-6}$  reciprocal ohms; there was therefore a gain in equivalent conductivity of 95 reciprocal ohms. The substance to the formation of which this phenomenon is due is volatile at 150°, and is, most probably, ammonium or methylammonium formate. It is shown that the sum of the ammonia and methylamine molecules produced per second, and the number of ion pairs absorbed per second, are in the ratio 2 : 3, whilst the ratio of caffeine molecules decomposed to the number of ion pairs absorbed is most probably 1 : 3, the extreme possible figures being 2 : 3 and 1 : 6. The decomposition of caffeine by means of penetrating radium rays therefore accords with the general rule, that the number of molecules destroyed is of the same order as the number of ion pairs from the total absorbed radiation (cf. Kailan, A., 1922, ii, 467). Although Leipen has shown (A., 1889, 1017) that the action of ozone on caffeine in aqueous suspension leads to the reaction  $C_8H_{10}O_2N_4 + 3O + 2H_2O = C_5H_6O_3N_2 + 2CO_2 + NH_2Me + NH_3$ , the formation of parabanic acid could not be detected. Moreover, a similar reaction involving hydrogen peroxide is improbable, since insufficient of the latter is formed to account for the quantity of caffeine decomposed (Kailan, *loc. cit.*). It is considered more likely that the action of the radium rays, or of the ions derived from them, is direct, or that, perhaps, activated oxygen plays a part in the reaction. W. S. N.

**Synthesis of Natural Cocaine.** R. WILLSTÄTTER, O. WOLFES, and H. MÄDER (*Annalen*, 1923, **434**, 111—139).—The methyl and ethyl esters of tropinonecarboxylic acid have now been obtained in large quantities. The *methyl* ester, m. p. 111°, obtained (using sodium and cymene) from methyl 1-methylpyrrolidinediacetate (Willstätter and Bommer, A., 1921, i, 122), forms a *hydrate*,  $C_{10}H_{15}O_3N \cdot 2.5H_2O$ , m. p. 100° (not sharp), a *monohydrochloride*, prisms, m. p. 180°, and a *benzoyl* derivative, needles, m. p. 75—76°, which has no marked anaesthetic action, and resists hydrogenation. Ethyl tropinonecarboxylate, b. p. 107°/0.5 mm., or 170°/25 mm., forms a *hydrate*,  $C_{11}H_{17}O_3N \cdot 2H_2O$ , m. p. 63—65°, a *picrate*, m. p. 135—136°, a *methiodide*, m. p. 190—192°, and a *hydrochloride*, m. p. 168°.

Methyl acetonedicarboxylate, with potassium hydroxide and methyl alcohol, affords the dipotassium derivative, which condenses with succindialdehyde and methylamine to give a 65% yield of methyl tropinonecarboxylate (the mother-liquors, after treatment with boiling sulphuric acid, affording a little tropinone).

On repeating the reduction of the last-named ester, followed by hydrolysis of the  $\psi$ -ecgonine methyl ester (m. p. 128°) (Willstätter and Bode, A., 1903, i, 361), a *hydrate* of the previously described



*r-ψ*-ecgonine was obtained; and also (in addition to *ψ*-ecgonine methyl ester), *r*-ecgonine methyl ester. The latter, when heated successively with hot potassium hydroxide and methyl alcohol containing hydrogen chloride, was converted into the *r-ψ*-ester.

The resolution of *r-ψ*-cocaine (benzoyl *r-ψ*-ecgonine methyl ester, m. p. 81.5°) has again been attempted, using *d*-tartaric, malic, *d*-camphor-, *d-α*-bromocamphor-β-, and *d-α*-bromocamphor-π-sulphonic acids. In all cases, however, partial racemates were obtained; the base at the same time was found to possess the simple formula, C<sub>17</sub>H<sub>21</sub>O<sub>4</sub>N. The following salts of *r-ψ*-cocaine are described: *hydrogen d-tartrate*, m. p. 164°, [M]<sub>D</sub><sup>20</sup> +39°; *d-α-bromocamphor-β-sulphonate*, m. p. 182—183°, [M]<sub>D</sub><sup>20</sup> +312°; *d-camphor-sulphonate*, m. p. 218°, [α]<sub>D</sub><sup>20</sup> +9.19°. For comparison, the corresponding salts of *d-ψ*-cocaine were prepared: *hydrogen-d-tartrate*, m. p. 139°, [M]<sub>D</sub><sup>20</sup> +191°; *d-α-bromocamphor-β-sulphonate*, m. p. 206—207°, [M]<sub>D</sub><sup>20</sup> +446°; *d-camphorsulphonate*, m. p. 222°, [α]<sub>D</sub><sup>20</sup> +37.31°.

When, however, the salt of *r-ψ*-ecgonine methyl ester with *d-α*-bromocamphor-β-sulphonic acid was crystallised from ethyl acetate-alcohol mixtures, the *d-base-d-acid* salt separated as prisms, m. p. 201°, [α]<sub>D</sub><sup>20</sup> +71.42—72.6°; the mother-liquors yielding the *l-base-d-acid* salt, m. p. 115°. Decomposition of the former salt gave *d-ψ*-ecgonine methyl ester, m. p. 116°, [α]<sub>D</sub><sup>20</sup> +19.5° (*hydrochloride*, [α]<sub>D</sub><sup>20</sup> +23.68°). With *d-α*-bromocamphor-π-sulphonic acid, *r-ψ*-ecgonine methyl ester gave a less soluble *l-base-d-acid* salt, m. p. 243°, [α]<sub>D</sub><sup>20</sup> +43.47°.

*d-ψ*-Ecgonine methyl ester gives the same *methiodide* (m. p. 209°) as is obtained from methyl iodide and the (cold) *l*-ester. The latter, with warm methyl iodide, however, gives the *methiodide* (m. p. 165°) described by Einhorn and Friedlaender (A., 1893, i, 537) as that of the *d*-ester. *r-ψ*-Ecgonine methyl ester or *r*-ecgonine methyl ester give the *methiodide* (m. p. 185°) already described by Willstätter and Bode (*loc. cit.*). The true *l*- and *dl*-ecgonine methyl ester *methiodides* (m. p., respectively, 164° and 162°) are formed (together with the *hydriodides*) by treating the corresponding esters with methyl iodide in presence of a solvent. The *methiodides* of the *ψ*-series are more stable towards alkali than their isomerides of the other series.

*r*-Ecgonine methyl ester, on benzylation, gave *r*-cocaine (m. p. 79—80°) (*hydrochloride*, m. p. 187°). Of the various salts of the base obtained by precipitation methods, only the *permanganate* was obtained crystalline, the *nitrate*, *hydriodides*, and *mercuri-iodides* separating as oils.

The resolution of *r*-cocaine was effected through the *hydrogen d-tartrate*, the salt of the *l*-base separating as the *dihydrate*, prisms, m. p. 114—115°. Using *l*-tartaric acid, *d*-cocaine *hydrogen-l-tartrate* was the less soluble salt. The identity of the active alkaloids was established crystallographically.

The product described by Willstätter and Bode (*loc. cit.*) as *ψ*-tropine-*O*-carboxylic acid is now shown to be *r*-ecgonine (as trihydrate). *dl*-Cocaine or *dl*-ecgonine methyl ester, on hydrolysis with

cold barium hydroxide, affords the same compound, which melts first at 93—118°, becoming solid and remelting, with decomposition, at 203° (slow heating) or 212° (rapid heating). The hemi-hydrochloride,  $(C_9H_{15}O_3N)_2 \cdot HCl$ , has m. p. 247° (decomp.) and the chloroaurate, m. p. 205° (one preparation having m. p. 175°, as recorded previously).

From the reduction product of tropinonecarboxylic ester, a third *r*-ecgonine was isolated as the *dihydrate*, prisms, m. p. 110° and 229° (with frothing). The *hydrochloride*,  $C_9H_{15}O_3N \cdot HCl \cdot H_2O$ , is sparingly soluble, and has m. p. 230—233°. Boiling concentrated hydrochloric acid converts the new ecgonine into *r*-anhydroecgonine, identical with the product of the action of hydrogen chloride (in glacial acetic acid) on *dl*-ecgonine or on *dl*- $\psi$ -ecgonine. The anhydro-compound crystallises with  $1H_2O$  and has m. p. 226—230° (decomp.), the *methiodide* of its methyl ester melting at 180°.

[With R. GOTTLIEB.]—The  $\psi$ -configuration favours anæsthetic action, the most powerful anæsthetic being *d*- $\psi$ -cocaine. The racemate of the  $\psi$ -series is more powerful than *l*- $\psi$ -cocaine or than *dl*-cocaine, whilst, in both series, the *d*-form, when injected subcutaneously, acts less powerfully than the *l*-forms on the central nervous system.

Crystal measurements [H. STEINMETZ and F. MÜLLBAUER] are given as follows:

*d*- $\psi$ -Ecgonine methyl ester-*d*- $\alpha$ -bromocamphor- $\beta$ -sulphonate (rhombic,  $a : b : c = 0.6338 : 1 : 0.3429$ ); *l*- $\psi$ -ecgonine methyl ester-*d*- $\alpha$ -bromocamphor- $\pi$ -sulphonate (rhombic  $a : b : c = 0.3598 : 1 : 0.6692$ ); *r*-cocaine (rhombic,  $a : b : c = 0.6192 : 1 : 0.6223$ ; *d*- and *l*-cocaine (synthetic and natural) (monoclinic,  $a : b : c = 0.8551 : 1 : 1.0248$ ;  $\beta = 106^\circ 56'$ ); and the new *r*-ecgonine dihydrate (triclinc,  $a : b : c = 1.2494 : 1 : \dots$ ;  $\alpha = 58^\circ 50'$ ,  $\beta = 122^\circ 7'$ ,  $\gamma = 113^\circ 2'$ ).

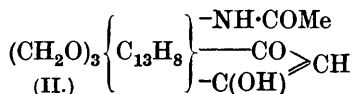
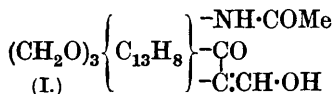
E. E. T.

**Action of the Grignard Reagent on Cocaine. Tropyldimethyl Carbinol.** S. FRÄNKEL and G. GRUBER (*Annalen*, 1923, 433, 241—246).—The action of an excess of magnesium methyl iodide on cocaine in ice-cold ethereal solution gives phenyldimethyl carbinol (*benzenesulphonate*, rhombic leaflets or large, pointed columns, m. p. 51.5°), and *tropyldimethylcarbinol*; the latter yields the syrupy *oxalate* and *tartrate*, hygroscopic *hydrochloride*, colourless needles, m. p. 162°, *dibenzoate*, clusters of needles, m. p. 90°, yellow *di-p*-nitrobenzoate, m. p. 103° (*hydrochloride*, m. p. 185°), and *di-p*-aminobenzoate, a powder, m. p. 178°. Colour reactions are given for the dibenzoate, the *di-p*-nitrobenzoate, and the *di-p*-aminobenzoate. The free carbinol, the dibenzoate, and the dinitrobenzoate have an anæsthetic action, the former being the more powerful. The diamino-benzoate has no anæsthetic action, but, like the free base, it has a bitter taste.

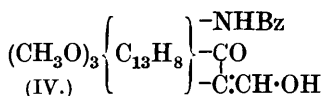
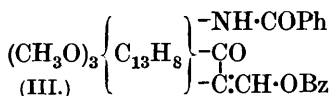
W. S. N.

**Constitution of Colchicine.** A. WINDAUS and H. SCHIELE (*Nachr. K. Ges. Wiss. Göttingen*, 1923, 17—36; from *Chem. Zentr.*, 1923, iii, 673—675; cf. Windaus, A., 1911, i, 904—906; 1915, i, 708—709).—The constitution of colchicine is discussed by

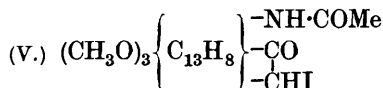
the authors. The methyl ether of colchicine is held to be an enolic form of a  $\beta$ -ketoaldehyde (I) or  $\beta$ -diketone (II).



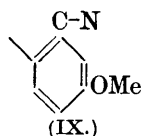
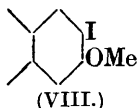
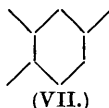
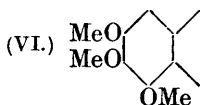
Colchicine gives the characteristic colour reaction for aldo- and keto-enols with ferric chloride. The ready hydrolysis of colchicine to colchicine also suggests the enolic structure. The dibenzoyl derivative (III) of trimethylcolchicinic acid (obtained by removal of one molecule of acetic acid from colchicine) gives no reaction with ferric chloride, whilst its hydrolytic product, *N*-benzoyltrimethylcolchicinic acid (IV), gives a deep green coloration.



The behaviour of colchicine with bromine and acetic acid, and also with iodine and potassium hydroxide suggests the keto-aldehyde formula (I). In the first case, tribromocolchicineic acid,  $C_{21}H_{20}O_7NBr_3$ , is obtained. This contains a carbonyl group which can occur only through oxidation of an aldehyde group. *N*-Acetyliodocolchicol (V) obtained in the latter case is to be considered as an iodophenol. Colchicine is therefore closely related to the aromatic *o*-hydroxy-aldehydes.

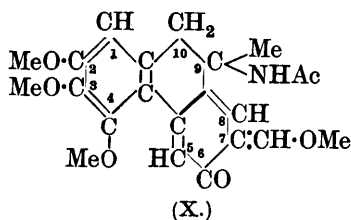


The authors demonstrate the existence of three six-atom carbon rings in colchicine. Colchicine, colchicine, trimethylcolchicinic acid, and *N*-acetyliodocolchicol all give, on oxidation with potassium permanganate, 3 : 4 : 5-trimethoxy-1 : 2-phthalic acid, suggesting the grouping (VI). Fusion with potassium hydroxide followed by oxidation gives terephthalic acid and trimellitic acid, which suggests the presence of a partly hydrogenated benzene ring of grouping (VII).



A third ring is demonstrated by the oxidation of *N*-acetyliodocolchicol methyl ether,  $C_{21}H_{24}O_5NI$ , with nitric acid and potassium permanganate. Amongst the products a compound is formed, which by reduction gives 4-methoxyphthalic acid; this the authors suppose to be 5-iodo-4-methoxybenzene-1 : 2-dicarboxylic acid arising from a ring (VIII). Oxidation of *N*-acetylcolchicol methyl ether gives 4-methoxy-*o*-phthalic acid from the third carbon ring, which suggests the grouping (IX). The three carbon rings

must be condensed, and these are shown by the authors to be in the phenanthrene grouping. *N*-acetylcolchinel methyl ether by hydrolysis with hydrochloric acid gives colchinel methyl ether hydrochloride, which contains four methoxyl groups and one amino-group. This can be degraded by the Hoffmann reaction into a quaternary ammonium hydroxide,  $C_{22}H_{31}O_4N$ , which on being heated in a vacuum loses water and trimethylamine, giving 2 : 3 : 4 : 6-tetramethoxy-9-methylphenanthrene, hexagonal tablets,

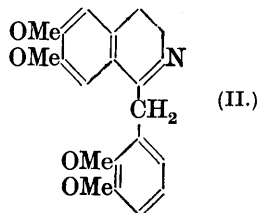
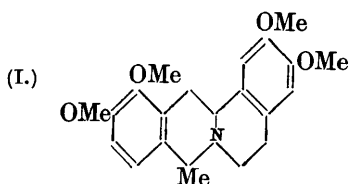


m. p. 111°. The latter by hydrolysis with hydriodic acid and subsequent reduction yields 9-methylphenanthrene,  $C_{15}H_{12}$ , m. p. 88°. Since colchicine,  $C_{22}H_{25}O_6N$ , gives hydroxycolchicine on oxidation with chromium trioxide, a reaction analogous to the oxidation of  $\alpha$ -tetrahydronaphthalene, a reactive

methylene group must be present. It is concluded that the constitution of colchicine is represented by the formula (X).

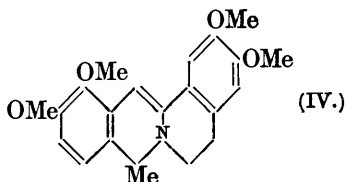
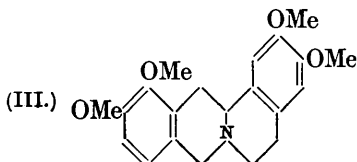
G. W. R.

**The Constitution of Corydaline.** E. SPÄTH and E. MOSETTIG (*Annalen*, 1923, **433**, 138—154).—A compound, colourless crystals, m. p. 111—112°, having the formula (I), has been synthesised by the following method. *o*-Vanillin methyl ether, hippuric acid, fused sodium acetate, and acetic anhydride are heated at 100°, giving an *azlactone*,  $C_{18}H_{15}O_4N$ , glistening, yellow needles, m. p. 167—168°, which is converted by the action of boiling, aqueous alkali hydroxide into benzoic acid, ammonia, and *o*-homoveratroylformic acid; the latter, without being isolated, is oxidised by means of hydrogen peroxide, giving *homo-o-veratric acid* (3 : 4-dimethoxyphenylacetic acid), m. p. 82—83°. The acid is now heated at 175—180° with homoveratrylamine; or its chloride, prepared by the action of phosphorus pentachloride, is treated in ethereal



solution with homoveratrylamine, and the solution shaken with dilute, aqueous alkali hydroxide solution. Either procedure gives the *amide*,  $C_6H_3(OMe)_2 \cdot NH \cdot CO \cdot CH_2 \cdot C_6H_3(OMe)_2$ , m. p. 130—130.5°. The action of phosphoric oxide on a boiling, toluene solution of the amide causes ring formation, with production of the *dihydroisoquinoline* derivative (II), (*picrate*, m. p. 172—174°), which is reduced by the action of tin on its boiling, aqueous-alcoholic hydrochloric acid solution to the similarly constituted, colourless, amorphous

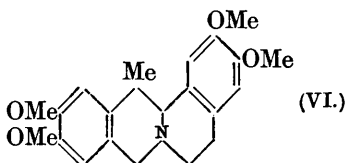
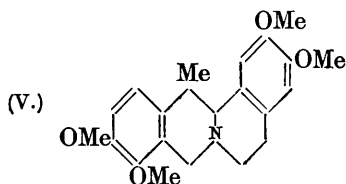
*tetrahydroisoquinoline* derivative (*m*-nitrobenzoyl derivative, yellow crystals, m. p. 148—149°). This compound gives resinous products when condensed with acetaldehyde diethylacetal, but can be condensed with methylal, by the action of boiling hydrochloric acid, to give the *base* (III), m. p. 158—159° (*hydrochloride*), which, being a compound of the tetrahydroberberine type, is dehydrogenated by heating at 100° with ethyl-alcoholic iodine. The *quaternary iodide* of the resulting *dihydro-base* is not fully purified, but is treated with a boiling ethereal solution of magnesium methyl iodide. The *methyl-dihydro-base* (IV), which is isolated from the



product, is difficult to purify owing to the ease with which it undergoes oxidation; the crude product has m. p. 100—110°. The final stage in the synthesis of the compound (I) is the reduction of the base (IV) by means of platinised zinc and hot, dilute sulphuric acid.

The formula (I) was at one time advanced by Gadamer, and by Haars (A., 1905, i, 462) as a possible one for corydaline. The compound having this structure is, however, quite different from either of the inactive corydalines. Consequently, the formulæ (V) and (VI), the former of which (cf. Späth and Lang, A., 1922, i, 168) has been accepted by Gadamer and Bruchhausen (A., 1922, i, 675), are the most probable for corydaline. It is possible, however, that it has a structure similar to that of bulbo-capnine, which contains a phenanthrene ring, and in which the nitrogen atom is monocyclically bound and carries a methyl group. In order to decide whether the nitrogen atom in corydaline takes part in one ring or in two, degradation has been carried out by the methods of Hofmann and of Emde.

Corydaline methiodide is too insoluble to be decomposed by means of sodium hydroxide at 100°; it is therefore treated in



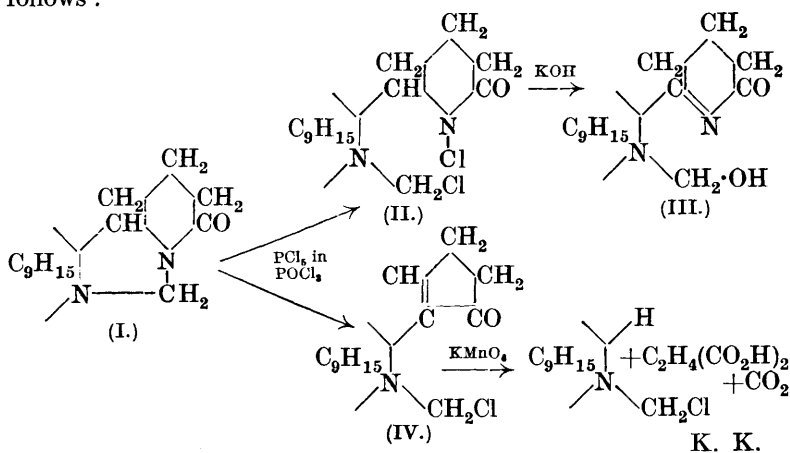
aqueous-alcoholic solution with silver nitrate, and, after removal of the silver iodide, the corydaline methonitrate solution is boiled with potassium hydroxide. The resulting crude methylcorydaline (Freund and Josephi, A., 1894, i, 100) is not purified, but is converted successively into the methiodide and the methochloride;

the latter is then boiled in aqueous solution with sodium hydroxide. The products are a nitrogen-free substance, trimethylamine, and traces of ammonia. The presence of dimethylamine could have been detected with certainty, since its condensation product with *m*-nitrobenzoyl chloride, *m*-nitrodimehylbenzamide, m. p. 84–85°, can readily be isolated from an aqueous solution containing 8% of trimethylamine hydrochloride and 0.77% of dimethylamine hydrochloride. Evidently the complete elimination of nitrogen from corydaline by Hofmann's method occurs in two, and not three, stages. This indicates, to some extent, that the nitrogen is bound in one ring only. Nevertheless, when the degradation is conducted by Emde's method, a nitrogen-free product is only obtained after three stages. Sodium amalgam is gradually added to a hot, aqueous solution of *corydaline methochloride*, colourless crystals; the resulting mixture of bases, which contains a crystalline compound,  $C_{23}H_{29}O_4N$ , evidently methylcorydaline (*ibid.*), is again converted into the methiodide, and methochloride, and treated with sodium amalgam. At this stage a hydrocarbon is not produced, and an almost quantitative yield of tertiary amine is obtained. The latter is again subjected to the same treatment, with the formation of trimethylamine and an unsaturated *hydrocarbon*, m. p. 87–88°, which passes, on catalytic hydrogenation, to an amorphous product.

The constitution of corydaline is therefore similar to that of berberine, and not to that of bulbocapnine. This agrees with the results of Herzig and Meyer (A., 1898, i, 53), who could not detect the presence of a methylimide group in corydaline by their method; their observations have been, in general, confirmed. It is probable that during the degradation by Hofmann's method, the corydaline alkylhalide (nitrate) partly decomposes into its original constituents, whilst simultaneously a strongly basic product is formed, containing monocyclically bound nitrogen. This could then form a quaternary salt, and undergo a further step in the degradation. Thus two stages will be accomplished in apparently one operation, and the production of a hydrocarbon, which really takes place in three steps, will appear only to require two. The use of the Hofmann degradation may therefore lead to misleading results, when applied to questions of alkaloid constitution. W. S. N.

**The Constitution of Matrine. III. and IV. Reaction between Matrine and Phosphorus Pentachloride.** HEISABURO KONDO and TOKUSABURO SANADA (*J. Pharm. Soc. Japan*, 1923, No. 498, 644–659; cf. A., 1921, i, 882; 1922, i, 269).—When matrine (formula I) (5 g.) is added to phosphoryl chloride (50 g.) containing phosphorus pentachloride (5 g.) at 80–100°, two substances are obtained, their amount differing according to the subsequent treatment. One, matrine monochloride (IV),  $(C_{15}H_{22}ONCl)_n$ , slightly yellowish, boat-like crystals, m. p. 240–242° (decomp.), is an unstable compound insoluble in almost all organic solvents. On treatment with dilute, acidified potassium permanganate solution it gives succinic acid and a base,  $C_{10}H_{18}NCl$ ; the latter corresponds with a volatile

base,  $C_{10}H_{19}N$ , obtained by the dry distillation of a mixture of matrine and zinc dust (A., 1921, i, 882). The chloroplatinate, yellow, rhombic prisms, m. p.  $309^\circ$  (decomp.), has not the formula  $(C_{15}H_{22}NCl)_2 \cdot H_2PtCl_6$ , but  $(C_{10}H_{18}NCl)_2 \cdot H_2PtCl_6$ . The monochloride gives also a chloraurate, a yellow, amorphous substance, m. p.  $180^\circ$  (decomp.), mercurichloride, m. p.  $287^\circ$  (decomp.), picrate, and dichromate. The other substance, matrine dichloride (II),  $C_{15}H_{24}ON_2Cl_2$ , light yellow, long, rhombic plates, m. p.  $146^\circ$ , is stable towards heat and potassium permanganate solution; [*chloroplatinate*, crystalline powder, m. p.  $234^\circ$  (decomp.); *chloraurate*, crystalline powder, m. p.  $224-225^\circ$  (decomp.)]. By treatment with 0.2*N*-alcoholic potash in the cold, the dichloride gave a compound (III),  $C_{15}H_{24}O_2N_2 \cdot HCl$ , one-third of which yielded matrine, and two-thirds an amorphous compound on reduction with glacial acetic acid and 3% sodium amalgam; the amorphous substance was converted into cinnamic acid and an amorphous base by oxidation with potassium permanganate solution. When the saponification is conducted at  $100^\circ$ , an amorphous base,  $C_{14}H_{25}ON$  (*chloraurate*, m. p.  $148^\circ$ ; *mercurichloride*, m. p.  $182^\circ$ ), and a potassium salt of an imino-acid,  $C_{15}H_{25}O_3N_2K$ , m. p.  $205^\circ$ , are produced. By reducing with glacial acetic acid and sodium amalgam or tin and hydrochloric acid, the dichloride is easily converted into matrine. From these results, the authors conclude that matrine is a saturated base not containing a double bond between carbon and nitrogen atoms, and that the chlorination causes the opening of a ring, one of the chlorine atoms becoming attached to the nitrogen atom which formed a lactam with the carbonyl group, and the other to the methylene group adjoining the nitrogen. The changes may be shown as follows:



**Spermine. I. The Base Isolated from Cholera Cultures by Kunz.** F. WREDE and E. BANIK (*Z. physiol. Chem.*, 1923, **131**, 29-37).—A base, supposed to be identical with spermine from human sperm, was isolated by Kunz (A., 1888, 1122), who attributed

to it the formula  $C_2H_5N$ . It has again been investigated. It forms a chloroplatinate,  $C_5H_{14}N_2 \cdot H_2PtCl_6$ , rhombs and needles, a phenylcarbimide,  $C_{19}H_{24}O_2N_4$ , fine, white needles, m. p.  $210^\circ$ , and is identical with cadaverine [pentamethylenediamine]. W. O. K.

**Spermine. II. The Base Isolated by Schreiner from Sperm.** F. WREDE and E. BANIK (*Z. physiol. Chem.*, 1923, **131**, 38—53).—A reinvestigation has been made of the base spermine, which Schreiner claimed to have isolated (A., 1879, 72). A base has been obtained in very small yield, forming a chloroaurate, containing C=7.78%, H=2.61%, N=4.03%, Au=47.40, 47.60, 48.41%, agreeing with the formula  $C_5H_{18}O_2N_2 \cdot H_2Au_2Cl_8$ , dense nodular, crystalline masses, m. p.  $216$ — $218^\circ$  (decomp.). No phenylcarbimide could be isolated, and therefore it is not piperazine, which forms a *phenylcarbimide*, fine crystals, m. p.  $305$ — $310^\circ$ , with sublimation, besides a *chloroaurate*, which does not melt at  $275^\circ$ . The trade article "Sperminum-Poehl" appears on analysis to consist of an inorganic phosphate, along with some organic contamination containing nitrogen. W. O. K.

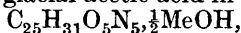
### Some Transformations of 3-Acetyl-2:4-dimethylpyrrole.

**Tripyrrylmethanes. I.** HANS FISCHER and H. AMMANN (*Ber.*, 1923, **56**, [B], 2319—2331).—3-Acetyl-5-aldehydo-2:4-dimethylpyrrole,  $\begin{matrix} \text{CAc} & \text{---} & \text{CMe} \\ | & & | \\ \text{CMe} & \cdot \text{C}(\text{CHO}) & \end{matrix} > \text{NH}$ , colourless needles, m. p.  $166^\circ$ , is

prepared in a maximal yield of 64.6% when a slow current of dry hydrogen chloride is passed into a suspension of 3-acetyl-2:4-dimethylpyrrole and hydrocyanic acid in anhydrous ether and the product is decomposed with cold water. The corresponding *aldazine*, decomp.  $299^\circ$ , the *phenylhydrazone*, colourless prisms, m. p.  $214^\circ$ , the *oxime*, colourless leaflets, m. p.  $203^\circ$ , and the *semicarbazone*, colourless prisms, m. p.  $236$  (decomp.), are described. The aldehyde is converted by concentrated hydrochloric acid into bis-3-acetyl-2:4-dimethylpyrrylmethene, m. p.  $200^\circ$  (cf. Piloty, Stock, and Dormann, A., 1914, i, 755), which is catalytically hydrogenated in the presence of glacial acetic acid and spongy platinum to bis-3-acetyl-2:4-dimethylpyrrylmethane, m. p.  $268^\circ$ .

During the preparation of the aldehyde, tri-3-acetyl-2:4-dimethylpyrrylmethane is invariably produced in a greater or less amount. It crystallises from methyl alcohol in colourless prisms, m. p.  $270^\circ$ , and is identical with the "intermediate product" obtained by Piloty, Krannich, and Will (A., 1915, i, 461) by the action of chloroform and potassium hydroxide solution on 3-acetyl-2:4-dimethylpyrrole and regarded as the substance,  $\begin{matrix} \text{CAc} & \text{---} & \text{CMe} \\ | & & | \\ \text{CMe} & \cdot \text{NH} & \end{matrix} > \text{C} \cdot \text{CH}(\text{OH}) \cdot \text{C} < \begin{matrix} \text{CMe} & \cdot \text{CAc} \\ | & & | \\ \text{NH} & \cdot \text{C} & \cdot \text{Me} \end{matrix}$

(cf. Wiedmann, *Diss.*, Munich, 1922). Much of the difficulty arising in the analysis of this compound is due to the fact that it crystallises from ethyl alcohol with half a molecule of solvent, from which it can be completely freed only with great difficulty. It separates from methyl alcohol or glacial acetic acid in the forms,

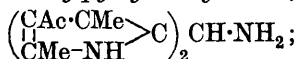




m. p. 270°, and  $C_{25}H_{31}O_5N_5 \cdot C_2H_4O_2$ , m. p. 187° (decomp.), respectively. All attempts to establish the presence in it of a hydroxyl group by means of the chlorides of phosphorus or hydrogen chloride were unsuccessful and led to the production of Piloty's methene hydrochloride. The constitution of the substance is placed beyond doubt by its synthesis from 3-acetyl-5-aldehydro-2:4-dimethylpyrrole and 3-acetyl-2:4-dimethylpyrrole under the influence of alcoholic potassium hydroxide, whereby it is found that the best yields are obtained when one molecular proportion of the aldehyde is treated with two molecular proportions of the pyrrole. It is further shown that the hydrolysis of Piloty's "intermediate product" by concentrated hydrochloric acid gives 3-acetyl-2:4-dimethylpyrrole (which is identified by the well-crystallised azo-dye produced with diazobenzenesulphonic acid), in addition to Piloty's dipyrlylmethene hydrochloride,

$$\begin{array}{c} \text{CAc} \cdot \text{CMe} \\ | \quad | \\ \text{CMe} - \text{NH} \end{array} > \text{C} \cdot \text{CH} : \text{C} < \begin{array}{c} \text{CMe} = \text{CAc} \\ | \\ \text{N}(\text{HCl}) : \text{CMe} \end{array}$$

The formation of the tripyrlylmethane compound in Piloty's experiments is readily explained, but its production by means of hydrocyanic acid is more difficult to interpret. It is tentatively ascribed to incomplete reaction of the acid, and combination of the aldehyde formed on addition of water with unchanged pyrrole. The course of the reaction appears, however, to be considerably influenced by slight changes in the experimental conditions. If the product of the action of hydrogen chloride and hydrocyanic acid on 3-acetyl-5-aldehydro-2:4-dimethylpyrrole is treated with well-cooled ammonia, a compound, colourless quadratic prisms, decomp. 167—168°, is obtained which, according to its analysis, is regarded as *bis*-3-acetyl-2:4-dimethylpyrlylmethylamine,



the investigation of the substance is not yet complete.

The action of chloroform and methyl-alcoholic potassium hydroxide solution on ethyl 2:4-dimethylpyrrole-3-carboxylate gives *tri*-3-carbethoxy-2:4-dimethylpyrlylmethane,  $C_{28}H_{37}O_6N_3$ , short, colourless prisms, m. p. 194°, which is converted by hydrochloric acid into *bis*-3-carbethoxy-2:4-dimethylpyrlylmethene, m. p. 213°, and ethyl 2:4-dimethylpyrrole-3-carboxylate.

*Bis*-3-acetyl-2:4-dimethylpyrlylmethene dissolved in boiling alcohol is converted by Schweizer's reagent into the copper salt,

$\text{Ac} \cdot \text{C} \begin{array}{c} \text{CMe} : \text{C} \cdot \text{CH} : \text{C} \cdot \text{CMe} \\ | \quad | \\ \text{CMe} \cdot \text{N} \cdot \text{Cu} \cdot \text{N} : \text{CMe} \end{array} > \text{CAc}$ , reddish-brown prisms with a green reflex. The corresponding *nickel* salt,  $C_{34}H_{38}O_4N_4Ni$ , red, hexagonal leaflets with an intensely green reflex, decomp. about 290°, and the *zinc* salt,  $C_{34}H_{38}O_4N_4Zn$ , cinnabar-red, hexagonal leaflets, are described; the zinc salt exhibits a green fluorescence when dissolved in alcohol.

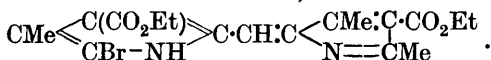
3-Acetyl-5-aldehydro-2:4-dimethylpyrrole is converted by the action of sodium ethoxide and hydrazine hydrate at 180° into a *substance*, colourless, volatile needles, m. p. 66°, which has not been investigated completely. Under similar conditions, 3-acetyl-

2 : 4-dimethylpyrrole is converted into cryptopyrrole in good yield, whereas 3-acetyl-2 : 4 : 5-trimethylpyrrole loses its acetyl residue and becomes transformed into 2 : 4 : 5-trimethylpyrrole. A liquid is isolated as by-product of the latter change, the picrate of which has m. p. 137°; its identity has not yet been established. H. W.

**Action of Bromine on Substituted Pyrroles and Syntheses of  $\alpha$ -Brominated Dipyrromethene Dyes.** HANS FISCHER and H. SCHEYER (*Annalen*, 1923, **434**, 237—251; Fischer, *Sitzungsber. Akad. München*, 1915, 401).—Ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate combines with bromine (1 mol.) to give a red, unstable *additive* compound (m. p. 120°, with gas evolution), which separates into its components on crystallisation or on keeping. Excess (4 mols.) of bromine converts the ester into *ethyl 4-methyl-2-bromomethylpyrrole-3 : 5-dicarboxylate* (colourless needles, m. p. 155—156°), which (1), when warmed with methyl (or ethyl) alcohol, gives the corresponding *2-methoxymethyl* (or *ethoxymethyl*) derivative, m. p. 79° (72°); (2) on reduction with hydrogen and platinum black is converted into the original 2 : 4-dimethyl ester; (3) with boiling water gives a *substance*,  $C_{24}H_{32}O_8N_2$  (colourless needles, m. p. 113—114°); and (4) with zinc dust and glacial acetic acid affords a *substance*,  $C_{13}H_{17}O_5N$  (needles, m. p. 120°).

Ethyl 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate with 1 mol. of bromine gives a well-defined but unstable *additive* compound, and with 4 mols. of bromine gives ethyl 3-bromo-4-methyl-2-bromomethylpyrrole-5-carboxylate (Fischer, A., 1922, i, 758). This substance, on warming with methyl (or ethyl) alcohol, affords the corresponding *2-methoxymethyl* (*ethoxymethyl*) derivative, m. p. 98—99° (101°), and, on warming with water, gives a mixture of substances.

Di- and tri-substituted pyrroles, with no substituent in position 2, when treated with an excess of bromine, afford crystalline dyes (cf. Fischer, *loc. cit.*), which are now shown to be (for the greater part), dipyrromethenes, giving well-defined zinc and copper salts, the latter being very similar to the copper salts of mesobilirubinogen. The mechanism of the formation of the dipyrromethenes is probably as follows (to take the case of the dye from ethyl 2 : 4-dimethylpyrrole-3-carboxylate): the 5-hydrogen atom in this compound reacts with the bromomethyl group in the first-formed ethyl 5-bromo-4-methyl-2-bromomethylpyrrole-3-carboxylate to give hydrogen bromide and a dipyrromethane, which then, in presence of excess of bromine, is oxidised to the methene,



This particular methene forms a *copper* salt,  $C_{36}H_{40}O_8N_4Br_2Cu$ , red rhombohedra with a green reflex (decomposing at 194—196°), and a *zinc* salt,  $C_{36}H_{40}O_8N_4Br_2Zn$ , red prisms with a golden reflex, m. p. 242°.

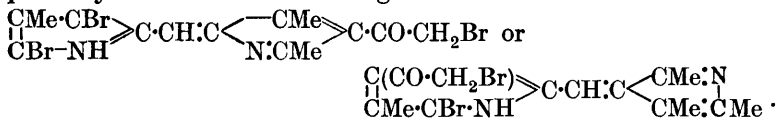
Ethyl 4-methyl-2-bromomethylpyrrole-3 : 5-dicarboxylate and ethyl 3-bromo-4-methyl-2-bromomethylpyrrole-5-carboxylate, when oxidised in presence of trisubstituted pyrroles, afford methene dyes. 2 : 4-Dimethylpyrrole with an excess of bromine affords 3 : 3' : 5'-

*tribromo-2 : 4 : 4'-trimethyldipyrromethene hydrobromide*, red needles, darkening at  $210^{\circ}$  and not melting at  $260^{\circ}$ . The free base forms red needles with a blue reflex, m. p. (if heated rapidly)  $192^{\circ}$  (with charring). Copper salt,  $C_{24}H_{20}N_4Br_6Cu$ , needles (red by transmitted and green by reflected light) decomposing at  $211^{\circ}$ . Zinc salt (red by transmitted and golden-yellow by reflected light) has a reddish-green fluorescence in alcoholic solution.

The zinc salt of bis-2 : 4-dimethyl-3-carbethoxypyrromethene, prepared for comparison, forms red plates, m. p.  $215^{\circ}$ , the alcoholic solution having a reddish-green fluorescence.

Hæmopyrrole affords (with excess of bromine), 5'-bromo-2 : 3 : 3'-trimethyl-4 : 4'-diethyldipyrromethene, which gives a copper salt (m. p.  $158^{\circ}$  [indef.]), red needles with a green reflex.

3-Acetyl-2 : 4-dimethylpyrrole behaves somewhat peculiarly with excess of bromine. The well-defined dye obtained ( $C_{14}H_{14}ON_2Br_4$ ) probably has one of the following formulæ :



5-Bromo-3-acetyl-2 : 4-dimethylpyrrole, when treated with bromine, gives the red compound,  $C_{14}H_{15}ON_2Br_5$ , the latter affording a zinc salt, red needles with a golden reflex.

Chloroform solutions of the above copper and zinc salts and also of the copper salt of bis-2 : 4-dimethylpyrromethene (A., 1923, i, 707) have been examined spectroscopically. E. E. T.

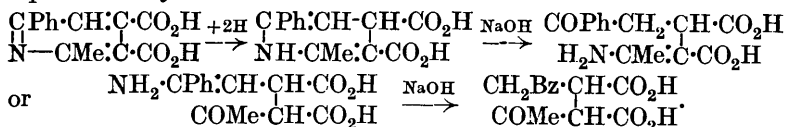
**Complex Salts.** G. SPACU and R. RIPAN (*Bul. Soc. Stiințe Cluj*, 1922, 1, 542—566; from *Chem. Zentr.*, 1923, iii, 601—602; cf. A., 1923, i, 832).—The authors have prepared a series of salts which show all variations between true complex salts and unstable compounds which are considered to be double salts. The dissociation of such double salts into their components is conditioned by the solvent. In non-dissociating solvents they behave as complex salts. The following complex or double salts are described : Double salt of the composition  $[\text{Mg}(\text{SO}_4)_2]_2[\text{Ni}(\text{H}_4\text{O}_2)_6]_2\cdot 2\text{H}_2\text{O}$ , formed by allowing a saturated equimolecular aqueous solution of magnesium sulphate and nickel sulphate to evaporate at  $25^{\circ}$ ; green crystals, losing water on keeping in air; *tetrapyrroline nickel magnesium sulphate*,  $[\text{Mg}(\text{SO}_4)_2]_2[\text{Ni}(\text{C}_5\text{H}_5\text{N})_4]$ , formed by warming and finally boiling magnesium nickel sulphate with pyridine; a green, crystalline powder which slowly loses pyridine in air; *monoaquopentapyridine nickel zinc sulphate*,  $[\text{Zn}(\text{SO}_4)_2][\text{Ni}(\text{C}_5\text{H}_5\text{N})_5\cdot\text{H}_2\text{O}]$ , prepared from zinc nickel sulphate and pyridine, a green, crystalline powder, fairly stable in air. Double salt,  $[\text{Mg}(\text{SO}_4)_3][\text{Co}(\text{H}_2\text{O})_6]_2\cdot 9\text{H}_2\text{O}$ , prepared by allowing a saturated equimolecular solution of magnesium sulphate and cobalt sulphate to evaporate; a pink, crystalline powder; complex salt,  $[\text{Mg}(\text{SO}_4)_3][\text{Co}(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})_4]_2$ , pink, crystalline powder which rapidly loses pyridine with decolorisation; *pentabenzylamineaquocobalt hexa-aquocobalt magnesium sulphate*,  $[\text{Mg}(\text{SO}_4)_3][\text{Co}(\text{C}_7\text{H}_5\text{N})_5\cdot\text{H}_2\text{O}][\text{Co}(\text{H}_2\text{O})_6]$ , a violet, crystalline powder; *hexapyridinecobaltmonopyridinepenta-aquocobaltcopper sulphate*,

$[\text{Cu}(\text{SO}_4)_3][\text{Co}(\text{C}_5\text{H}_5\text{N})_6][\text{Co}(\text{C}_5\text{H}_5\text{N})(\text{H}_2\text{O})_5]$ , a violet powder losing pyridine on keeping in air; complex salt,  $[\text{CuCl}_6][\text{Co}(\text{C}_5\text{H}_5\text{N}, \text{HCl})_3]_2$ , obtained by the action of a strong ethyl-alcoholic solution of hydrogen chloride on the preceding compound; a green, crystalline powder, stable in air; complex salt,  $[\text{CuBr}_6][\text{Co}(\text{C}_5\text{H}_5\text{N}, \text{HCl})_3]_2 \cdot \text{H}_2\text{O}$ , similarly prepared, dark violet crystals; complex salt,

$[\text{CoBr}_6][\text{Cu}(\text{C}_5\text{H}_5\text{N}, \text{HCl})_3]_2$ , crystals, stable in air; complex salt,  $[\text{Cu}(\text{SO}_4)_2][\text{Co}(\text{C}_7\text{H}_9\text{N})_3(\text{H}_2\text{O})_3]_2$ , a greyish-green, crystalline powder, stable in air. G. W. R.

**Action of Bromine on 2-Aminopyridine.** J. P. WIBAUT and G. M. KRAAY (*Rec. trav. chim.*, 1923, **42**, 1084—1091).—An aqueous solution of 2-aminopyridine, at  $0^\circ$ , absorbs bromine vapour to give 3:5-dibromo-2-aminopyridine, m. p.  $104.1$ — $104.5^\circ$ , identical with the product obtained indirectly from 3:5-dibromo-1-methyl-2-pyridone by Fischer and Chur (A., 1916, i, 741), who found, for the latter compound, the m. p.  $180^\circ$  (Wibaut and Kraay give  $179.5$ — $180.5^\circ$ , Decker and Kaufmann [A., 1911, i, 1023] giving  $176^\circ$ ). The dibromoaminopyridine, prepared by either method, gives an acetyl derivative, m. p.  $160$ — $161^\circ$ , a benzoyl derivative, m. p.  $181$ — $182^\circ$ , and a picrate, m. p.  $232$ — $232.4^\circ$ . Fischer and Chur, for the last three substances, obtained the respective m. p.  $102^\circ$ ,  $142$ — $143^\circ$ , and  $228^\circ$ . E. E. T.

**The Course of the Reduction of Pyridinecarboxylic Acids to Nitrogen-free Products.** O. MUMM and K. BRODERSEN (*Ber.*, 1923, **56**, [B], 2295—2301).—It has been established that in the remarkable reduction of pyridinecarboxylic acids to nitrogen-free products the group  $\cdot\text{CH}\cdot\text{N}\cdot\text{CH}\cdot$  is converted into the complex  $\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot$ . It appears probable that the primary product is a dihydrocyclic derivative, which is converted by the sodium hydroxide derived from the sodium amalgam into an open-chain dialdehyde. In view of their unstable nature, there is, however, little probability of the isolation of such compounds. The authors have therefore directed their attention to derivatives containing substituents in the 2- and 6-positions which should give rise to the more stable ketones, and have selected the readily accessible 6-phenyl-2-methylpyridine-3:4-dicarboxylic acid (cf. Mumm and Böhme, A., 1921, i, 439). Under suitable conditions, the acid is transformed into  $\beta$ -benzoyl- $\alpha$ -acetylmethylsuccinic acid whilst, in addition, the isolation of very unstable, unsaturated nitrogenous products has been achieved. The course of the change may therefore be represented by the scheme:



The reduction of an alkaline solution of 6-phenyl-2-methylpyridine-3:4-dicarboxylic acid by sodium amalgam (2 atomic proportions) leads to the formation of  $\beta$ -benzoyl- $\alpha$ -acetylpropionic acid,  $\text{CH}_2\text{Bz}\cdot\text{CH}(\cdot\text{CH}_2\cdot\text{CO}\cdot\text{Me})\cdot\text{CO}_2\text{H}$ , long, flattened rhombohedra, m. p.  $83^\circ$ , and after resolidification,  $135^\circ$  (*phenylhydrazones*, m. p.

204°), which is readily converted into the corresponding *lactone*, m. p. 135°, found to be identical with the synthetic product (cf. Miethke, *Dissert.*, Kiel, 1922). With four atomic proportions of sodium, 6-phenyl-2-methylpyridine-3:4-dicarboxylic acid gives  $\gamma$ -phenyl- $\alpha$ -acetonyl- $\gamma$ -butyrolactone,  $\begin{array}{c} \text{CHPh}\cdot\text{CH}_2 \\ | \quad \diagup \\ \text{O} \quad \text{CO} \end{array} > \text{CH}\cdot\text{CH}_2\cdot\text{COMe}$ , or

$\alpha$ -benzoylmethyl- $\gamma$ -valerolactone,  $\begin{array}{c} \text{CHMe}\cdot\text{CH}_2 \\ | \quad \diagup \\ \text{O} \quad \text{CO} \end{array} > \text{CH}\cdot\text{CH}_2\text{Bz}$ , a very vis-

cous, almost colourless liquid, b. p. 198—220°/0.5—0.6 mm., whereas with six atomic proportions of the metal  $\alpha\beta'$ -hydroxypropyl- $\gamma$ -phenyl-

$\gamma$ -butyrolactone,  $\begin{array}{c} \text{CHPh}\cdot\text{CH}_2 \\ | \quad \diagup \\ \text{O} \quad \text{CO} \end{array} > \text{CH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$  (which could not

be satisfactorily purified), is produced. The *barium* salt,  $(\text{C}_{13}\text{H}_{17}\text{O}_4)_2\text{Ba}$ , and the *silver* salt, m. p. 185° (decomp.), of the corresponding acid are described. The lactone is isomerised by alcoholic hydrogen chloride into  $\alpha\beta'$ -hydroxy- $\beta'$ -phenylethyl- $\gamma$ -valero-

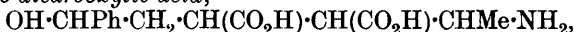
lactone,  $\begin{array}{c} \text{O} \quad \text{CO} \\ | \quad \diagup \\ \text{CHMe}\cdot\text{CH}_2 \end{array} > \text{CH}\cdot\text{CHPh}\cdot\text{OH}$ , a pale yellow liquid, b. p. 180—

183°/13 mm., from which the corresponding *silver* salt, m. p. 185°, is obtained. When distilled under greatly diminished pressure,  $\alpha\beta'$ -hydroxypropyl- $\gamma$ -phenylbutyrolactone undergoes a peculiar shortening of the side-chain, which results in the formation of

$\gamma$ -phenyl- $\alpha$ -methylbutyrolactone,  $\begin{array}{c} \text{CO}\cdot\text{CHMe} \\ | \quad \diagup \\ \text{O} \quad \text{CHPh} \end{array} > \text{CH}_2$ , crystals, m. p.

about 60°. The *barium* salt, short, coarse crystals, m. p. (indefinite) 236—250° (decomp.), and the *silver* salt of the corresponding acid are described.

The reduction of 6-phenyl-2-methylpyridine-3:4-dicarboxylic acid in ice-cold alkaline solution by a large excess of sodium amalgam leads to the production of a mixture of  $\epsilon$ -amino- $\alpha$ -hydroxy- $\alpha$ -phenyl-hexane- $\gamma\delta$ -dicarboxylic acid,

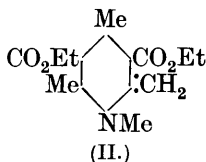
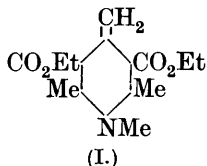


colourless needles, m. p. 260°, which readily loses water, probably with ring closure and then gives a *hydrochloride*,  $\text{C}_{14}\text{H}_{17}\text{O}_4\text{N}\cdot\text{HCl}$ , long, colourless needles, m. p. 220°, and an isomeric *dicarboxylic acid*,  $\text{C}_{14}\text{H}_{19}\text{O}_5\text{N}$ , a colourless, extremely hygroscopic powder. H. W.

**Pyridonemethides [Methylenedihydropyridines].** O. MUMM and G. HINGST (*Ber.*, 1923, **56**, [B], 2301—2313).—The authors have endeavoured to isolate simple members of the pyridonemethides. Since, however, these substances are expected to be highly unstable, they have chosen as initial material the readily accessible ethyl 2:4:6-trimethylpyridine-3:5-dicarboxylate with the object of thereby securing relative crystallisability and stability in the methide.

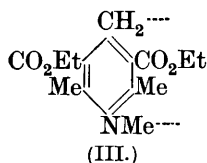
Ethyl 2:4:6-trimethylpyridine-3:5-dicarboxylate is readily converted by methyl sulphate into the corresponding *methosulphate*, colourless, prismatic rods, m. p. 172—174°, which is transformed by aqueous potassium cyanide solution into *ethyl 4(?2)-cyano-1-methyl-2:4:6-trimethyldihydropyridine-3:5-dicarboxylate*, colourless, matted needles, m. p. 92°, which decomposes when heated into

the pyridonemethide (see later). The methosulphate is transformed by 2*N*sodium hydroxide solution into *ethyl trimethylmethylenedihydropyridine-3:5-dicarboxylate* (annexed formulæ, I and II),



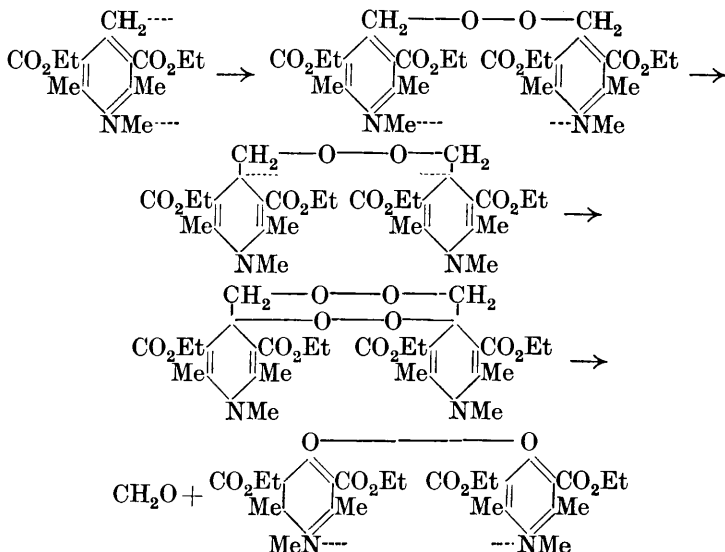
which is obtained in two interconvertible forms, yellow needles and yellowish-red plates, m. p. 74—75° when slowly heated; the prismatic variety is the more stable. The corresponding *perchlorate*, colour-

less, prismatic rodlets, m. p. 141°, and the *picrate*, yellow, prismatic crystals, m. p. 131—132°, are described. The substance is converted by methyl hydrogen sulphate into the methosulphate of ethyl 2:4:6-trimethylpyridine-3:5-dicarboxylate, m. p. 172—173°. It combines with iodine to give the *di-iodo*-derivative,  $\text{C}_{15}\text{H}_{21}\text{O}_4\text{NI}_2$ , a reddish-brown solid which could not be recrystallised. In its chemical activity, the pyridonemethide resembles closely the diarylquinonemethides, and for this reason the radicle formula



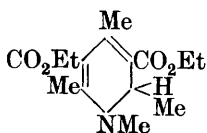
(III) is also possible. The chemical behaviour is most easily explicable on the assumption that it is an equilibrium mixture of forms I and III. It is oxidised on exposure to air in the solid condition, more rapidly in solution to a *dipyridone*,  $(\text{C}_{14}\text{H}_{19}\text{O}_5\text{N})_2$ , a hygroscopic, amorphous, brownish-black powder which yields dark

red solutions. Since the pyridones described previously do not show any tendency towards polymerisation, the dipyridone must be regarded as a primary product. The course of the change is very probably represented by the scheme :



The hypothesis is in harmony with the amount of oxygen absorbed, and the intense colour of the compound is explained by the presence of the two quadrivalent nitrogen atoms of which the free valencies partly saturate one another.

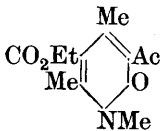
The pyridonemethide adds smoothly two atomic proportions of hydrogen in the presence of hexane and spongy platinum, and is converted thereby into the unsymmetrical *ethyl 1 : 2 : 4 : 6-tetramethyldihydropyridine-3 : 5-dicarboxylate* (annexed formula), a yellow



liquid, b. p. 145—155°/0.2 mm. It appears in this case to function as an  $\alpha$ -pyridonemethide.

The dihydro-compound is hydrogenated in glacial acetic acid solution to *ethyl 1 : 2 : 4 : 6-tetramethyltetrahydropyridine-3 : 5-dicarboxylate*, a pale yellow, mobile liquid, b. p. 115—122°/0.3 mm. Cautious hydrolysis of pyridone-

methide by 2*N*-sodium hydroxide at the atmospheric temperature leads to the formation of *ethyl 3-acetyl-1 : 4 : 6-trimethylpyrid-2-one-4-carboxylate* (annexed formula), colourless, lustrous leaflets,



m. p. 90.5—91°, which is transformed successively into the corresponding *carboxylic acid*, rhombic plates, m. p. 221°, and 3-acetyl-1 : 4 : 6-trimethylpyrid-2-one. The first and third of these compounds appear to be identical with the "*N*-methyl-dicarbocollidiniumdehydride" and "*N*-methylcarbo-

collidiniumdehydride" isolated by Hantzsch from the methiodide of ethyl 2 : 4 : 6-trimethylpyridine-3 : 5-dicarboxylate. The constitution of these compounds is deduced from the observation that they are converted by concentrated sulphuric acid at 180—220° into 1 : 4 : 6-trimethylpyrid-2-one, colourless, rhombic plates, m. p. 84—85°, which is further identified as the dibromo-compound,  $C_8H_9ONBr_2$ , colourless crystals, m. p. 169° (cf. Simonsen and Nayak, T., 1915, 107, 792). Their formation is explained by assuming that the action of the sodium hydroxide causes a temporary fission of the ring with the production of a  $\beta$ -ketonic acid, from which a cyclic compound is again formed with co-operation of the terminal carboxy-group.

H. W.

**An Application of the Colorimetric Law of Dilution.** J. PICCARD and J. H. DARDEL (*Ber.*, 1923, 56, [B], 2253—2254).—The application of the colorimetric dilution law (cf. Piccard, A., 1911, ii, 561) to the reduction product of benzylpyridinium chloride (cf. Emmert, A., 1920, i, 331) has been effected in the expectation that an equilibrium of the type quadrivalent nitrogen  $\rightleftharpoons$  trivalent carbon would not be disturbed by dilution, whereas an equilibrium of the kind radicle  $\rightleftharpoons$  double molecule would be displaced in the customary manner. Since the intensity of the colour is not diminished by cooling the solutions to  $-20^\circ$ , it appears impossible to regard the coloured compounds as compounds with free valencies. This conclusion has been drawn independently by Emmert (A., 1922, i, 1064; 1923, i, 383).

H. W.

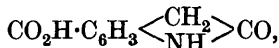
**Isatin-4-carboxylic Acid.** J. VON BRAUN and G. HAHN (*Ber.*, 1923, 56, [B], 2343—2347).—The ready preparation of the nitro-

phthalonic acid (von Braun, this vol., i, 48) has led the authors to an extended investigation of isatin-4-carboxylic acid which closely resembles isatin except in that it gives derivatives which dissolve in alkali.

Isatin-4-carboxylic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix}\text{CO}\\\text{NH}\end{smallmatrix}\rangle\text{CO}$ , decomp. above  $200^\circ$ , is readily prepared by the reduction of nitrophthalonic acid in alkaline solution by ferrous hydroxide; the bluish-black *disodium* salt and the *ethyl* ester, yellow leaflets, m. p.  $140^\circ$ , are described. Somewhat unexpectedly, it is converted by an excess of phosphorus pentachloride into *isatincarboxyl chloride*,  $\text{C}_9\text{H}_4\text{O}_3\text{NCl}$ , a black powder. *Isatin-4-carboxylic acid*  $\beta$ -phenylhydrazone crystallises in orange-coloured needles, decomp.  $200^\circ$ ; the  $\beta$ -*anil*, a Bordeaux-red, crystalline powder, decomp. above  $200^\circ$ , and the yellow  $\beta$ -*oxime*, decomp. above  $200^\circ$ , are described. Isatin-4-carboxylic acid is converted by *o*-phenylenediamine into the quinoxaline derivative,  $\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{C}\cdot\text{N}\rangle\text{C}\cdot\text{N}\rangle\text{C}_6\text{H}_4$ , the *monosodium* and *disodium* salts of which are described. *Dioxindole-4-carboxylic acid*,

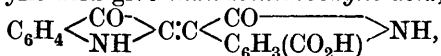


an almost colourless substance, decomp. above  $200^\circ$ , is prepared by the reduction of isatin-4-carboxylic acid with sodium amalgam by which it is reduced further to *oxindolecarboxylic acid*,

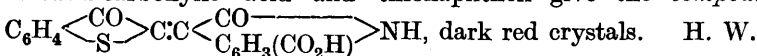


decomp. above  $280^\circ$ . The latter acid, together with isatin-4-carboxylic acid, is obtained when an alcoholic solution of dioxindole-carboxylic acid is boiled.

Acetophenone readily condenses with isatin-4-carboxylic acid in the presence of alkali to give *atophancarboxylic acid* (2-phenylquinoline-4:5-dicarboxylic acid), slender, colourless crystals (the *potassium* salt is described). The acid passes readily into the corresponding *anhydride*, yellow needles, m. p.  $226^\circ$ . Indoxyl and isatin-4-carboxylic acid give *indirubincarboxylic acid*,



bluish-black crystals with a coppery reflex, which is decomposed by molten alkali into a *substance*,  $\text{C}_{17}\text{H}_{12}\text{O}_5\text{N}_2$ , decomp. above  $270^\circ$ . Isatin-4-carboxylic acid and thionaphthen give the *compound*



**Tri-indolylmethanes and Aldehydes, Ketones, Ketonic Esters, and Keto-nitriles of Substituted Indoles.** HANS FISCHER and K. PISBOR (*Ber.*, 1923, **56**, [B], 2313—2319).—The ready applicability of Gattermann's aldehyde synthesis and of Hoesch's ketone synthesis to substituted pyrroles (A., 1922, i, 758, 1055) has led the authors to utilise these methods with substituted indoles.

A solution of 2-methylindole and chloroacetonitrile in anhydrous chloroform is converted by dry hydrogen chloride into the *ketimine*



*hydrochloride*, m. p. 170°, which is hydrolysed to 3-chloroacetyl-2-methylindole,  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CMe} \end{smallmatrix} \text{C} \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$ , identical with the compound described by Salway (T., 1913, 103, 351). It is converted by potassium cyanide in aqueous alcoholic solution into 3-cyanoacetyl-2-methylindole, small, yellow leaflets, m. p. 184°. 2-Methylindole is similarly transformed successively by anhydrous hydrocyanic acid and hydrogen chloride into the *imine hydrochloride*, m. p. about 180°, and 2-methylindole-3-aldehyde, slender needles, m. p. 198°. In like manner, ethyl indole-2-carboxylate, m. p. 119°, gives *ethyl 3-aldehydoindole-2-carboxylate*, pointed prisms, m. p. 185°, which is hydrolysed to 3-aldehydoindole-2-carboxylic acid, colourless leaflets, m. p. 247°. The ester is converted by hippuric acid in the presence of acetic anhydride and anhydrous sodium acetate into the corresponding *azlactone*,  $\text{C}_{21}\text{H}_{16}\text{O}_4\text{N}_2$ , yellow needles, decomp. 242°. The action of ethyl cyanoacetate on 2-methylindole in the presence of chloroform and gaseous hydrogen chloride leads to the isolation of the very stable *imine* of *ethyl 2-methylindole-3-acetate*,  $\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_2$ , small, colourless prisms, m. p. 151°, which does not appear to be converted into the corresponding ketonic ester even when warmed with sodium hydroxide solution. 2-Methylindole is transformed by two molecular proportions of acetonitrile into the *imine hydrochloride*, needles, and subsequently into 3-acetyl-2-methylindole, m. p. 195°.

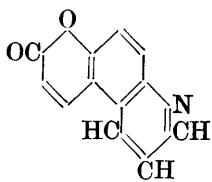
A mixture of 3-aldehyde-2-methylindole and 2-methylindole is converted by alcoholic potassium hydroxide solution into trimethyltri-indolylmethane, colourless crystals, m. p. 319°, which is identical with the substance isolated by Ellinger and Flamand (A., 1914, i, 881). The constitution of the compound is established by the observation that it is converted by perchloric acid into 2-methylindole and di-indolylmethene perchlorate, m. p. 248°.

H. W.

### Skraup's Quinoline Synthesis applied to 6-Aminocoumarin.

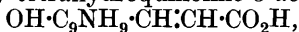
H. KONDO and TETSUKICHI UI (*J. Pharm. Soc. Japan*, 1923, No. 498, 615—628).—6-Nitrocoumarin was prepared by adding nitric acid (25 g., *d* 1.51) to a solution of coumarin (25 g.) in concentrated sulphuric acid (50 c.c.), the yield being 90%. It was then reduced electrolytically to 6-aminocoumarin, using a perforated copper plate as an electrode, current density 6—7 amperes, and 2.5—3.0 volts, the yield being 66%. When a mixture of 6-aminocoumarin (5 g.) and concentrated sulphuric acid (25—30 g.) is heated with glycerol (12 g.), nitrobenzene (2.7 g.), and fuming sulphuric acid (7—8 g.) in a reflux apparatus, the first violent reaction occurs at 120—135° and the second at 180—190°. The condensation product, *coumaroquinoline*, forms slightly brown needles, m. p. 232° (*mercurichloride*, colourless, hexagonal plates, m. p. 213°; *potassium chromate* compound, orange-yellow, rhombic plates; *chloroaurate*, yellow, short needles, m. p. 207°; *chloroplatinate*, orange-red, short needles, m. p. 286—290° [decomp.]; *picrate*, yellow, long needles, m. p. 214° [decomp.]). By the use of arsenic acid instead of nitrobenzene,

a purer compound is obtained. The annexed formula is ascribed to coumaroquinoline (cf. Marckwald, A., 1893, i, 603; 1894, i, 474; Claus, A., 1894, i, 174; 1898, i, 333).



By heating coumaroquinoline with methyl iodide in a sealed tube at  $100^\circ$  for three hours, the *methiodide*,  $C_{12}H_{17}O_2N, MeI$ , orange-red, rhombic plates, m. p.  $252^\circ$  (decomp.), was obtained; it gave the *methyrate*,  $C_{12}H_{17}O_2N, MeOH$ , a brown syrup, on treatment with freshly prepared silver hydroxide. The *methochloride*,  $C_{12}H_{17}O_2N, MeCl$ , light yellow, long needles, m. p.  $236^\circ$  (decomp.), gave a *chloroplatinate*, orange-brown, long prisms, m. p.  $250^\circ$  (decomp.); *chloroaurate*, yellow, hexagonal, long prisms, m. p.  $206^\circ$ ; *mercurichloride*, colourless, thin needles, m. p.  $236^\circ$  (decomp.); and *picrate*, yellow, hay-like crystals, m. p.  $214^\circ$  (decomp.).

By heating coumaroquinoline with concentrated hydrochloric acid and tin on a water-bath, a *tetrahydro-compound*, yellow, rectangular plates, m. p.  $143^\circ$ , was formed, the four hydrogen atoms being added to the pyridine nucleus. The tetrahydro-compound gave an *acetyl* derivative, colourless, rhombic plates, m. p.  $149-149.5^\circ$ ; and a tertiary *amine*, a volatile oil, b. p.  $263-265^\circ$ , when heated in a sealed tube with hydrogen iodide and red phosphorus. Coumaroquinoline, when heated with 0.2*N*-alcoholic potash, did not react, whilst tetrahydrocoumaroquinoline by the same treatment gave 6-hydroxy-tetrahydroquinoline-5-acrylic acid,



white, hay-like crystals, which did not melt below  $285^\circ$ . K. K.

**Preparation of Condensation Products of the Aromatic Series containing Nitrogen and Sulphur.** LEOPOLD CASSELLA & Co. (D.R.-P. 370854; from *Chem Zentr.*, 1923, iv, 538-539; cf. A., 1923, i, 917).—Sulphur monochloride in excess is allowed to act at temperatures not exceeding  $50^\circ$  on aromatic amines containing an alkyl group in the para-position, or on salts of such amines. The reaction is allowed to take place in a solvent or diluent which is indifferent to sulphur monochloride, preferably a nitrohydrocarbon, acetic acid, or anhydrous formic acid. By the action of sulphur monochloride on *p*-toluidine in nitrobenzene solution at  $15-40^\circ$ , a *condensation product* is obtained which gives an orange-yellow picrate. From the hydrochloric acid solution after neutralisation with sodium acetate, or alkali hydroxides, a compound,  $R \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{SO}$ , separates on keeping. It condenses with chloroacetic acid, giving *p*-toluidine-*o*-thiolacetate; the inner *anhydride* has m. p.  $152^\circ$ . *m*-Xylidine yields similarly a *condensation product* which gives an orange-yellow, crystalline *picrate*. *m*-Xylidine *o*-thiolacetate, obtained therefrom, gives an inner *anhydride*, m. p. about  $160^\circ$ . Compounds of the formula given above on treatment with alkalis give *o*-aminothiophenols.

G. W. R.

**The Preparation and Properties of 1-Thiolbenzthiazole, its Homologues and Derivatives.** L. B. SEBRELL and C. E. BOORD (*J. Amer. Chem. Soc.*, 1923, **45**, 2390—2399).—Thiolbenzthiazole, and its derivatives, may be prepared by heating with sulphur at 206—293°, (a) the corresponding diarylthiocarbamide (cf. Romani, A., 1922, i, 467; also Bruni and Romani, *Giorn. Chim. Ind. Appl.*, 1921, **3**, 351), (b) the zinc salt of the corresponding arylthiocarbamic acid, (c) the ammonium salt of the acid, (d) a mixture of carbon disulphide and the relevant arylamine. Bruni and Romani (*loc. cit.*; cf., also, A., 1921, i, 734), who also use phenylthiocarbamide or methyleneaniline, suppose that phenylthiocarbimide is first produced. They do not, however, take into account the concurrent production of an alkali-insoluble substance, which, in fact, they did not further investigate. This is now shown to be 1-anilinobenzthiazole (Hofmann, A., 1887, 823); it is formed in greatest quantity (16·5% theory) when thiocarbamilide is used, the simultaneous yield of thiolbenzthiazole being 73·3%. Thus a large proportion of starting material is accounted for. Moreover (Jacobson and Frankenbacher, A., 1891, 1048), 1-anilinobenzthiazole is not formed by the action of aniline on the 1-thiol derivative. It is considered that essentially the same mechanism will satisfactorily explain the concurrent production of 1-anilino- and 1-thiol compounds. The tautomeric thiol form of thiocarbamilide should exist in geometrically isomeric forms. Sulphurisation of the *trans*-form,  $\text{NHPh}\cdot\overset{\text{SH}}{\underset{\text{N}\cdot\text{Ph}}{\text{C}}}$ , and subsequent elimination of hydrogen sulphide, will yield 1-anilinobenzthiazole, whilst sulphurisation of the *cis*-form,  $\text{NHPh}\cdot\overset{\text{SH}}{\underset{\text{Ph}\cdot\text{N}}{\text{C}}}$ , and the removal of aniline, will give 1-thiolbenzthiazole. Also, a greater yield of the latter is obtained from phenyldithiocarbamic acid or its salts (75—80%) than from phenylthiocarbimide (60%). It is therefore likely that phenyldithiocarbamic acid (or its derivatives) also undergoes direct sulphurisation, the appropriate hydrosulphide being then eliminated. It is improbable that thiocarbamilide is an intermediate stage when dithiocarbamates are used, because this would be expected to yield a greater quantity of alkali-insoluble residue than is actually obtained.

Losanitch's work (A., 1892, 55) on the ammonium salts of arylthiocarbamic acids is confirmed. The zinc salts are obtained in a purer form by the action of aqueous or ammoniacal zinc acetate on the ammonium salts than by adding zinc oxide to a mixture of the amine and carbon disulphide (Krulla, A., 1913, i, 1174). Zinc salts of the thiolbenzthiazoles are prepared either by the interaction of the ammonium salt and ammonium zincate in aqueous solution, or by the action of a zinc salt on the thiazole in aqueous-alcoholic solution. Normal lead salts are obtained by the action of a lead salt on the thiazole in aqueous-alcoholic solution; or an aqueous solution of its sodium salt may be used. The action of lead hydroxide on the thiazole in alkaline solution gives the basic lead salt.

Disulphides are prepared from 1-thiolbenzthiazole and its derivatives by the action of alcoholic iodine, with or without the addition of alkali (cf. Hofmann, *loc. cit.*).

1-Thiolbenzthiazole is prepared by the methods given above, in the yields, (a) 74.0%, (b) 77.5%, (c) 74.0%, (d) 76.6%. It gives an amorphous, slightly yellow disulphide, m. p. 176°, a white, amorphous zinc salt, a bright yellow normal lead salt, and a white, amorphous basic lead salt. 1-Thiol-3-methylbenzthiazole, white needles, m. p. 186°, is obtained in the following yields: (a) 49.0%, (b) 37.0%, (c) 67.0%, (d) 45.5%. It gives a disulphide, white needles, m. p. 162°, a white, amorphous zinc salt, a yellow, amorphous normal lead salt, and a white, amorphous basic lead salt. 1-Thiol-4-methylbenzthiazole, pale yellow plates, m. p. 163° (disulphide, white plates, m. p. 195°), is obtained by the method (c) in 69.5% yield. 1-Thiol-5-methylbenzthiazole, very pale yellow crystals, m. p. 181° (disulphide, white needles, m. p. 201—202°, white, amorphous zinc salt), is obtained in the yields (a) 68.0%, (c) 71.5%, (d) 57.9%.

1-Thiol-3:5-dimethylbenzthiazole, pale yellow crystals, m. p. 250.5°, disulphide, slender, white needles, m. p. 193°, is obtained in the yields (a) 17.2%, (b) 32.4%, (c) 34.5%, (d) 30.4%.

1-Thiol-5-ethoxybenzthiazole, long, cream-coloured needles, m. p. 198°, is obtained in the yields (a) 58.4%, (b) 59.3%, (c) 73.0%, (d) 55.6%, but only the third method gives a product that can be purified readily.

1-Thiol-5-methoxybenzthiazole, pale yellow needles, m. p. 201°, is prepared by any of the four methods, but is always difficult to purify; the yield by the fourth method is 62.0%.

Attempts to prepare substituted thiolbenzthiazoles from *o*-anisidine, *o*- or *p*-chloro- or -bromo-aniline, and from *p*-aminophenol, have been unsuccessful. Benzidine and carbon disulphide give a product, m. p. above 250°, which is insoluble in alkali.

W. S. N.

**Constitution of Antipyrine.** H. THOMS and J. SCHNUPP (*Annalen*, 1923, 434, 296—312).—Of the two formulæ proposed for antipyrine, that usually accepted and due to Knorr is now shown to be correct, whereas the phenol-betaine formula of Michaelis (cf. A., 1902, i, 305) is definitely misleading. This has been shown by studying the catalytic hydrogenation of antipyrine and related compounds. It is found that whilst 2-methyl-5-pyrazolones resist hydrogenation (evidence of strong valency interaction between positions 2 and 5), hydrogenation can be effected under certain conditions, whereas if the Michaelis formula were correct, simple hydrogenation such as occurs (at the 3:4-position) would be extremely unlikely, although to be anticipated on the basis of the Knorr formula.

Whilst hydrogen and palladium (Willstätter) and hydrogen and colloidal palladium (Skita) effected no reduction of antipyrine, even at high pressures, this substance was readily reduced by the Sabatier-Senderens method at 160—180° to give 1-phenyl-2:3-di-

methyl-5-pyrazolidone, whilst at 180—220°, 1-phenyl-2 : 3-dimethylpyrazolidine was obtained.

Pyrazole and 1-phenylpyrazole are readily converted into the corresponding pyrazolines by Willstätter's method at the ordinary temperature, the conversion of the phenyl compound so obtained into the phenylpyrazolidine requiring a temperature of 70—80°. 1-Phenyl-3-methylpyrazoline, readily formed by the reduction of the corresponding pyrazole, is less easily reduced than phenylpyrazoline to the pyrazolidine.

1-Phenyl-5-pyrazolone is reduced (at 70—80°) by the Willstätter method, giving 1-phenyl-5-pyrazolidone, 1-phenyl-3-methylpyrazolone undergoing the corresponding reduction less rapidly. 1-Phenyl-2-methyl-5-pyrazolone is not reduced under similar conditions.

Nitrosoantipyrine is so rapidly reduced to 4-aminoantipyrine (Willstätter method) that any molecular instability induced by the nitroso-group could not be detected.

1-Phenyl-3 : 4 : 4-trimethyl-5-pyrazolone differs from other pyrazolones in being reducible (at the ordinary temperature and 860 mm.) to 5-hydroxy-1-phenyl-3 : 4 : 4-trimethylpyrazoline. In 4-keto-1-phenyl-3-methyl-5-pyrazolone, however, the 4- and not the 5-carbonyl group is reduced (the product being 4-hydroxy-1-phenyl-3-methyl-5-pyrazolone), which is additional evidence of the interaction of groups in the 2 : 5-positions.

Knorr's conception of the antipyrine molecule ("half-benzene" formula, etc.) also falls in line with the instability of 3 : 4-additive compounds. Antipyrine dibromide readily loses hydrogen bromide, giving 4-bromoantipyrine. Nitrogen peroxide, when added to a solution of antipyrine in light petroleum, gives a brown, crystalline *additive* compound, which with water affords nitroso- and nitroantipyrine. Similarly, cyanogen bromide combines with antipyrine in ethereal solution to give an *additive* compound, decomposed by water to give 4-bromoantipyrine. E. E. T.

**Synthesis of Pyrazolealdehydes.** I. C. A. ROJAHN and K. FAHR (*Annalen*, 1923, **434**, 252—264).—Whereas six of the best-known methods for the preparation of an aldehyde from the corresponding acid proved valueless in the pyrazole series, the method of Rosenmund (*A.*, 1921, ii, 320) gave good, although variable, results. It was found that a catalyst "regulator" was unnecessary, the use of dry hydrogen free from oxygen being, however, essential. In presence of traces of oxygen, acid anhydrides were obtained instead of aldehydes.

5-Chloro-1-phenyl-3-methylpyrazole-4-aldehyde, colourless needles, m. p. 142—143° (*phenylhydrazone*, m. p. 174°; *semicarbazone*, m. p. 214—215°) was obtained in small quantities by the Étard oxidation of 5-chloro-1-phenyl-3 : 4-dimethylpyrazole, and in good yield by reducing 5-chloro-1-phenyl-3-methylpyrazole-4-carboxyl chloride, using a palladium-barium sulphate catalyst in presence of xylene, at 150—160°. In presence of "sulphured" quinoline and traces of oxygen, the main product was the *anhydride*, needles, m. p. 178°.

The acid gives an *ethyl* ester, m. p.  $74^{\circ}$ , an *amide*, m. p.  $195^{\circ}$ , an *anilide*, m. p.  $156^{\circ}$ , and a *dihydrazide*,  $C_{22}H_{18}O_2N_6Cl_2$ , m. p.  $248^{\circ}$ .

3-Chloro-1-phenyl-5-methylpyrazole-4-carboxylic acid (needles, m. p.  $216^{\circ}$ ), gives an *ethyl* ester (needles, m. p.  $93-94^{\circ}$ ) and a *chloride*, m. p.  $67^{\circ}$ , b. p.  $235-240^{\circ}/20-25$  mm. The corresponding *aldehyde* (needles, m. p.  $103-104^{\circ}$ ) forms a *semicarbazone* (m. p.  $182^{\circ}$ ) and an *aminoguanidine* derivative (nitrate),  $C_{12}H_{14}O_3N_7Cl$ , m. p.  $204-205^{\circ}$  (decomp.).

1-Phenyl-3:5-dimethylpyrazole-4-carboxyl chloride has m. p.  $64^{\circ}$  and b. p.  $208-210^{\circ}/20$  mm. The corresponding *aldehyde* forms needles, m. p.  $123-124^{\circ}$  (*phenylhydrazone*, m. p.  $140-141^{\circ}$ , *semicarbazone*, m. p.  $191-192^{\circ}$ ). The acid *anhydride* has m. p.  $189.5^{\circ}$ .

1:3-Diphenyl-5-methylpyrazole-4-carboxyl chloride has m. p.  $82^{\circ}$ , and b. p.  $235-240^{\circ}/17$  mm., the corresponding *aldehyde* (needles, m. p.  $131-132^{\circ}$ ) giving a *semicarbazone* and *aminoguanidine* derivative (nitrate),  $C_{18}H_{19}O_3N_7$  (m. p.  $207^{\circ}$  and  $208^{\circ}$  [decomp.], respectively), whilst the corresponding acid *anhydride* has m. p.  $205^{\circ}$ .

1-Phenyl-5-methylpyrazole-4-carboxyl chloride has m. p.  $147^{\circ}$  and b. p.  $260-270^{\circ}/25$  mm., the corresponding *anhydride* having m. p.  $156^{\circ}$ . The *phenylhydrazone* of the corresponding *aldehyde* has m. p.  $145^{\circ}$  (decomp.).

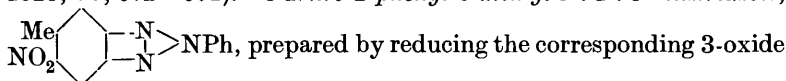
5-Chloro-1-phenyl-3-methylpyrazole-4-aldehyde, when heated with hydrazine hydrate, gave the corresponding *hydrazone*(?), m. p.  $189-190^{\circ}$ , or, at higher temperatures, the *hydrazone* of 1-phenyl-3-methyl-5-hydroxypyrazole-4-aldehyde, m. p.  $201-202^{\circ}$ , which on benzoylation gave the N-benzoyl derivative (m. p.  $163^{\circ}$ ) of 1'-benzoyl-1-phenyl-3-methyldipyrzole (cf. A., 1917, i, 480). E. E. T.

**Preparation of Unsymmetrical C.C.-Dialkylbarbituric Acids.** E. LAYRAUD (Brit. Pat. 191008).—New unsymmetrical C.C.-dialkylated derivatives of barbituric acid, viz., *ethylisobutylbarbituric acid*, *ethylisoamylbarbituric acid*, *propylbutylbarbituric acid*, *propylisobutylbarbituric acid*, and *propylisoamylbarbituric acid* can be produced by alkylising a monoalkylbarbituric acid as described in Brit. Pat. 1945/03, or by the direct condensation of carbamide or of its generators with a dialkylmalonic ester, chloride, amide, etc., in presence of a condensing agent such as a metallic alkoxide as in Brit. Pat. 1664/03, or by condensing dialkylcyanoacetic ester with carbamide or its generators in presence of an alkali alkoxide, and splitting off the imino-group by treatment with an acid as described in Brit. Pat. 18246/03. Silver ethylbarbiturate, prepared by treatment of the free acid in aqueous solution with ammoniacal silver nitrate, is heated for six hours under pressure at  $150^{\circ}$  with *isobutyl iodide* in an alcohol solvent. The *ethylisobutylbarbituric acid* obtained has m. p.  $173-174^{\circ}$ . *Ethylisoamylbarbituric acid*, m. p.  $154-155^{\circ}$ , is similarly prepared. The former acid can also be produced by heating *ethylisobutylmalonic ester*, carbamide, and sodium ethoxide together in alcoholic solution under pressure at  $110^{\circ}$  for five hours. *Propylbutylbarbituric acid*, m. p.  $153^{\circ}$ , is prepared by heating *propylbutylcyanoethyl acetate* with carbamide in alcoholic solution in presence of sodium ethoxide under reflux for six hours

and hydrolysing the sodium salt of the iminopropylbutylbarbituric acid thus produced. *Propylisobutyl-* and *isoamylbarbituric* acids, m. p. 164—165° and 134°, respectively, are similarly obtained.

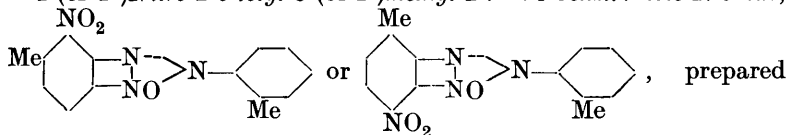
T. S. W.

**Reduction of Azimino-oxides.** A. ANGELETTI (*Gazzetta*, 1923, **53**, 672—674).—5-Nitro-2-phenyl-6-methyl-2 : 1 : 3-benztriazole,



(cf. Giua and Giua, A., 1923, i, 608) by means of hydrazine hydrate, crystallises in lustrous needles, m. p. 131—132°.

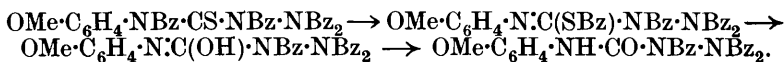
4-(or 1-)Nitro-2-o-tolyl-5-(or 4-)methyl-2 : 1 : 3-benztriazole N-oxide,



by treating 2 : 3 : 4-trinitrotoluene with o-tolylhydrazine, crystallises in silky flocks of pale yellow needles, m. p. 202—203°, and in alcoholic solution gives with potassium hydroxide first a green and then a deep blue coloration. Saturation of its alcoholic solution with hydrogen chloride results in no coloration, although under the same conditions the nitroazo-compounds give a bright carmine-red colour (cf. Giua and Giua, *loc. cit.*). When reduced by means of hydrazine hydrate it gives 4-(or 1-)nitro-2-o-tolyl-5-(or 4-)methyl-2 : 1 : 3-benztriazole,  $C_{14}H_{12}O_2N_4$ , which forms crystals, m. p. 164—165°, dissolves in concentrated sulphuric acid without coloration and, in alcoholic solution, gives a deep reddish-violet coloration with potassium hydroxide.

T. H. P.

**Action of Acid Chlorides on Semicarbazides.** E. FROMM, M. SOFFNER, and M. FREY (*Annalen*, 1923, **434**, 285—295).—A study of the action of benzoyl chloride (alone or in presence of sodium hydroxide, hot or cold), on 4-o-tolylthiosemicarbazide (m. p. 148°; the benzaldehyde and acetone semicarbazones, melting, respectively, at 159° and 182°) and on 4-o-anisylthiosemicarbazide (m. p. 156°; giving semicarbazones with benzaldehyde and acetone, melting, respectively, at 174° and 140°). Both thiosemicarbazides, when treated with excess of benzoyl chloride and sodium hydroxide, give, in the cold, unstable, yellow tetrabenzoyl derivatives (both melting at 154°). The yellow anisyl derivative, on crystallisation or keeping, becomes colourless, owing to decomposition; on boiling its chloroform solution and treating with alkali, it is converted into colourless tribenzoyl-4-o-anisylsemicarbazide, m. p. 136° :



Tolyl- and anisyl-thiosemicarbazides give (cf. Pulvermacher, A., 1894, 304) 1-monobenzoyl derivatives (m. p. 138° and 157°, respectively). If the monobenzoyl-anisyl compound is heated with 1

equivalent of benzoyl chloride, or if the original thiosemicarbazide is heated with excess of this reagent, 3-thiol-5-phenyl-4-anisyl-1 : 2 : 4-triazole (m. p. 232°) is formed (benzoyl derivative, m. p. 176°).

If 4-o-tolylthiosemicarbazide is heated (1) with a slight excess of benzoyl chloride, there is obtained a substance,  $C_{23}H_{20}ON_4S$ , m. p. 188°, converted by alcoholic potassium hydroxide into potassium benzoate, and a second substance,  $C_{16}H_{20}O_2N_4S$ , m. p. 154°; whilst (2), using a large excess of benzoyl chloride, dibenzoyl-2 : 5-ditoluidino-1 : 3 : 4-thiodiazole, m. p. 252°, is obtained. The de-benzoylated compound, 2 : 5-o-toluidino-1 : 3 : 4-thiodiazole, may be obtained (e.g., by oxidation with iodine) from di-o-tolylhydrazodithiodicarbonamide,  $C_7H_7 \cdot NH \cdot CS \cdot NH \cdot NH \cdot CS \cdot NH \cdot C_7H_7$  (m. p. 179°), which is evidently formed in the above reaction by the condensation (with loss of hydrazine) of 2 mols. of 4-o-tolylthiosemicarbazide, and is also obtainable by the action of o-tolylthiocarbimide on the latter compound.

Phenyl-o-tolylhydrazodithiodicarbonamide and the corresponding o-tolyl-o-anisyl derivative melt, respectively, at 180° and 164°.

3-Thiol-4-toluidino-4-tolyl-1 : 2 : 4-triazole has m. p. 180° and with lead acetate gives the compound  $C_{18}H_{14}O_2N_4SPb$ , m. p. above 350°.

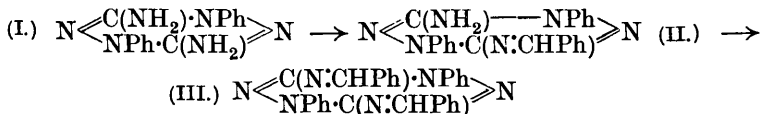
Di-o-anisylhydrazodithiodicarbonamide (from hydrazine sulphate, alkali, and anisylthiocarbimide, or from the last-named compound and anisylthiosemicarbazide) has m. p. 146°, and is converted by hot dilute sodium hydroxide into 3-thiol-5-anisidino-4-anisyl-1 : 2 : 4-triazole, m. p. 208° (benzoyl derivative, m. p. 192°; mercurichloride, m. p. above 350°), together with a little 3 : 5-dithiol-4-anisyl-1 : 2 : 4-triazole, isolated as the lead derivative.

Di-o-anisylhydrazodithiodicarbonamide, on oxidation with iodine, affords 2 : 5-dianisidino-1 : 3 : 5-thiodiazole (hydrochloride, needles; benzoyl derivative, m. p. 240°).  
E. E. T.

**Action of Cyanogen Halides on Phenylhydrazine. VII. Derivatives of Guanazine.** G. PELLIZZARI (*Gazzetta*, 1923, 53, 661—667; cf. A., 1922, i, 585).—The action of cyanogen halides on phenylhydrazine yields the isomeric  $\alpha$ - and  $\beta$ -cyanophenylhydrazines,  $CN \cdot NPh \cdot NH_2$  and  $NHPh \cdot NH \cdot CN$ . The latter is readily transformed into the dimeric diphenylaminoguanazole (cf. A., 1911, i, 338), which is comparable with the so-called diphenylurazine, shown by Busch to be anilinophenylurazole (A., 1901, i, 488). It is now found that, by treatment with acetic anhydride,  $\alpha$ -cyanophenylhydrazine may be converted into the dimeride, diphenylguanazine. This polymerisation appears to be preceded by acetylation, the first product being  $\alpha$ -cyano- $\beta$ -acetylphenylhydrazine, which then yields diacetyldiphenylguanazine,  $2CN \cdot NPh \cdot NH_2 \rightarrow 2CN \cdot NPh \cdot NHAc \rightarrow NH : C \begin{smallmatrix} NPh \cdot NAc \\ NAc \cdot NPh \end{smallmatrix} C : NH$ . This compound may be de-acetylated by stages to acetyldiphenylguanazine and diphenylguanazine, and may also be acetylated further to tetra-acetyldiphenylguanidine. The formation of the latter confirms the structure assumed for diphenylguanazine, but it may also react according to the tautomeric form (I), since with benzaldehyde



it yields benzylidene and dibenzylidene derivatives, to which only the formulæ II and III can be attributed :



*Diacetyldiphenylguanazine* (see above) forms minute, lustrous, white crystals, m. p. 268°. The *monoacetyl* compound,  $\text{C}_{16}\text{H}_{16}\text{ON}_6$ , crystallises in tufts of silky, white needles, m. p. 228°, and exhibits slight basic properties.

*Diphenylguanazine*,  $\text{NH}:\text{C} \begin{array}{c} \text{NPh} \cdot \text{NH} \\ \text{NH} \cdot \text{NPh} \end{array} \text{C}:\text{NH}$  or (I) (see above), crystallises in lustrous, white lamellæ, m. p. 198°, exhibits the normal molecular weight in freezing acetic acid or naphthalene, and reduces hot ammoniacal silver nitrate solution and Fehling's solution and, in alcoholic solution, cupric oxide.

*Tetra-acetyldiphenylguanazine*,  $\text{NAc} \begin{array}{c} \text{NPh} \cdot \text{C}(\text{NAc}) \\ \text{C}(\text{NAc}) \cdot \text{NPh} \end{array} \text{NAc}$ , crystallises in lustrous lamellæ, m. p. 188—189°, with previous softening.

*Benzylidenediphenyldiaminodihydrotetrazine* (II), forms pale yellow, lustrous crystals, m. p. 183°, and *diaminodiphenyldibenzylidenedihydrotetrazine* (III), deep yellow, lustrous needles, m. p. 150°  
T. H. P.

**The Influence of Sulphur on the Colour of Azo-dyes.** W. R. WALDRON and E. EMMET REID (*J. Amer. Chem. Soc.*, 1923, **45**, 2399—2417).—A number of azo-dyes containing sulphur are prepared and contrasted with similarly constituted substances not containing sulphur. The sulphur atom has a decided bathochromic effect, provided it is joined directly to the ring carrying the azo-chromophore group. If it is separated from the ring, or if it is present as a sulphone group, it has little effect.

Sodium *p*-nitrophenyl sulphide (cf. Brand and Wirsing, A., 1913, i, 406) is quite stable when pure and dry. Its preparation, and that of *p*-nitrobenzyl bromide, are described in detail.

The following *p*-nitrophenyl alkyl sulphides,  $\text{R} \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , are prepared by the action of an alkyl halide on sodium *p*-nitrophenyl mercaptan in boiling aqueous-alcoholic solution:  $\text{R}$ =methyl, m. p. 72°, ethyl, m. p. 44°, isopropyl, m. p. 44·5°,  $\beta$ -hydroxyethyl, m. p. 59° (yellow needles); benzyl, phenacyl, m. p. 118° (yellow plates); propyl,  $d_{25}^{25}$  1·1963, isobutyl,  $d_{25}^{25}$  1·1573, butyl,  $d_{25}^{25}$  1·1625, isoamyl,  $d_{25}^{25}$  1·1335 (brown oils). The  $\beta$ -hydroxyethyl derivative is converted by boiling with hydrobromic acid into the  $\beta$ -bromoethyl compound, yellow plates, m. p. 58°. Esters of *p*-nitrophenyl mercaptan are obtained by the use of benzoyl chloride, carbonyl chloride, or thiocarbonyl chloride, but not of toluene-*p*-sulphonyl chloride or *m*-nitrobenzenesulphonyl chloride. The *thiobenzoate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{COPh}$ , yellow plates, has m. p. 123·7°; the *dithiocarbonate*,  $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S})_2\text{CO}$ , a yellow powder, has m. p. 174·5°; the *trithiocarbonate*, m. p. 141°, is a buff powder. The nitrophenyl

alkyl sulphides are reduced by means of iron dust and acetic acid, or hydrochloric acid, giving the following *p*-aminophenyl alkyl sulphides: methyl,  $d_{25}^{25}$  1.1425, ethyl,  $d_{25}^{25}$  1.1010, isopropyl, propyl, isobutyl,  $d_{25}^{25}$  1.0421, butyl, isoamyl, benzyl,  $d_{25}^{25}$  1.1321, which are colourless oils, but darken rapidly in the light; phenyl, m. p. 95.8°, phenacyl, m. p. 111.5°. The following *p*-nitrophenylsulphones,  $R \cdot SO_2 \cdot C_6H_4 \cdot NO_2$ , which are prepared by the gradual addition of saturated chromic acid solution to a boiling solution of the nitrothioether in 80% acetic acid, are white plates or needles: methyl, m. p. 142.5°; ethyl, m. p. 138.5°; isopropyl, m. p. 115.3°; propyl, m. p. 114°; isobutyl, m. p. 73°; butyl, m. p. 56.4°; isoamyl, m. p. 62.5°; phenyl, m. p. 142°; benzyl, m. p. 172°. Reduction of these nitrosulphones gives the following *p*-aminophenylsulphones,  $R \cdot SO_2 \cdot C_6H_4 \cdot NH_2$ , which are white plates or needles: R=methyl, m. p. 133°; ethyl, m. p. 89.3°; isopropyl, m. p. 122°; propyl, m. p. 97°; isobutyl, m. p. 83.7°; butyl, m. p. 109°; isoamyl, m. p. 110°; phenyl, benzyl, m. p. 218.5°.

The action of *p*-nitrobenzyl bromide in alcoholic solution at 60° on sodium methylmercaptide, or ethylmercaptide, gives *p*:*p*'-dinitrodibenzyl sulphide, but by a similar method the following sulphides are obtained: *p*-nitrobenzyl butyl sulphide, an oil,  $d_{25}^{25}$  1.1462; *p*-nitrobenzyl isoamyl sulphide, an oil,  $d_{25}^{25}$  1.1513; phenyl *p*-nitrobenzyl sulphide, white plates, m. p. 79°. These sulphides give, on reduction, the corresponding aminosulphides: butyl, an oil,  $d_{25}^{25}$  1.0321; isoamyl, an oil,  $d_{25}^{25}$  1.0307; phenyl, m. p. 72°; and, on oxidation, the *p*-nitrobenzyl sulphones: butyl, m. p. 139.5°; isoamyl, m. p. 117°; phenyl, m. p. 209.5°, which form white plates, and are decomposed by the action of hot 20% sodium hydroxide solution, giving a red solution and a yellow precipitate, m. p. 195°, which is free from sulphur (probably  $NO_2 \cdot C_6H_4 \cdot CH : CH \cdot C_6H_4 \cdot NO_2$ ). The *p*-aminobenzylsulphones are produced by the reduction of the nitrosulphones: butyl, m. p. 95°; isoamyl, m. p. 126°; phenyl, m. p. 180°, all of which form needles.

The action of sodium *p*-nitrophenyl sulphide (2 mols.) in aqueous-alcoholic solution at 65–70° on halides, such as methylene iodide, ethylene bromide, benzylidene chloride, mustard gas, or its sulphone, etc., gives *p*:*p*'-dinitrodiphenyl derivatives of the general formula,  $(NO_2 \cdot C_6H_4)_2X$ , where X has the structures mentioned in the following list:  $-CH_2 \cdot S-$ , pale yellow plates, m. p. 108°;  $-S \cdot CH_2 \cdot S-$ , olive plates, m. p. 179°;  $-S \cdot [CH_2]_2 \cdot S-$ , yellow plates, m. p. 136°;  $-S \cdot [CH_2]_3 \cdot S-$ , yellow plates, m. p. 110°;  $-S \cdot CHPh \cdot S-$ , yellow needles, m. p. 150.5°;  $-S \cdot [CH_2]_2 \cdot S \cdot [CH_2]_2 \cdot S-$ , yellow plates, m. p. 86.5°;  $-S \cdot [CH_2]_2 \cdot SO_2 \cdot [CH_2]_2 \cdot S-$ , pale yellow plates, m. p. 170°. These give, on reduction by means of iron and acetic acid, the corresponding *p*:*p*'-diaminodiphenyl derivatives, which have, respectively, the following characteristics: flat needles, m. p. 93°; red needles, m. p. 99°; red needles, m. p. 111°; an oil; white needles, m. p. 131°; red needles, m. p. 93°, and white needles, m. p. 149°. Oxidation of the dinitro-sulphides by means of chromic acid in acetic acid solution gives, in general, the corresponding dinitrosulphones, but *p*:*p*'-dinitrodiphenyldithiomethane,  $R \cdot S \cdot CH_2 \cdot S \cdot R$ , is broken

down into sulphonic acids :  $-\text{CH}_2\cdot\text{SO}_2^-$ , m. p.  $195^\circ$ ;  $-\text{CH}_2\cdot\text{SO}_2\cdot\text{CH}_2^-$ , m. p.  $260^\circ$ ;  $-\text{SO}_2\cdot[\text{CH}_2]_2\cdot\text{SO}_2^-$ , m. p.  $235^\circ$  (decomp.);  $-\text{SO}_2\cdot[\text{CH}_2]_3\cdot\text{SO}_2^-$ , m. p.  $208^\circ$ ;  $-\text{SO}_2\cdot[\text{CH}_2]_2\cdot\text{SO}_2\cdot[\text{CH}_2]_2\cdot\text{SO}_2^-$ , m. p.  $235^\circ$  (decomp.), of which the first forms white plates, and the others white needles. The reduction of the dinitro-sulphones presents great difficulty. The action of iron and acetic acid on dinitrodiphenylsulphone gives *p* : *p'*-diaminodiphenylsulphone (Fromm and Wittmann, A., 1908, i, 631), but from the  $-\text{SO}_2\cdot\text{CH}_2^-$  compound a substance is obtained, m. p.  $215^\circ$  (decomp.), which appears to be a nitroamino-sulphone, whilst dinitrodibenzylsulphone yields a white, tarry material. The last two reductions are, however, readily effected by the use of tin and alcoholic hydrochloric acid. *p*-Aminophenyl-*p*-aminobenzyl sulphone forms white plates, m. p.  $216^\circ$ ; di-(*p*-aminobenzyl)sulphone, yellow needles, has m. p.  $187\cdot5^\circ$ .

Dyes are prepared from the *p*-aminophenyl alkyl or aryl sulphides, the analogous sulphones, the *p*-aminobenzyl alkyl or aryl sulphides, and from the corresponding sulphones. The base, or its sulphate, dissolved in dilute hydrochloric acid, is diazotised by means of sodium nitrite at  $5^\circ$ . The solution, after keeping for thirty minutes, is added to a slight excess of *R*-salt, dissolved in two equivalents of sodium carbonate solution, at  $5^\circ$ . Dyes are made in the same way from thioanisidine or its sulphone, the following intermediates being also used : salicylic acid, Schaeffer's salt, Neville and Winther's acid, L-acid, and chromotrope acid, and these dyes are compared with those similarly derived from *p*-toluidine and *p*-anisidine. All these dyes are acid colours, dyeing animal fibres from a boiling, slightly acid bath (sulphuric acid), containing sodium sulphate. Dyes are also prepared from the *p* : *p'*-diaminodiphenyl compounds,  $(\text{NH}_2\cdot\text{C}_6\text{H}_4)_2\text{X}$  (sulphides and sulphones). The base is tetrazotised at  $5^\circ$  as before, and, after keeping for thirty minutes, the solution is coupled at  $5^\circ$  with sodium salicylate (1 mol.). After keeping for three hours the liquid is warmed at  $35^\circ$ , and kept over-night; the second molecule of sodium salicylate is then added. These acid chrome colours are used in a boiling solution containing acetic acid and sodium sulphate, to which, if the dye is to be chromed, dichromate is subsequently added, and the boiling continued. Thioaniline, its sulphone, and the diamine from mustard gas,  $(\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot[\text{CH}_2]_2)_2\text{S}$ , are tetrazotised and coupled with the other intermediates mentioned above; for comparison, similar dyes are prepared from benzidine. Additional dyes are made from the same bases by tetrazotising, and coupling with H-acid, in alkaline solution, or with naphthionic acid or  $\gamma$ -acid, in neutral solution. These colours are applied to cotton by the use of a boiling solution containing sodium chloride.

All the dyes derived from *R*-salt and the amino-sulphides,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SR}$ , are red, except that, when  $\text{R}=\text{Me}$  or  $\text{Ph}$ , the colour is Bordeaux or scarlet. The bathochromic effect of the sulphur atom is therefore so decided that the nature of the adjacent group *R* makes little difference in the colour of the dye. But this is not so if the sulphur atom is removed from the benzene nucleus; for

whilst the dye derived from the base containing the group  $-S\cdot CH_2Ph$  is deep red, that obtained from the isomeric base containing the group  $-CH_2\cdot S\cdot Ph$  is tangerine, and so is that from the base containing  $-CH_2\cdot S\cdot C_5H_{11}$  (*iso*). In the last two the oxidation of the sulphur atom to  $-SO_2-$  does not alter the colour, although, in those dyes containing the  $-S\cdot C_6H_4\cdot N:N-$  group, oxidation of the sulphur atom to  $-SO_2-$  completely destroys the bathochromic effect. In fact, the sulphone group is actually hypsochromic. Thus the dyes from  $NH_2\cdot C_6H_4\cdot SO_2R$  are gold coloured, whilst that from aniline and *R*-salt is orange. In this series also, the actual nature of *R* scarcely affects the colour. It is curious that the dye derived from the base,  $NH_2\cdot C_6H_4\cdot S\cdot CPh$ , is scarlet; this is ascribed to the overwhelming effect of oxidation, even of the group beyond the sulphur atom.

Since the alkyl group present in the sulphide or sulphone is of little consequence, further comparisons are made between dyes containing the groups  $-Me$ ,  $-OMe$ ,  $-SMe$ , and  $-SO_2Me$ . *p*-Toluidine (*a*), *p*-anisidine (*b*), *p*-thioanisidine (*c*), and its sulphone (*d*) are diazotised and coupled with salicylic acid, Schaeffer's salt, Neville and Winther's acid, *L*-acid, *R*-salt, and chromotrope acid. In the following list of colours the second refers to the chromed salicylic acid. (*a*) Yellow, yellow, orange, scarlet, red, scarlet, cardinal. (*b*) Yellow, yellow, scarlet, scarlet, red, red, heliotrope. (*c*) Yellow (darker), old gold, red, red, bordeaux, bordeaux, violet. (*d*) Gold, old gold, gold, orange, old gold, gold, red. The following order of the auxochromes mentioned, with respect to the colour of the dye, holds, therefore, regardless of the nature of the second constituent:  $-SMe$ ,  $-OMe$ ,  $-Me$ ,  $-SO_2Me$ .

The chromed colours obtained from salicylic acid and diamines of the type  $(NH_2\cdot C_6H_4)_2X$  are as follows:  $X=S$ , old gold,  $-CH_2\cdot S-$  or  $-CH_2\cdot S\cdot CH_2-$ , old gold,  $-S\cdot CH_2\cdot S-$ , old gold (but deeper),  $-S\cdot [CH_2]_2\cdot S-$  or  $-S\cdot [CH_2]_2\cdot S\cdot [CH_2]_2\cdot S-$ , gold, whilst the dye from benzdine is gold. These results also show that the sulphur atom exerts its greatest influence on colour when directly connected with the ring. The sulphone of thioaniline gives an old gold, but darker than that from thioaniline itself; the dyes from the mustard gas amine and its sulphone are practically identical.

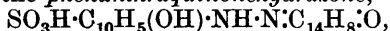
The following colours are for the dyes derived from (*a*) benzdine, (*b*) thioaniline, (*c*) its sulphone, and (*d*) the diamine from mustard gas, when diazotised and coupled with salicylic acid (chromed), Schaeffer's salt, Neville and Winther's acid, *L*-acid, *R*-salt, chromotrope acid,  $\gamma$ -acid, Chicago acid, and *H*-acid: (*a*) yellow, maroon, heliotrope, claret, purple, purple, violet, purple, blue; (*b*) gold, scarlet, red, claret, claret, heliotrope, claret, lilac, purple; (*c*) gold, orange, scarlet, burnt orange, burnt orange, claret, claret, maroon, maroon; (*d*) yellow, scarlet, red, red, red, heliotrope, red, violet, lilac. In this series, the interposition of a sulphur atom, or of groups, between the benzene nuclei, destroys the mutual influence of the latter; the colours obtained are, for that reason, lighter than when benzdine is used, in spite of the effect, in series (*b*) and (*d*), of a bathochromic sulphur atom. The dyes from  $\gamma$ -acid and

the diamine bases having the groups  $-\text{S}\cdot\text{CH}_2\cdot\text{S}-$ ,  $-\text{S}\cdot[\text{CH}_2]_2\cdot\text{S}-$ , and  $-\text{S}\cdot[\text{CH}_2]_3\cdot\text{S}-$  are red, red, and maroon, respectively. That these diamine bases are unlike benzidine is illustrated by the fact that they do not form fast direct cotton dyes. The following colours refer to cotton, coloured with the dyes obtained from (a) benzidine, and (b), (c), (d), the three bases just mentioned, and naphthionic acid,  $\gamma$ -acid, and  $H$ -acid: (a) red, violet, blue; (b) burnt orange, claret, blue; (c) burnt orange, claret, blue; (d) gold, maroon, violet.

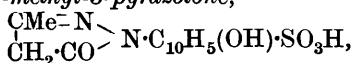
W. S. N.

***J*-Acid (iso- $\gamma$ )[6-Amino- $\alpha$ -naphthol-3-sulphonic Acid].** M. BATTEGAY and A. WOLFF (*Bull. Soc. chim.*, 1923, **33**, [iv], 1481—1510).—Of the forty-seven known aminonaphtholsulphonic acids, only two, *J*-acid and *M*-acid (5-amino- $\alpha$ -naphthol-3-sulphonic acid) yield derivatives which dye cotton fabrics directly. The authors show that *J*-acid itself and those of its derivatives in which the aminogen group is replaced by such substituents as chlorine or the hydrazine group only have a feeble affinity for cellulose, but the replacement of the hydrogen group by methylpyrazolone results in a high degree of affinity. Comparative study of the monoazo-colours derived from *J*-acid or of its derivative diazo-compounds clearly shows the great influence of the aminogen group on affinity for cellulose. The colours derived from the acid itself are more powerful dyes than those derived from the chloro- or methylpyrazolone derivatives. In replacing the amino-group by a hydrazine group the tinctorial power of the resulting substance chiefly depends on the nature of the ketone condensed with the hydrazine. Comparison with aldehydic condensation products was not possible, as the reaction stops at the intermediate stage and the final dehydration involves partial decomposition. Derivatives of aromatic  $\alpha$ -diketones have great tinctorial power for cellulose. They may be considered as derivatives of *J*-acid in which the aminogen group is replaced by the azo-group. The authors regard them as *o*-oxyazo-dyes. The general conclusion is drawn that the derivatives of two of the many isomeric aminonaphtholsulphonic acids possess their special tinctorial properties in virtue of their more symmetrical structure.

The following derivatives of the acid are described, together with their chemical and tinctorial properties: the 4 : 4'-tetramethyldiaminodiphenylketohydrazone,  $\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{NH}\cdot\text{N}:\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , an orange-red powder, prepared by direct condensation in presence of hydrochloric acid with subsequent hydrolysis of the resulting hydrochloride; the phenanthraquinonehydrazone,



small, red grains, prepared as the calcium salt by condensing the hydrazine of the acid with phenanthraquinone in presence of calcium carbonate; the isatinhydrazone,  $\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{NH}\cdot\text{N}:\text{C}_8\text{NH}_5\text{O}$ , obtained in an impure condition as calcium salt by a similar method; 1-sulphonaphthol-3-methyl-5-pyrazolone,



a white powder, formed on condensing the hydrazine of the acid with acetoacetic ester, which readily couples with the diazo-compound of *p*-nitroaniline; the *tartrazine*, dark brown powder prepared from the hydrazine and sodium dihydroxytartrate; the *m*-nitrobenzaldehydehydrazone,  $\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , orange-red, hygroscopic crystals, which do not appear to have undergone the final change involving loss of the elements of water; sodium 6-chloro- $\alpha$ -naphthol-3-sulphonate, white crystals; the 4-diazo-*m*-xylidine derivative, red powder; the 2-diazo-*m*-xylidine derivative of the sodium salt of 6-chloro- $\alpha$ -naphthol-3-sulphonic acid, orange-red powder with bronze sheen; the 4- $\beta$ -naphthylaminediazo-derivative, small crystals with bronze sheen; the 2- $\beta$ -naphthylamine diazo-derivative of 6-chloro- $\alpha$ -naphthol-3-sulphonic acid, brown powder; 6-methylpyrazolone- $\alpha$ -naphthol-2-diazo-*m*-xylidine-3-sulphonic acid, dark red powder; 6-methylpyrazolone- $\alpha$ -naphthol-2-diazo- $\beta$ -naphthylamine-3-sulphonic acid, orange-red powder. [Cf. *B.*, 49.] H. J. E.

**The Specific Ash of Proteins.** R. MIESES (*Biochem. Z.*, 1923, **142**, 312—316).—A study has been made of the ash content of the various protein fractions of ox-serum. The fractions insoluble in water contain a high proportion of ash insoluble in water, whilst the reverse holds for the water-soluble fractions. In the albumin, the percentage of calcium is greater than that of phosphate; they are approximately the same in the soluble globulin, and in a reverse ratio in the insoluble globulin. J. P.

**Carbophosphide and its Action on Blood-serum.** G. CUNEO (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 230—237).—The passage of hydrogen phosphide through a 20% solution of carbonyl chloride in toluene results in the formation of *carbophosphide*,  $\text{CO}(\text{PH}_2)_2$ , as a yellow powder which has no definite melting point and decomposes at above 250°. This compound remains unaltered in either a vacuum or a desiccator, but in moist air undergoes slow oxidation with formation of carbon dioxide, gaseous hydrogen phosphide, and oxygenated phosphorus compounds.

When blood-serum is centrifuged and repeatedly filtered and then treated with about 0.4% of carbophosphide at 38—40°, a *phospho-albumin* is gradually precipitated. This compound contains phosphorus in organic combination, reddens blue litmus paper, and dissolves readily in very dilute alkali hydroxide or carbonate solution or in disodium hydrogen phosphate or sodium acetate solution. In alkaline solution, it remains unaltered for months and has a characteristic odour resembling that of ozone. It contains 14.31% N and 2.91—3.03% P, and when dissolved in 1% sodium carbonate solution and injected subcutaneously, intravenously, or intraperitoneally into the dog, produces rise in temperature.

[With E. MARAGLIANO.]—Carbophosphide causes increased appetite in many cases, exerts an inhibiting effect in general, and especially gastro-intestinal, putrefaction, often reduces the frequency

of epileptic attacks, and is advantageous in all conditions in which administration of phosphorus is indicated. T. H. P.

### Physical Chemistry of the Globulins. II. Acid Globulins.

M. ADOLF (*Koll. Chem. Beihefte*, 1923, **18**, 223—274; cf. A., 1923, i, 396).—The physico-chemical relationships of the globulins have been investigated with respect to the acids, hydrochloric, sulphuric, phosphoric, oxalic, trichloroacetic, and acetic. It is shown that the different acids in the presence of an excess of albumin exhibit a definite power of dissolving globulin, which appears to be independent of the strength and basicity. None of the salts so produced is neutral but all are somewhat hydrolysed. The combining power of globulin in acid solutions is different in the different acids and is apparently not connected with the strength or basicity of the acid. It increases with acids in the order acetic < phosphoric < hydrochloric < sulphuric. In the case of the two acids last-named, the process of combination appears to be a time process. Determinations of the residual conductivity and the mobility of the ions show that there is no reason for assuming that in acid solutions further basic valencies come into action. The increased viscosity in excess of acid is not entirely dependent on the albumin concentration, for it increases with the different acids in the opposite sense to the combining power. From electrometric measurement of the hydrogen- and chlorine-ions and from residual conductivity measurements, it is shown that the viscosity maximum and the ionisation maximum coincide, and a minimum in both these factors also coincides. A correlation of the measurements shows that a portion of the acid is molecularly combined with the globulin. The quantity of combined acid is dependent on the nature of the acid anion and is inversely proportional to the hydration as determined by viscosity measurements. The ionic conductivity of the positive globulin-ion in combination with various acids has been found in excess of acid saturated with albumin to be 50 ohms<sup>-1</sup>. In spite, therefore, of the formation of molecular compounds with acids, the globulin acid compounds behave as salts. From the present work and that previously published, globulin is found to have a valency of seven. J. F. S.

### Physical Chemistry of the Globulins. III. Globulin Salts.

M. ADOLF (*Koll. Chem. Beihefte*, 1923, **18**, 273—313; cf. preceding abstract).—Globulin salt solutions of high albumin content and exactly known salt concentration have been prepared, which it is shown display all the characteristic properties of natural globulin solutions. In a *N*/10-solution of an alkali chloride  $3.2 \times 10^{-3}$  equivalents are combined with 1 g. of globulin, hence on the basis of the previously determined molecular weight of globulin, a single molecule is combined with 4 mols. of alkali chloride. By means of electrical conductivity measurements, transport experiments, and electrometric measurements of the chloride-ion concentration, it is shown that globulin salt compounds ionise according to the equation  $\text{GM}^+ + \text{Cl}^- \rightleftharpoons \text{GMCl}$ , the ion containing the globulin being positively charged. The ionic conductivity of the positive ion of the globulin

salt is found to be 50 ohms<sup>-1</sup>. The globulin salt has a not inconsiderable viscosity which is apparently independent of the nature of the anion of the salt. From electrometric measurements of the hydrogen-ion concentration, it is shown that globulin salt solutions in an excess of salt solution have a small but definite hydrogen-ion concentration which is due to hydrolysis of the globulin salt. In a solution containing 0.1*N* potassium chloride and 2.3% of globulin the degree of hydrolysis is 0.1% and is uninfluenced by a further addition of salt. The turbidity of the solution and the hydrogen-ion concentration increase with increasing dilution, and precipitation commences at a hydrogen-ion concentration 10<sup>-5</sup>. The metallic portion of the salt is contained in the coagulum, hence the hydrolysis is to be expressed  $\text{GMX} + \text{H}_2\text{O} \rightleftharpoons \text{GM}\cdot\text{OH} + \text{HX}$ . Small quantities of acids precipitate globulin from globulin salts and the precipitate redissolves in an excess of acid to form an acid globulin, even in the presence of an excess of the salt. Alkali hydroxides combine with globulin salts in considerable quantities, and no precipitation takes place on progressively neutralising the alkali; the compounds thus produced behave in a manner analogous to that of the alkali globulinate solutions under similar conditions. Globulin is still to be found in solution after one-third and one-half saturation with ammonium sulphate. The so-called isoelectric point of globulin is dependent on the quantitative relations of the globulin and the buffer solution, and on the nature of the buffer solution, and indicates that value of the hydrogen-ion concentration at which the particular globulin salt ceases to have a definite existence, and the acid present is no longer sufficient to hold the globulin present in solution. The results of the present work indicate that the salt is combined with the nitrogen of the amino-group,  $\text{R}(\text{NH}_2\text{KCl})\cdot\text{CO}_2\text{H}$ . J. F. S.

**Silk Fibroin.** I. R. BRILL (*Annalen*, 1923, **434**, 204—217).—An investigation, by X-ray methods, of the physical structure of fibroin from nine different sources (cf. Herzog and Jancke, A., 1921, i, 12, etc.). The interpretation of results obtained in such investigations is discussed in detail. It is concluded that fibroin is a mixture of at least two proteins, of which one is crystalline (the unit silk crystal) and is present in all the samples examined. It is suggested, among other things, that the silk protein consists of a compound formed from alanine and glycine in equimolecular proportions, these, as is indicated by the symmetry relationships observed, possibly being united to form a ring, formed of four *d*-alanylglycine anhydride groupings, combined as in a polypeptide. E. E. T.

**Chemistry of Hæmoglobin. I. The Preparation of Hæmoglobin.** R. M. FERRY (*J. Biol. Chem.*, 1923, **57**, 819—828).—The corpuscles from citrated horse-blood are washed six times with 1.5% sodium chloride solution and then placed in a high speed centrifuge (Sharples). The resulting paste is diluted with three to four times its own volume of water, which causes nearly complete hæmolysis, and solid sodium chloride is



then added to give a 2% solution. This is again centrifuged and the solution so obtained purified first by dialysis for three days in collodion membranes, and finally by the method of negative pressure dialysis. All the operations are carried out in a cold room at 2°. A solution of practically pure hæmoglobin, together with a crystalline deposit, is thus obtained. The freedom of the solution from other proteins may be tested by a cataphoresis method. At  $p_H$  6.5 to 6.2 hæmoglobin and the other serum proteins migrate to opposite poles.  
E. S.

**An Electrochemical Study of Hæmoglobin.** J. B. CONANT (*J. Biol. Chem.*, 1923, 57, 401—414).—When dipped into a solution of hæmoglobin, an inert electrode shows a fairly definite potential which varies with the degree of oxygenation. This is the oxidation-reduction potential of the system hæmoglobin-methæmoglobin. By following the change electrometrically, using potassium ferricyanide and sodium hyposulphite as oxidising and reducing agents, respectively, it has been found that the reduction of methæmoglobin involves only one hydrogen equivalent, thus suggesting that the change is from a ferri- to a ferro-compound. By passing oxygen or carbon monoxide through the system the potential is raised but is again lowered on removing the gases. These variations in the potential are due to changes in the ratio of free hæmoglobin to methæmoglobin; the conversion of hæmoglobin into oxyhæmoglobin is a process of oxygenation and not of oxidation. The author tentatively expresses the above relations between hæmoglobin, methæmoglobin, and oxyhæmoglobin by means of formulæ which emphasise the analogy between these substances and Manchot's aminoferrocyanides (cf. A., 1913, i, 1311). The reduction of hæmatin to hæmochromogen appears to involve the addition of two hydrogen atoms.  
E. S.

**Differentiation of Oxyhæmoglobins by Means of Mutual Solubility Tests.** K. LANDSTEINER and M. HEIDELBERGER (*J. Gen. Physiol.*, 1923, 6, 131—135).—The solubilities of specimens of pure oxyhæmoglobin derived from different species are additive, which confirms the view, already suggested by serological tests, that they are different substances.  
C. R. H.

**Distribution of Nitrogen in Globin.** A. HUNTER and H. BORSOOK (*J. Biol. Chem.*, 1923, 57, 507—514).—Using Van Slyke's method, the following results were obtained for the distribution of nitrogen in purified globin: ammonia-*N* 5.37, humin-*N* 1.90, arginine-*N* 8.0, histidine-*N* 12.7, lysine-*N* 11.1, amino-*N* of filtrate 57.0, non-amino-*N* of filtrate 3.3%. Estimations of the tryptophan and tyrosine content by Folin and Looney's method (A., 1922, ii, 539) gave values of 2.61 and 4.63%, respectively. Fürth and Lieben's method, which was used by Kiyotaki (A., 1923, i, 399) for the estimation of tryptophan in globin, is criticised. Making certain assumptions, the authors calculate from their results that the globin molecule contains 2 tryptophan, 4 tyrosine, 4 arginine, 8 histidine, 10 lysine, and about 100 other amino-acid radicles.  
E. S.

**Is the Pentose of the Nucleotides formed under the Action of Insulin?** L. B. WINTER and W. SMITH (*Nature*, 1923, **112**, 829—830; cf. A., 1923, i, 727, and Berkeley, A., 1923, i, 1259).—The substance, which responds to the  $\alpha$ -naphthol test, but is without reducing action on copper salts, gives little indication that it contains a pentose. When the  $\alpha$ -naphthol test is modified by the use of concentrated hydrochloric acid instead of sulphuric acid, a positive reaction is obtained only shortly after the sugar has been extracted from the tissue, and then only faintly; after some weeks, the test may fail entirely. It is believed that the substance is of a true carbohydrate nature, and its presence in normal tissues is indicated. It is pointed out that the fact that the islets of Langerhans tissue contain unusually large amounts of pentose compounds need not lead to the conclusion that the function of insulin is to convert the sugar reserves of the body into pentose derivatives. A. A. E.

**Yeast-nucleic Acid. V. Methods of Preparation of Yeast-nucleic Acid.** H. STEUDEL and S. IZUMI (*Z. physiol. Chem.*, 1923, **131**, 159—165).—It has been shown that yeast-nucleic acid, unlike thymus-nucleic acid, is easily decomposed by alkali at room temperature (SteuDEL and Peiser, A., 1923, i, 720). This makes it doubtful whether processes such as that of Altmann (*Arch. Anat. Physiol.*, 1889, 526) yield unchanged yeast-nucleic acid. Various preparations of yeast-nucleic acid have been prepared using Altmann's process, but keeping the temperature below 0°, and also by the method of Clarke and Schryver (A., 1918, i, 130), in which an extract is made with sodium chloride solution instead of with alkali. The value P/N for various fractions has been determined. It is not constant, and the variation may be due to some extent to the difficulty of working with the limited apparatus available. A value for P/N approximately equal to 1.65 has been obtained from two of the best preparations, and this agrees approximately with Levene's formula (requiring P/N=1.699). W. O. K.

**Conductivity Titration of Gelatin Solutions with Acids.** D. I. HITCHCOCK (*J. Gen. Physiol.*, 1923, **6**, 201—205).—The conductivity titration method of Kolthoff (A., 1920, ii, 420, 421, 501) has been applied to gelatin. The results show a combining weight of 1,160 for gelatin, which is in agreement with the value found previously by the hydrogen electrode method. C. R. H.

**Density and Hydration in Gelatin Sols.** T. SVEDBERG and B. A. STEIN (*J. Amer. Chem. Soc.*, 1923, **45**, 2613—2620).—The variation in density of gelatin sols in different concentrations of acetic, nitric, hydrochloric, sulphuric, and phosphoric acids has been determined. It is found that for all the acids used the density increases with an increase in hydrogen-ion concentration up to a maximum value at about  $p_H$  5.0, after which the density curves drop toward a minimum at about  $p_H$  4.7. The curves for the variation of viscosity of proteins with change in Sørensen values also have a maximum at  $p_H$  3.0—3.2, dropping to a minimum at

the isoelectric point,  $p_H$  4.7, as shown by Loeb and Pauli. The similarity of the density curves to the viscosity curves adds further verification to Pauli's hypothesis of hydration of proteins. The acids may be arranged in the following series representing their effect on the hydration of proteins; acetic < phosphoric < hydrochloric < sulphuric < nitric. It is shown that the effect of alkali and alkaline-earth chlorides on hydration is of the same order as that of the acids, and that the kations may be arranged in a series in the order of their effectiveness thus:  $Sr > Ca > Na, K > Li$ . Non-electrolytes do not affect the hydration to nearly as great an extent as do acids and salts. The anomalous action of methyl and ethyl alcohols seems to indicate that these substances favour hydration.

J. F. S.

### Phthalic Anhydride as a Means of Hydrolysing Proteins.

P. BRIGL and E. KLENK (*Z. physiol. Chem.*, 1923, **131**, 66—96).—Treatment of ethyl phthalylglycollate, m. p. 111—113°, with concentrated aqueous ammonia results in the formation of the diamide of phthaloylglycine, fine needles, m. p. 255° (decomp.). Phthalic anhydride and glycylglycine, fused together at 200° for five minutes or at 180° for forty-five minutes, yield *phthalylglycylglycine*, thin needles, m. p. 232° (copper salt, bundles of needles; *ethyl ester*, fine white needles, m. p. 190°). When heated above 200°, phthalylglycylglycine decomposes, and phthalylglycine is formed. Phthalylglycylglycine along with unchanged material is also obtained from phthalic anhydride and diketopiperazine. From *dl*-leucylglycine and phthalic anhydride, *phthalyl-leucylglycine* is obtained. It is a yellow, amorphous compound, which melts indefinitely between 35° and 65°, but forms a well-defined *ethyl ester*, m. p. 126°, which on treatment with methyl-alcoholic ammonia yields the *diamide* of *phthaloyl-leucylglycine*, m. p. 211° (decomp.). When heated, this compound is converted into the *monoamide* of *phthalyl-leucylglycine*, rhombic plates, m. p. 211°.

Eighty-seven g. of elastin was heated with 130 g. of phthalic anhydride at 200° for about fifteen minutes. The excess of phthalic anhydride was removed by extraction with benzene and then with ether. The residue was dissolved in methyl alcohol and a fraction (A) precipitated with copper acetate. The filtrate, concentrated to a syrup, was stirred up with chloroform, thus being divided into two fractions, one soluble in chloroform (C), and one insoluble (B). Fraction (A) was further divided into two fractions by precipitating the copper with hydrogen sulphide and separating the fraction of the organic compound insoluble in cold water and cold alcohol, (A<sub>1</sub>) from that soluble in cold water and cold alcohol (A<sub>2</sub>). Fraction C was converted into its ethyl ester and separated into a fraction (C) insoluble in warm ethyl acetate, a fraction (C<sub>1</sub>) which separates on cooling and a fraction (C<sub>2</sub>) soluble at room temperature. Analyses of these various fractions are given.

W. O. K.

**The Influence of Colloids on Ferments. I.** L. PINCUSSEN (*Biochem. Z.*, 1923, **142**, 212—221).—A study has been made of the influence of colloidal iron, at varying hydrogen-ion concentration\*

trations, on pepsin, rennin, trypsin, malt diastase, takadiastase, and ptyalin, acting on appropriate substrates. No general rule is applicable, the results being very variable and not always in accord with the adsorption theory. In general, the colloidal iron diminished the action of the enzyme to an extent dependent on the  $p_H$ , but in certain cases an increased activity was observed. At the isoelectric point the added colloid had little or no effect on the enzyme. Indications were obtained that an enzyme may retain its activity even when adsorbed, and the interaction of the colloid and substrate may also play a part in determining the final effect.

J. P.

**Amylase.** L. AMBARD (*Bull. Soc. Chim. biol.*, 1923, **5**, 693—716).—A study has been made of the power of adsorbing amylase possessed by the amyloses (A., 1912, i, 832), by dextrin and by glycogen. This power increases with the molecular weight, and is taken to be a function of the grouping of the specific intra-molecular linkings of the substances concerned.

The rest of the paper is a consideration of the effect on the rate of hydrolysis of adsorption of enzyme by substrate. C. R. H.

**An Amylase Preparation with Limited Powers of Hydrolysis.** K. SJÖBERG (*Z. physiol. Chem.*, 1923, **131**, 116—130).—By extraction of malt with water and dialysis of the resulting solution, an enzyme has been obtained which converted only about 30% of starch into maltose. The rate of reaction is maximal at  $p_H$  6. The presence of dextrose decreases the velocity constant of the reaction, a concentration of 3% of either sugar reducing it to about 27% of the original value. In the same way, the products of intermediate hydrolysis also exert an inhibitory action. From the hydrolysis product, a substance dialysed through a collodion membrane which produced a reddish-violet colour with iodine, presumably a dextrin. The non-dialysable part is more sparingly soluble in water than the original starch, gives a pure blue colour with iodine, and does not reduce Fehling's solution,  $[\alpha]_{H_g}^{18} + 158^\circ$  (in 1% solution). It has some retarding influence on the hydrolysis of starch by the enzyme, and is provisionally called an amylose, but is not identical with the substance isolated by Pringsheim and Fuchs (A., 1923, i, 965). W. O. K.

**The Limiting Hydrolysis of Starch and a Complement of the Amylases.** II. H. PRINGSHEIM and K. SCHMALZ (*Biochem. Z.*, 1923, **142**, 108—116).—The hydrolysis of starch by maltase-free preparations of amylases (malt, salivary, and pancreatic) proceeds beyond the supposed limiting value of 70 to 78% maltose formation, and in many cases a quantitative production of the sugar has been observed. The effects of varying quantities of enzyme of different ages, and of temperature, on the extent of the hydrolysis have been studied. The complement present in yeast which accelerates the action of amylases, more particularly those of saliva and of the pancreas, on starch (cf. A., 1923, i, 965) only seems to do so above the limiting value. The complement, which is

destroyed by boiling, has a marked effect in reactivating old preparations of malt extract which have lost much of their amylolytic power. Maltose has been isolated directly in a crystalline condition from a starch hydrolysate, showing a 96% concentration of the sugar by titration. J. P.

**The Influence of Colloids on Ferments. II.** J. HAGIHARA (*Biochem. Z.*, 1923, **142**, 222—227).—Various preparations of pure cholesterol had no effect on the activities of different diastases between  $p_H$  4.0 and 6.0. Between  $p_H$  6.8 and 10.0, their activity was decreased by cholesterol. A Heyden preparation of cholesterol, which gave anomalous results, was found to contain a protective protein colloid to which the differences from pure cholesterol were traced. Lecithin, at all reactions between  $p_H$  4.0 and 9.8 decreased the action of the diastases, with the exception that, when present in acid solution in great dilution, it was without effect. J. P.

**The Differentiation of Animal and Plant Diastases.** T. KOGA (*Biochem. Z.*, 1923, **142**, 159—174).—In contradistinction to diastases of animal origin, the action of those from vegetable sources (malt, takadiastase from *Aspergillus* and the diastase of *Amylomyces delamar*) is not increased by blood-serum or by sodium chloride. Yeast and malt extracts are similarly devoid of activating influences on plant diastases. On the other hand, the diastases present in *Bacillus coli* and *B. pyocyaneus* are markedly activated by blood-serum and are therefore allied to animal diastases. The use of blood-serum as a means of differentiating animal and plant diastases is suggested. J. P.

**The Occurrence of Glycerophosphatase in Takadiastase.** S. AKAMATSU (*Biochem. Z.*, 1923, **142**, 184—185).—Takadiastase contains a glycerophosphatase capable of hydrolysing commercial sodium glycerophosphate to the extent of 82% in twelve days. J. P.

**The Hydrolysis of Lecithin by Takadiastase.** S. AKAMATSU (*Biochem. Z.*, 1923, **142**, 186—187).—As in the case of synthetic glycerophosphoric acid (cf. preceding abstract), the glycerophosphoric acid residue present in egg-yolk lecithin is also hydrolysed by takadiastase. J. P.

**Sulphatase. II.** C. NEUBERG and K. LINHARDT (*Biochem. Z.*, 1923, **142**, 191—194).—The sulphatase found in takadiastase (A., 1923, i, 1148) hydrolyses pure potassium *p*-cresol sulphate, forming potassium sulphate and *p*-cresol. The reaction is diminished in the presence of magnesium carbonate and sodium acetate, and proceeds best in alkaline solution. Pre-war takadiastase preparations still contain active sulphatase. J. P.

**Ferments and Light. III. Urease. II.** L. PINCUSSEN and N. KATO (*Biochem. Z.*, 1923, **142**, 228—238).—Sunlight acting on urease solutions at  $p_H$  6.4 diminishes the activity both of the active constituent and of "Stable Component-X" (cf. A., 1923, i, 1034). Potassium hydrogen phosphate at  $p_H$  5.6 affords a partial

protection to the active component, but even in the dark the activity of the other constituent is decreased by phosphate. Ultra-violet light destroys the active enzyme both in the presence and absence of phosphate, but has not such a marked effect as sunlight in inhibiting Component-X. J. P.

**Possible Sources of Insulin.** C. H. BEST and D. A. SCOTT (*J. Metabolic Research*, 1923, **3**, 177—179).—The presence of insulin in potatoes, rice, wheat, beet-roots, and celery was demonstrated by the preparation of extracts from these plants which when administered to rabbits caused a marked lowering of the blood-sugar. CHEMICAL ABSTRACTS.

**Preparation of Insulin.** C. H. BEST and D. A. SCOTT (*J. Biol. Chem.*, 1923, **57**, 709—723).—The various methods which have been devised for the preparation of insulin are reviewed and the method at present in use at the University of Toronto is described. Although the preparation of insulin by extraction of the pancreas with acidified water has yielded promising results, the yields are considerably smaller than those obtained by alcoholic or acetone extraction; moreover, the aqueous extracts are more difficult to purify. E. S.

**Concentration of Insulin by Adsorption on Benzoic Acid.** P. J. MOLONEY and D. M. FINDLAY (*J. Biol. Chem.*, 1923, **57**, 359—361).—Impure solutions of insulin may be purified, or dilute solutions concentrated, by adsorption on benzoic acid. For this purpose, the insulin solution is treated with a solution of sodium benzoate and the benzoic acid precipitated by addition of hydrochloric acid, the process being repeated, if necessary, on the filtrate. The insulin may be recovered by suspending the precipitate in water and extracting the benzoic acid with ether. If, however, considerable amounts of impurities are present, this method of recovery is not applicable and other methods (*e.g.*, solution of the precipitate in glacial acetic acid and precipitation of the insulin in a solid form with ether) must be employed. E. S.

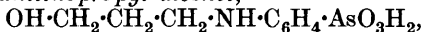
**Action of Proteolytic Enzymes on Insulin.** E. J. WITZEMANN and L. LIVSHIS (*J. Biol. Chem.*, 1923, **57**, 425—435).—Insulin is inactivated by trypsin, papain, and pepsin; this indicates that it has a protein-like nature. The suggestion is made that the action of insulin is due to a particular group or grouping which may be present either in a protein, a peptone, or a polypeptide. E. S.

**Preparation of Derivatives of Arsenobenzene Stable in Solution.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.P. 375718; from *Chem. Zentr.*, 1923, iv, 537).—Stable solutions of arsenobenzene derivatives may be obtained by mixing, for example, solutions of the methylene sulphonylate and the carbamate of 4-aminoarsenophenyldimethylpyrazolone; 4-aminoarsenophenyldimethylpyrazolone carbamate, and 3 : 3'-diamino-4 : 4'-dihydroxyarsenobenzene methylenesulphonylate; dimethylhexaminoarsenobenzene and 3 : 3'-diamino-4 : 4'-dihydroxyarsenobenzene methylene

sulphoxylate; dimethylhexaminoarsenobenzene and a mixture of the carbamate and methylene sulphoxylate of 4-aminoarsenophenyldimethylpyrazolone; 4-aminoarsenophenyldimethyl pyrazolone and the sodium salt of 4-aminoarsenophenyldimethylpyrazolone glycine.

G. W. R.

**Arsinated N-Arylamino-alcohols.** C. S. HAMILTON (*J. Amer. Chem. Soc.*, 1923, **45**, 2751—2754).—Ethylene chlorohydrin and sodium *p*-arsanilate react in boiling, aqueous solution to give  $\beta$ -*p*-arsinoanilinoethyl alcohol,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$ , colourless needles, m. p. 167—168°; the sodium, ammonium, and barium salt are described. The use of trimethylene chlorohydrin gives  $\gamma$ -*p*-arsinoanilinopropyl alcohol,



colourless crystals, m. p. 160—161°; the sodium, ammonium, and barium salts are described. These arsino-compounds are reduced by means of hot, aqueous sodium hyposulphite to give, respectively,  $\beta$ -*p*-arsenoanilinoethyl alcohol,  $(\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{As})_2$ , and  $\gamma$ -*p*-arsenoanilinopropyl alcohol,  $(\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{As})_2$ , both of which are yellow compounds, which do not melt at 250°. Condensation could not be effected between a chlorohydrin and *m*-arsanilic acid, 2-amino-*p*-tolylarsinic acid, or 3-amino-4-hydroxyphenylarsinic acid. Of the two sodium salts mentioned above, the propane derivative is apparently the more toxic, and has the higher trypanocidal action.

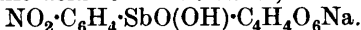
When *p*-arsanilic acid, sodium hydroxide solution, and ethylene dibromide are boiled under reflux, the product contains, besides unchanged material, *s*-*di-p*-arsinoanilinoethane,



which does not melt at 250°, and gives a colourless, crystalline sodium salt.

W. S. N.

***o*-Amino- and *o*-Acetamido-phenylstibinic Acids.** A. D. MACALLUM (*J. Soc. Chem. Ind.*, 1923, **42**, 468—471r).—*o*-Nitrophenylstibinic acid was prepared from *o*-nitroaniline by a slight modification of the diazo-method of Schmidt (A., 1920, i, 900). Molecular-weight determinations of this and the other compounds described, by the cryoscopic method, indicate a unimolecular structure. When boiled with an excess of sodium hydrogen tartrate, *o*-nitrophenylstibinic acid forms a tartrate,

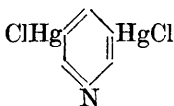


The acid can be reduced with ferrous sulphate or ferrous hydroxide in alkaline solution to *o*-aminophenylstibinic acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SbO}_3\text{H}_2$ , which forms a brown powder soluble in 200 parts of water. It forms a lead salt,  $\text{C}_{12}\text{H}_{14}\text{O}_6\text{N}_2\text{Sb}_2\text{Pb}\cdot 8\text{H}_2\text{O}$ , and a barium salt,  $\text{C}_6\text{H}_8\text{O}_3\text{NBaSb}\cdot 4\text{H}_2\text{O}$ . The amino-acid can be acetylated with acetic anhydride in neutral solution at 0° to *o*-acetamidophenylstibinic acid, which does not melt below 250°. *Di-o*-chlorophenylstibinic acid,  $(\text{C}_6\text{H}_4\text{Cl})_2\text{SbO}_2\text{H}$ , is formed from antimony oxide and *o*-chlorodiazobenzene chloride; its chloride has m. p. 105—110°. The acid is sparingly soluble in alkalis.

E. H. R.

**Mercury Derivatives of Pyridine.** G. SACHS and R. EBERHARTINGER (*Ber.*, 1923, **56**, [B], 2223—2226).—Mercuration of pyridine can be effected in much the same manner as that of benzene but at a somewhat higher temperature. The mercuri-complex enters in the  $\beta$ -position to the nitrogen atom; substitution thus proceeds in the normal manner for pyridine.

A solution of mercury acetate in pyridine is heated during two and a half hours at 175—180°, the product is dissolved in water and treated with sodium chloride whereby *pyridine-3:5-dimercurichloride* (annexed formula) is precipitated as a pale-brown, amorphous, odourless powder, decomp. 220°. The mother-liquors from the chloride are treated with sodium iodide, which causes the separation of *pyridine-3-mercuri-iodide*,



$C_5H_4NIHg$ , a yellow, amorphous powder, m. p. 68—69°. The constitution of the mercuri-derivatives is elucidated by converting them by means of a solution of bromine and sodium bromide into 3:5-dibromopyridine, m. p. 110°, and 3-bromopyridine, respectively; the latter substance is identified as the additive compound with mercuric chloride,  $C_5H_4NBr.HgCl_2$ , colourless, microscopic needles, m. p. 196—196.5°. Since, however, the yields of the bromopyridines are not quantitative, it is possible (although not probable) that isomeric mercuri-derivatives may also be produced. H. W.

**Mercury Compounds of Purine Derivatives.** L. ROSENTHALER and A. ABELMANN (*Ber. Deut. pharm. Ges.*, 1923, **33**, 186—190).—The following compounds are precipitated by the addition of a 10% solution of mercurous nitrate to a solution in nitric acid of caffeine, theobromine, and theophylline, respectively: *Caffeine mercuronitrate*,  $C_8H_{10}O_2N_4.HgNO_3$ , forms microscopic crystals which have no definite m. p. and decompose at 245—250°. The aqueous solution has a feebly acid reaction and is very sensitive towards bases, even aniline causing the liberation of mercurous oxide. The substance, from which caffeine is extracted by means of chloroform, gives all the reactions of mercurous compounds. *Theobromine mercuronitrate*,  $C_7H_8O_2N_4.HgNO_3$ , crystallises in prisms, which do not melt below 300°. It is sparingly soluble in cold water and, when heated with water, undergoes partial decomposition with liberation of metallic mercury. *Theophylline mercuronitrate*,  $C_7H_8O_2N_4.HgNO_3$ , forms amorphous masses not melting below 300°. Towards weak bases it behaves like the caffeine analogue and towards water like the theobromine compound. A different type of compound, having the formula  $(C_7H_7O_2N_4)_2Hg$ , is precipitated on mixing a solution of theophylline in dilute acetic acid with a cold, saturated, aqueous solution of mercuric acetate. It forms microscopic needles which do not melt below 300°, and is converted into caffeine on methylation. The corresponding derivative of theobromine is not obtainable by the above method, and caffeine, containing no free imido-hydrogen atom, is also incapable of reacting thus with mercuric acetate. W. T. K. B.



## Physiological Chemistry.

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**The Consumption of Oxygen in Sea Organisms when exposed to the Atmospheric Air.** IVAN GJAJA (*Glas. Acad. Sci. Belgrade*, 1923, 105, 35—41).—Experiments with the sea-gastropod *Trochus* and the sea-urchin *Echinocardis* show that both organisms are able to live a certain time when exposed to atmospheric air. The results were compared with the consumption of oxygen in some land-organisms (*Helix nemoralis*, *Rana esculenta*). The amount of oxygen consumed was found to be respectively: *Trochus* and *Helix nemoralis* 1.3 c.c., *Echinocardis* 3.1 c.c., *Rana esculenta* 0.66—1.32 c.c. of oxygen per hour and per g. of dry organic substance. The experiments were made at approximately the same temperature.  
S. S. M.

**Physiology of Muscular Exercise. V. Oxygen Relationships in the Arterial Blood.** H. E. HIMWICH and D. P. BARR (*J. Biol. Chem.*, 1923, 57, 363—378).—During and after short periods of vigorous leg exercise (cf. A., 1923, i, 623, 624) there is a rise in the oxygen content, oxygen capacity, and oxygen saturation of arterial blood. The factors which cause this change are discussed in detail and the conclusion is drawn that the increased diffusion of oxygen through the lungs is mainly responsible. With longer periods of exercise it is probable that there is a decrease in the oxygen content of arterial blood owing to the continued rise in the circulation rate.  
E. S.

**The Transport of Carbon Dioxide in the Blood of Marine Invertebrates.** T. R. PARSONS and W. PARSONS (*J. Gen. Physiol.*, 1923, 6, 153—166).—The blood of the lower marine invertebrates can take up no more carbon dioxide than can sea-water; that of the higher forms can take up twice or three times as much. The form of the carbon dioxide dissociation curves obtained indicates that the hæmocyantin in the blood of these animals plays a similar part in the carrying of carbon dioxide to that played by hæmoglobin in the blood of vertebrates.  
C. R. H.

**Ether Anæsthesia. II. Anæsthetic Concentration of Ether for Dogs.** E. RONZONI (*J. Biol. Chem.*, 1923, 57, 761—788).—Using the method of Shaffer and Ronzoni (this vol., ii, 69) for the ether estimations, it has been found that during ether anæsthesia the concentration of ether in arterial blood varies directly with that in alveolar air, and depends on the distribution coefficient between air and blood at body temperature. During the induction of anæsthesia, and with a continued administration of a constant amount of ether, the concentration in arterial is greater than in venous blood. This is probably due to the great solubility of ether in the depot fat. For the same reason, the concentration is higher in venous blood during the elimination of the ether. An ether tension in alveolar air of 33—41 mm. produces respiratory failure

in dogs when anaesthesia is induced rapidly; after several hours, a tension of 27—34 mm. is sufficient.

E. S.

**Distribution of Phosphorus in the Blood.** T. F. ZUCKER and M. GUTMAN (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 133—136).—Estimations made on the fresh, protein-free filtrate of human blood by Tisdall's method gave 2.66 mg. of inorganic phosphorus in a total phosphorus content of 19.43 mg. Boiling for two hours caused the hydrolysis of 9.73 mg. of the remaining phosphorus in organic combination.

CHEMICAL ABSTRACTS.

**The Inorganic Phosphorus and Calcium in Maternal and Fœtal Blood.** A. F. HESS and M. MATZNER (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 75—76).—Tests were made on the maternal blood before, and forty-eight hours after, parturition, and on the cord blood of infants. The calcium did not vary significantly from the normal. The average inorganic phosphorus content for twenty-one infants was 3.71 mg.%; the mothers' blood contained 2.89 mg.% when taken from one to two days after parturition. The maternal blood during pregnancy averaged 2.77 mg.% of inorganic phosphorus for twelve individuals. The normal inorganic phosphorus content of the blood of young infants is 4.5 mg.%. The estimations were made on the whole blood by Bell and Doisy's method.

CHEMICAL ABSTRACTS.

**Rickets in Relation to the Inorganic Phosphate and Calcium in Maternal and Fœtal Blood.** AL. H. HESS and M. J. MATZNER (*Amer. J. Diseases Children*, 1923, **26**, 285—289).—The inorganic phosphorus of the new-born is generally lower than that of infants of one month of age or older. However, even when the percentage was within rachitic range, rickets was not evident. No relationship was found between the percentage of inorganic phosphorus in the blood of the new-born and the occurrence of rickets during the first year of life.

CHEMICAL ABSTRACTS.

**Calcium and Phosphorus in the Blood Plasma in Rickets and Tetany.** J. H. HESS, J. K. CALVIN, C. C. WANG, and A. FELCHER (*Amer. J. Diseases Children*, 1923, **26**, 271—279).—In moderate rickets, the phosphorus, or calcium, or both, may be moderately lowered; in severe rickets the phosphorus is markedly reduced, whilst the calcium may or may not be lowered. In rickets complicated by tetany, the calcium is reduced, whilst the phosphorus may or may not be reduced.

CHEMICAL ABSTRACTS.

**Fat Transport in the Body. Changes in the Lipoid Content of the Blood and Lymph during Fat Absorption in the Dog.** H. C. ECKSTEIN (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 74—75).—The thoracic lymph of an eighteen-hour fasting dog was collected before and after the introduction of olive oil into the duodenum. The total fatty acids increased rapidly during fat absorption; the phosphatides remained unchanged. Phosphatides were not synthesised during the passage of the fat components through the intestinal wall.

CHEMICAL ABSTRACTS.

**Insulin and Glycolysis.** G. S. EADIE, J. J. R. MACLEOD, and E. C. NOBLE (*Amer. J. Physiol.*, 1923, **65**, 462—476).—Insulin added to defibrinated blood (dog and rabbit) in vitro, or injected into the animals previously to drawing the blood, does not accelerate the rate of glycolysis in the blood samples. In mixtures of blood, muscle juice, and phosphates, insulin decidedly retarded glycolysis, whereas Cohnheim's extract of pancreas had no influence. The action of insulin is thought to be an extravascular or intracellular process.

CHEMICAL ABSTRACTS.

**Changes in the Permeability of Red Blood-corpuscles in Non-electrolytic Solutions.** R. HÖBER and A. MEMMESHEIMER (*Pflüger's Archiv*, 1923, **198**, 564—570; from *Chem. Zentr.*, 1923, iii, 686).—Red blood-corpuscles washed with an isotonic solution show decreased absorption of "vital colouring" ("vital färbender") basic dyes in comparison with corpuscles washed with isotonic sodium chloride solution of the same reaction. The difference is not observed with "non-vital colouring" acid dyes. Glycine has the same inhibitory effect on dye absorption as sugar.

G. W. R.

**The Distribution of Chlorine in the Blood.** L. CSÁKI (*Biochem. Z.*, 1923, **142**, 360—369).—The average chloride content of red blood-corpuscles is 60% of that of the plasma, the extreme values found, including both normal and pathological cases, being 43% and 78%. A similar difference is shown by defibrinated and hirudin blood. The chloride content of both native and hirudin serum after spontaneous coagulation is the same as that of the corresponding plasma, but a marked alteration in the distribution of the chlorine occurs after defibrination, on passing carbon dioxide, and on previously administering large doses of sodium hydrogen carbonate. Corpuscles from defibrinated blood, in contact with isotonic sodium sulphate or dextrose solutions, lose chloride and after some hours the external solution contains more than the corpuscles (cf., also, A., 1922, i, 1086).

J. P.

**Does Dextrose in Blood Undergo Modification by other Blood Constituents before Oxidation in the Tissues?** T. BÜDINGEN (*Z. Klin. Med.*, 1923, **97**, 147—168; from *Chem. Zentr.*, 1923, iii, 634).—The combustion of dextrose is facilitated by preliminary moistening with blood. It is supposed that by reaction of dextrose with mineral salts in blood, "dextrates" are formed which are more readily combustible than the sugar itself. It is suggested that such dextrates occur in blood. Proteins and certain amino-acids such as tyrosine, leucine, glycine, and aspartic acid also increase the combustibility of dextrose. Iron compounds containing hydroxyl groups show a similar effect, but iron and iron oxides are without effect. The rate of oxidation of sugar in blood is increased by the addition of certain salts, whilst under pathological conditions the rate of oxidation may be diminished. The increase in the respiratory quotient after injection of dextrose is held to be due to the blood-sugar becoming more readily oxidised through reaction with the kations present.

G. W. R.

**The Potassium Content of Human Serum.** L. WILKINS and B. KRAMER (*Arch. Intern. Med.*, 1923, **31**, 916—922).—Normal human serum contains 18—22 mg. of potassium per 100 c.c. Increases were observed only in nephritis (25—26 mg.) and in tetany (23—29 mg.). There was no apparent relation between an increased potassium and a decreased calcium content. The ingestion of 1.3 g. of potassium iodide three times daily for a long time did not increase the potassium content of the serum, but after the ingestion of 2, 10, and 15 g. of potassium chloride, the potassium content of the serum was increased to 25, 30, and 35 mg., respectively, in about two hours, with subsequent return to normal.

## CHEMICAL ABSTRACTS.

**Mode of Occurrence of Proteins in Plasma and Serum.**

**I. Are Serum Proteins combined with Alkalis?** R. MOND (*Pflüger's Archiv*, 1923, **199**, 187—193; from *Chem. Zentr.*, 1923, iii, 570).—In normally reacting blood only a very small proportion of the sodium present in the serum is combined with proteins, which are principally present in forms other than salts. A minimal buffer effect occurs between the neutral point and the isoelectric point for globulins. The buffering (? titration) curve is markedly sigmoid.

G. W. R.

**The Organic Constituents of the Saliva.** H. B. LEWIS and H. UPDEGRAFF (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 168—169).—Human saliva contained approximately 30% as much uric acid as the blood; the values ranged from 0.6 to 2.9 mg. per 100 c.c. Benedict's method applied to a filtrate obtained by a modified Folin and Wu precipitation method was used. The salivary glands were not readily permeable to dextrose. CHEMICAL ABSTRACTS.

**Cholesterol in Duodenal Contents.** J. J. HERTZ and M. KAHN (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 167—168).—In the fasting state, the cholesterol in the duodenal contents of different individuals varied from 25 to 105 mg. in 10 c.c. Concentrated magnesium sulphate solution introduced into the duodenum caused a rapid increase in the cholesterol content, indicating an outpouring of concentrated bile. CHEMICAL ABSTRACTS.

**Fat and Protein Absorption after Comprehensive Resection of the Intestine.** O. SCHUMM and A. PAPENDIECK (*Z. physiol. Chem.*, 1923, **131**, 54—59).—After resection of 3.7 m. of the intestine, about four-fifths of the fat consumed was excreted in the faeces, which also contained about two-thirds of the nitrogen in the food. W. O. K.

**Investigations on Iodine Metabolism. I. Experiments with Physiological Quantities of Iodine on Adults.** T. VON FELLEBERG (*Biochem. Z.*, 1923, **142**, 246—262).—Iodine, taken in physiological quantities, is excreted chiefly by the kidney, but also in variable amounts in the faeces, nasal excrement, and in the sweat. Potassium bromide, sodium fluoride and chloride, and copious water drinking do not affect the excretion of iodine. A Turkish bath

increases the iodine excretion by the skin, but the total is not increased. Physical exercise and fevers increase the total excretion, whilst during fasting and sleeping it diminishes. Iodine equilibrium is attained on a daily intake of about 14 micrograms (cf. *Biochem. Z.*, 1923, 139, 371). If the intake is increased, a readily mobilised "actual" reserve is built up, which is distinguished from the potential reserve of the thyroids. The course of iodine metabolism is dependent to a certain extent on the nature of the iodine compound administered, thus iodine fats are more readily absorbed than iodides. J. P.

**Energetic Metabolism in Mouse and Rat.** I. GJAJA and BRANDIMIR MALEŠ (*Glas. Acad. Sci. Belgrade*, 1905, 1—34).—The energetic metabolism in mouse and rat was measured by the consumption of oxygen. The first series of experiments with mice at constant temperatures showed that in the whole interval from 1.5° to 40° (the lethal temperature) the amount of oxygen consumed was almost constant from the beginning of the experiment. In a second series of experiments with mice and rats, the temperature during the experiment was changed in order to examine the influence of various temperatures on the consumption of oxygen. The consumption of oxygen increases with decreasing temperature owing to the production of complementary heat in the organism to compensate loss by radiation. A third series of experiments on mice has shown that the temperature at which the animal produces a complementary heat does not depend on the size of the animal, but depends rather on its greater or lesser protection by fur, the beginning of the production of a complementary heat being at a higher temperature in the case of a badly protected animal. S. S. M.

**Metabolism of Fixed Base during Fasting.** J. L. GAMBLE, G. S. ROSS, and F. F. TISDALL (*J. Biol. Chem.*, 1923, 57, 633—695).—The discussion which is developed in this paper is based on the conception that, since the osmotic pressure and  $p_H$  of the body-fluids are to a large extent dependent on the concentration in them of total fixed base, the maintenance of an approximately constant value of the latter is the chief result of the processes of acid-base metabolism. During starvation, the following causes contribute to an increased excretion of acidic radicles: destruction of tissue protoplasm with the production of sulphuric and phosphoric acids, reduction in the total volume of the body-fluids, and the production of ketonic acids owing to the incomplete oxidation of fat. The first two processes also liberate fixed base, which is available for the excretion of acidic radicles; in addition, a certain quantity of calcium is derived from the calcium deposits of the body. The total amount of base available is, however, insufficient for the excretion of the acids produced by the above causes, and two regulatory mechanisms come into play to adjust this and so maintain the concentration of total fixed base in the plasma and, consequently, in the other body-fluids. These are, the excretion of urine of an acidity greater than that of the plasma, and the production of ammonia in the kidney. Calculations, made from estimations of the inorganic constituents

of the plasma and urine of four epileptic children undergoing periods of fast, approximately confirm these views, which are discussed in great detail in the original. E. S.

**Estimation of the Alkali Retention in Growth.** A. T. SHOHL (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 139—140).—The acids and bases in the food, urine, and faeces were estimated in terms of *N* solutions. The alkali retention expressed in c.c. of 0.1*N* solution per kg. of body-weight amounted to 11 c.c. in infants. Of the alkali retained, 2 c.c. was required for protein increase, 4 c.c. for the alkaline reserve, and about 57 c.c. for the formation of bone.

CHEMICAL ABSTRACTS.

**The Physiology of Sleep. I. The Effects of Prolonged Sleeplessness on Man.** N. KLEITMAN (*Amer. J. Physiol.*, 1923, **66**, 67—92).—Experimental insomnia in man (forty to one hundred and fifteen hours) produced no change in the blood-sugar, alkaline reserve of the blood and plasma, hæmoglobin content, or certain other factors. Increased excretion of phosphates and acids is apparently due to sleep. There is a greater excretion of chlorine in the day time; the same is true in insomnia, but there is a tendency to reversal in a subject who sleeps during the day. The excretion of total nitrogen and of creatinine shows little diurnal variation, and is unaffected by either insomnia or reversed routine.

CHEMICAL ABSTRACTS.

**Composition of Herring Ova. III. Researches on Ova, Using Micro-methods.** H. STEUDEL and S. OSATO (*Z. physiol. Chem.*, 1923, **131**, 60—64).—Micro-estimations show that there are, in 100 herring ova, 1.546 mg. of total N, 0.0054 mg. of ammonia N, 0.1054 mg. of urea N, 0.0024 mg. of creatinine, and an amount of a reducing substance corresponding with 0.2 mg. of dextrose. The total nitrogen is 13.59% of the weight of the dried eggs, and this corresponds with the value 13.23% obtained by using micro-methods on larger quantities of eggs. W. O. K.

**The Composition of Herring Ova. IV.** H. STEUDEL and E. TAKAHASHI (*Z. physiol. Chem.*, 1923, **131**, 99—106).—In the aqueous extract of herring ova, the following substances have been isolated and identified: guanidine, adenine, histidine, arginine, lysine, and cystine. Colour reactions indicate the presence of small quantities of tyrosine, tryptophan, and of creatinine. W. O. K.

**The Composition of Herring Ova. V. The Monoamino-acids of the Skins of the Ova.** S. OSATO (*Z. physiol. Chem.*, 1923, **131**, 151—158).—The monoamino-acids of the skin of 38.7 g. of herring ova have been investigated, using Fischer's ester method, and the following constituents have been isolated: alanine, 0.1 g.; valine, 1.1 g.; leucine, 4.3 g.; glutamic acid, 0.16 g.; proline, 0.6 g.; tyrosine, 6.27%; cystine, 0.71%, tryptophan, 2.02%. The last three have been estimated by the method of Folin and Looney (*A.*, 1922, ii, 539). W. O. K.

**The Concentration of Various Anions and Kations in Cerebrospinal Fluid and Serum.** J. B. PINCUS and B. KRAMER (*J. Biol. Chem.*, 1923, **57**, 463—470).—Analyses have been made of the serum and cerebrospinal fluid of normal and pathological subjects. The results show that, in the cerebrospinal fluid of a normal individual, the concentration of inorganic phosphorus is considerably, and of potassium somewhat, smaller than in the serum; chlorides, on the other hand, have a much higher concentration than in the serum, whilst that of sodium and of hydrogen carbonate is the same in both fluids; the concentration of calcium is 40—50% of that of the serum. The Donnan membrane equilibrium appears to be important in determining the relation between the concentration of the various constituents in the two body-fluids. E. S.

**Lipase Production by the Liver.** P. V. PREWITT (*Amer. J. Physiol.*, 1923, **65**, 287—295).—The isolated dog liver perfused with defibrinated dog blood may increase or decrease in lipolytic activity under various conditions. The lipolytic activity of the liver was determined by extraction with water and testing the hydrolysing power of the extract on ethyl butyrate. The lipase content of the unperfused liver is very much greater than that of the perfused organ, the marked decrease in liver-tissue following the initial perfusion not being accounted for by the slight increase in the lipase of the perfusion fluid. The addition of secretin to the perfusion fluid results in an increased lipase content of the liver-tissue. Although hepatic lipase does not seem to be increased by the action of pilocarpine, interchange of lipase between liver and blood is apparently facilitated under its influence. The lipolytic activity of the liver is not altered immediately by asphyxia, but changes are induced which are favourable to increased activity during subsequent perfusion.

CHEMICAL ABSTRACTS.

**The Physiology of the Polyamyloses. II. Glycogen Formation and Animal Combustion.** H. VON HOESSLIN and H. PRINGSHEIM (*Z. physiol. Chem.*, 1923, **131**, 168—176).—Perfusion of the surviving liver of the guinea-pig with a solution of maltose or of tetra-amylose does not result in the formation of glycogen. No excretion of tetra-amylose takes place after administration of tetra-amylose to the living animal, neither is there any increase of glycogen in the liver. A similar result is obtained with hexa-amylose. No increase of dextrose appeared in the urines of two diabetic patients after administration of 50 g. of tetra-amylose.

W. O. K.

**Chemical Study of Several Marine Molluscs of the Pacific Coast. The Liver.** P. G. ALBRECHT (*J. Biol. Chem.*, 1923, **57**, 789—794).—Analyses are presented of the liver of certain marine molluscs (abalone, Pismo clam, *Cryptochiton*, *Ischnochiton*, owl limpet). All had a relatively high iron content; creatine, creatinine, and uric acid were absent; urea was present in all except the abalone; and all contained those enzymes which are known to be present in the alimentary canal. The last result supports the view that the

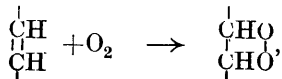
enzymes have their origin in the liver. An active uricase was found in the abalone and Pismo clam. E. S.

**The Effect of Quinine on the Iodine Content of the Thyroid Gland.** H. SUGATA (*Amer. J. Physiol.*, 1923, **65**, 282—286).—Quinine sulphate administered to dogs (fasting or fed) in daily doses of 0.2 to 0.3 g. per kg. caused a considerable increase in the iodine content and concentration of the thyroid. High external temperature (35°) also causes an increase in iodine, whilst a decrease is produced by starvation. It is believed that endogenous protein metabolism is fundamentally responsible for the distribution of iodine in the body.

CHEMICAL ABSTRACTS.

**A New Autoxidisable System of the Cell.** O. MEYERHOF (*Pflüger's Archiv*, 1923, **199**, 531—566).—Experiments similar to those of Hopkins and Dixon (cf. A., 1923, i, 167) were performed to investigate the oxygen uptake of systems consisting of a sulph-hydryl compound and muscle treated in various ways. The sulph-hydryl compounds employed were thioglycollic acid and cysteine. It was found that with a system of thioglycollic acid and the dried muscle powder prepared according to Hopkins and Dixon, the uptake of oxygen might be twelve times the amount necessary to convert the sulph-hydryl compound to the corresponding disulphide. It was then found that after prolonged extraction with alcohol and ether the muscle powder lost its power of taking up oxygen, this power being retained in a substance precipitated by acetone from the concentrated ethereal extracts. Next it was shown that a mixture of lecithin and thioglycollic acid reacted in the same way as the muscle powder, and finally, that, of the constituents of lecithin, linolenic acid alone possessed this property. It is therefore probable that linolenic acid is the heat stable substance of unspecified nature described by Hopkins and Dixon.

All the above reactions proceed best in an acid solution ( $p_H$  about 3), and may be entirely inhibited in neutral or alkaline solution; moreover, the uptake of oxygen ceases when the reaction for the  $-SH$  group disappears. The amount of oxygen taken up is about 5 c.c. per g. of dried muscle, or, in the case of linolenic acid, two molecules of oxygen to each molecule of acid; estimation of the iodine value before and after oxidation shows that only two of the double bonds have disappeared; these must therefore have been oxidised to a peroxide linking



as is known to occur in the spontaneous oxidation of linolenic acid.

A close analogy is drawn between the oxidation of lecithin in these experiments and that which takes place in the presence of iron.

A consideration of the kinetics of the reaction and of the other experimental facts enumerated leads the author to suggest that the course of physiological oxidation by the agency of such substances as glutathione is not, as generally accepted,  $2R\cdot SH + O =$



$\text{RS}\cdot\text{SR} + \text{H}_2\text{O}$ , and  $\text{RS}\cdot\text{SR} + \text{H}_2\text{O} + \text{M} = 2\text{R}\cdot\text{SH} + \text{MO}$  (M being an oxidisable constituent of the muscle), but  $2\text{R}\cdot\text{SH} + \text{O}_2 = \begin{array}{c} \text{R}\cdot\text{SH}\cdot\text{O} \\ \text{R}\cdot\text{SH}\cdot\text{O} \end{array}$  and  $\begin{array}{c} \text{R}\cdot\text{SH}\cdot\text{O} \\ \text{R}\cdot\text{SH}\cdot\text{O} \end{array} + 2\text{M} = 2\text{R}\cdot\text{SH} + 2\text{MO}$ .

According to this theory, it is only the reduced form of such a substance as glutathione which actually takes part in this process of tissue oxidation. C. R. H.

### **The Antagonism between Magnesium- and Calcium-ions.**

W. BAUMECKER (*Biochem. Z.*, 1923, **142**, 142—158).—Magnesium and calcium chlorides inhibit the imbibition of water by fibrin to the same extent, whereas on muscle pulp the former, in certain low concentrations, causes an increased, the latter a diminished imbibition, whilst mixtures of the two salts show a balanced antagonistic action. On the living isolated frog-muscle, the narcotic action of magnesium is unaccompanied by imbibition until the narcosis has become irreversible. Calcium salts cause a marked loss of water. Unlike sodium salts, calcium does not remove the reversible paralysis caused by magnesium. The antagonism between magnesium and calcium on the living muscle is therefore not brought about by their action in causing imbibition or loss of water, but is effected through the myoneural junction. The narcotic action of magnesium on the end-plate is only observed in Ringer solutions containing calcium. It is concluded that magnesium replaces the calcium which is necessary for the proper functioning of the end-plates. J. P.

**Behaviour of Calcium Phosphate and Calcium Carbonate (Bone Salts) precipitated in various Media, with Applications to Bone Formation.** J. C. WATT (*Biol. Bull. Marine Biol. Lab.*, 1923, **44**, 280—308).—Calcium phosphate, when precipitated in water or in colloidal solutions, is constantly granular and amorphous in character, and is apparently uninfluenced by the nature of the solution. On the other hand, calcium carbonate, when precipitated in water, shows a great diversity of crystalline form; in colloidal solutions, it exhibits two main forms, irregular crystalline and spherical, respectively. Mixtures obtained by simultaneous precipitation of both salts in the same solution admit of identification of each salt separately. The character of the spherules and crystals is influenced by the presence of normal or pathological constituents of blood, especially lecithin and acetone, and by the hydrogen-ion concentration of the colloidal solution. Large spherules, after persisting for months, may undergo structural change, finally dissolving; the substance is then deposited in the crystalline form. The mechanism of the formation of bone in animals is discussed.

CHEMICAL ABSTRACTS.

**A Method of Micro-incineration Applicable to Histochemical Researches.** A. POLICARD (*Bull. Soc. chim.*, 1923, **33**, [iv], 1551—1558).—The author has devised a method of studying the distribution of mineral salts in histological sections. The section

is placed on a platinum slide, carefully dried, then raised to a dull red heat for twelve to fifteen minutes. A very slow current of air facilitates the burning off of the organic matter, and is stated to be preferable to oxygen for that purpose. Glass is inadmissible for the slide material as it softens at the temperature required for the operation. Unglazed porcelain may be used. The ash resulting from the incineration forms a "mineral plan" of the section dealt with. This is examined microscopically by reflected light, and it is stated that this examination clearly shows the distribution and relative quantities of mineral matter. The presence and distribution of iron, in particular, is readily studied by the intensity of coloration of the ash by the ferric oxide resulting from the combustion.

H. J. E.

**Asteriasterol—a New Sterol from the Starfish and the Sterols of certain other Marine Echinoderms.** I. H. PAGE (*J. Biol. Chem.*, 1923, **57**, 471—476).—A sterol, m. p. about 70°, to which the name *asteriasterol* is given, has been isolated from *Asterias forbesi*. It forms an *acetate*, m. p. 97°, and a *benzoate*, m. p. 125°. The colour reactions which it gives with various sterol reagents are described. The sterols present in *Echinarachnius parma* and *Arbacia punctulata* are identical, and those in *Cumingia tellinoides*, *Choctopus pergamentaceus*, and *Arenicola cristata*, probably identical, with cholesterol.

Oxycholesterol gives an immediate deep violet coloration with arsenious chloride which changes to bright blue on gently heating and to bright green on vigorously boiling.

E. S.

**Glycerophosphatase in Human Organs.** E. FORRAI (*Biochem. Z.*, 1923, **142**, 282—290).—The possibility has been investigated of the presence of glycerophosphatase in various dried human organs examined soon after death. The observations of Grosser and Husler (A., 1912, ii, 367) were confirmed and, in addition, the enzyme was found in the adrenals, thyroids, testes, and in carcinomas. Amyloid kidneys contained less, and in a case of eclampsia muscle contained more than the normal organs. None of the organs in which the enzyme was found is of mesodermal origin. It is supposed that the enzyme originates in the epithelial layers.

J. P.

**The Distribution of Calcium and Inorganic Phosphorus in Milk.** P. GYÖRGY (*Biochem. Z.*, 1923, **142**, 1—10).—That portion of the calcium and inorganic phosphate of human milk and of cow's milk which is indiffusible (50—60% in the former and 30—40% in the latter) diminishes with increasing hydrogen-ion concentration, and at the isoelectric point of casein all the calcium and phosphate of the milk is dialysable. During the tryptic digestion of milk at constant  $p_H$ , the diffusible calcium and phosphate increases, and similar results were obtained on a casein solution to which calcium chloride and a phosphate mixture had been added. It is concluded that the non-diffusible calcium phosphate of milk is combined with the casein in the form of a

complex double compound, and not simply adsorbed by the protein (cf. Van Slyke and Bosworth, *J. Biol. Chem.*, 1914, **14**; 1915, **20**; 1916, **24**).  
J. P.

**Copper as a Constituent in Woman's and Cow's Milk. Its Absorption and Excretion by the Infant.** A. F. HESS, G. C. SUPPLEE, and B. BELLIS (*J. Biol. Chem.*, 1923, **57**, 725—729).—Raw cow's milk contains 0.55 mg. of copper per litre and commercially pasteurised milk 0.6—0.7 mg. per litre. Analyses of two specimens of human milk gave values of 0.4 and 0.61 mg. per litre, respectively. The constant presence of copper in the urine of both infants and adults indicates that it is absorbed from the alimentary canal.  
E. S.

**Urinary Acidity. II. The Increased Acidity produced by Eating Prunes and Cranberries.** N. R. BLATHERWICK and M. L. LONG (*J. Biol. Chem.*, 1923, **57**, 815—818).—The increased acidity of the urine which is produced by eating prunes or cranberries (A., 1914, i, 627) is due to the excretion of hippuric acid. The benzoic acid present in the fruit appears to be insufficient to account for all the hippuric acid excreted, which must therefore be derived from some other source.  
E. S.

**Synthesis of Hippuric Acid in the Animal Organism. VI. The Influence of the Protein of the Diet on the Synthesis and Rate of Elimination of Hippuric Acid after the Administration of Benzoates.** W. H. GRIFFITH and H. B. LEWIS (*J. Biol. Chem.*, 1923, **57**, 697—707; cf. A., 1923, i, 1261).—The rate of synthesis of hippuric acid by rabbits, following the administration of sodium benzoate, is increased when the hydrolytic products of proteins containing glycine are administered simultaneously with the benzoate, but not when the proteins do not contain this amino-acid. It is therefore improbable that any readily available precursors of glycine are produced during the ordinary metabolism of proteins.  
E. S.

**Allantoin. I. The Influence of Amino-acids on the Excretion of Allantoin by the Rabbit.** A. A. CHRISTMAN and H. B. LEWIS (*J. Biol. Chem.*, 1923, **57**, 379—395).—The excretion of allantoin by rabbits was decreased markedly by the administration of amino-acids (glycine, alanine, glutamic acid) or urea, and to a smaller degree by gelatin.  
E. S.

**Several Cases of Cystinuria.** J. M. LOONEY, H. BERGLUND, and R. C. GRAVES (*J. Biol. Chem.*, 1923, **57**, 515—531).—Using recent methods of estimation, the authors have examined several cases of cystinuria and have confirmed older work. The total amount of cystine excreted is composed of two fractions: a small and constant amount derived from endogenous metabolism, and a larger fraction which is proportional to the protein intake. An increased excretion of cystine is not accompanied by an increased elimination of other amino-acids. In the absence of the administration of sodium hydrogen carbonate or of atophan, practically

the whole of the neutral sulphur in the urine is due to cystine; the administration of sodium hydrogen carbonate, however, decreases the excretion of cystine and disturbs the distribution of the neutral sulphur. E. S.

**The Proteic Acids of the Urine. III. Oxyproteic Acid.** S. EDLBACHER (*Z. physiol. Chem.*, 1923, **131**, 177—178; cf. *Z. physiol. Chem.*, 1922, **120**, 71; **127**, 186).—The so-called "oxyproteic acid" of urine appears to consist essentially of urea, contaminated with some impurities, as it is decomposed by urease with the formation of ammonia, and gives the characteristic crystalline compound with Naphthol Yellow-S (dinitronaphthol-sulphonic acid). These results agree with those of Freund and Sittenberger-Kraft (A., 1923, i, 511). W. O. K.

**Fat Metabolism in Avitaminosis. II. The Total Fat, Neutral Fat, Cholesterol, and Cholesterol Ester in the Blood of Normal, Starving, Avitaminosed, and Phosphorus Poisoned Rats.** K. ASADA (*Biochem. Z.*, 1923, **142**, 44—52).—The total and neutral fat, cholesterol, and cholesterol ester have been determined in the blood of normal, starving, and avitaminosed rats, with and without simultaneous phosphorus poisoning. The blood-fat is highest in the avitaminosed rat and least in the starved rat. After phosphorus poisoning, the total blood-fat in the normally fed animal is unchanged, in starvation it is increased to approximately the normal level, and in avitaminosis associated with phosphorus administration it is markedly increased, but later sinks to sub-normal values. The variations in the amounts of cholesterol and of the ester are parallel to the changes in total fat under the three conditions of experiment. After poisoning with phosphorus, the ester especially is increased, this being most marked in the early stages of avitaminosis. J. P.

**Fat Metabolism in Avitaminosis. III. The Fat and Cholesterol Content of the Liver after Phosphorus Poisoning in Normal, Starved, and Avitaminosed Rats.** K. ASADA (*Biochem. Z.*, 1923, **142**, 165—180).—In avitaminosed rats, the total and neutral fat of the liver diminishes, but after prolonged vitamin-free feeding it again rises, still keeping within sub-normal limits. The liver cholesterol progressively decreases and does not run parallel to the altered fat content. In the starved animals the diminution of liver fat is marked, whilst the cholesterol is increased. After phosphorus poisoning, which greatly lowers the liver-fat and cholesterol of the starved animal, the liver of the avitaminosed animal is but slightly less rich in fat and cholesterol than that of the normally fed but poisoned rat, but both show a much greater fat content than do the similarly treated but non-poisoned animals. In advanced avitaminosis the phosphorus poisoned liver, which is practically free from glycogen, contains more fat than the normal poisoned liver. Starved and avitaminosed rats are much more susceptible to death from phosphorus poisoning than are normally fed animals. The water content of avitaminosed livers first in-

creases, then diminishes, in relation to normal conditions. After phosphorus poisoning, it is increased in the starved rat, lessened in avitaminosis, and unchanged in the normal rat. J. P.

**The Content of Copper and Zinc in Normal and Carcinomatous Tissues.** H. J. TAVERNE (*Nederl. Tijdschr., Geneeskunde*, 1923, **67**, i, 2810—2812; from *Chem. Zentr.*, iii, 946).—In a mammary carcinoma, normal tissue contained 0.94 mg. of copper and 3.74 mg. zinc per kg., whilst the cancerous material contained 0.54 mg. of copper and 3.65 mg. of zinc per kg. G. W. R.

**Effect of Treatment with Insulin on the Hydrogen-ion Concentration and Alkali Reserve of the Blood in Diabetic Acidosis.** G. E. CULLEN and L. JONAS (*J. Biol. Chem.*, 1923, **57**, 541—552).—The treatment of diabetic patients with insulin causes the alkali reserve and the  $p_H$  of the plasma, both of which are lowered, to return concurrently to the normal. E. S.

**[Physiological] Action of Acetylene. III. The Gases of the Blood of Rabbits during the Administration of Acetylene.** R. SCHOEN and G. SLIWKA (*Z. physiol. Chem.*, 1923, **131**, 131—145; cf. A., 1923, i, 727).—During inhalation of a constant mixture of acetylene and oxygen, the acetylene content of the arterial and venous blood of rabbits gradually increases and saturation is reached after seventeen minutes, 88% saturation being reached after five minutes. The presence of acetylene in the air breathed does not influence the oxygen content of the arterial blood, but the carbon dioxide content constantly decreases. After ceasing the administration of the acetylene, increased breathing occurs and acetylene is rapidly expired. W. O. K.

**[Physiological] Action of Acetylene. IV. Critical Remarks on the Action of Acetylene.** H. WIELAND (*Z. physiol. Chem.*, 1923, **131**, 146—150).—The author has suggested (A., 1922, i, 497) that ethylene and nitrous oxide differ from other inhalation anaesthetics such as chloroform and ether, as they have no effect on anoxybiotic processes, and now replies to criticisms of this view by Bart (*Verh. Deutsch. pharmakol. Ges.*, 1922, **2**, 7) and by Meyer and Hopff (A., 1923, i, 632). W. O. K.

**The Influence of Guanidine on the Frog.** K. ŠAHOVIĆ (*Glas. Acad. Sci. Belgrade*, **105**, 42—44).—Injections of a solution of guanidine in the frog causes the same symptoms of tetany as was observed by Paton and Findlay with rabbits, mice, and rats. S. S. M.

**Behaviour of Quinoline in the Animal Organism.** B. SCHEUNEMANN (*Arch. exp. Path. Pharm.*, 1923, **100**, 51—60).—The three quinoline derivatives, observed by Fühner (A., 1906, ii, 692) to occur in the urine after administration of quinoline, have been studied in the urine of the rabbit after oral administration of 20 g. of quinoline tartrate. Two of them have been identified as 8-hydroxyquinoline and 6-hydroxyquinoline; the third one is probably 6-hydroxy-4-quinolone. C. R. H.

## Chemistry of Vegetable Physiology and Agriculture.

**The rôle of Bacteria in the "Lactic Acid Fermentation of Dextrose by Peptone." III and IV.** O. ACKLIN (*Biochem. Z.*, 1923, **142**, 117—141, 351—359).—III. A further study has been made of the action of bacteria-bearing peptones in producing the fermentation observed by Schlatter (A., 1922, i, 1096) in dextrose-peptone-bicarbonate mixtures. The supposed autocatalytic fermentation (*J.S.C.I.*, 1923, 993A, 1145A) can be fully reproduced in sterile peptones inoculated with bacteria from preparations showing the fermentation. The incubation period and the quantitative course of the process is dependent solely on the extent of active bacterial infection. Schlatter ascribed variations in the activities of different peptones to their variable phosphate content, and postulated the existence of an active organic combination between the peptone and phosphoric acid. The author finds that in peptones poor in phosphates (Witte) added phosphate increases the extent of bacterial fermentation up to a limit determined by the hydrogen-ion concentration. On the other hand, peptones rich in phosphorus (Siegfried) showed no increased fermentation on the addition of phosphates. A careful study has been made of the effect of phosphate and acetate buffers on the  $p_H$  of the fermentation mixtures and on the general course of the action of the bacteria. The optimum  $p_H$  lies between 6·8 and 7·2, being rather nearer the former value than the latter. If sodium acetate is substituted for sodium hydrogen carbonate the fermentation is still observed but in less degree, as measured by acid or gas formation, which diminish with increasing acetate concentration. During the fermentation in the presence of sodium acetate the  $p_H$  becomes more acid than is the case when bicarbonate is present.

IV. The course of the fermentation in inoculated peptone is not appreciably influenced by the sterilisation methods employed. The peptone may be sterilised by ultra-filtration through a De Haën filter of 0·78 $\mu$ . J. P.

**Lactic Acid Fermentation of Dextrose by Peptone.** E. BAUR (*Z. physiol. Chem.*, 1923, **131**, 65).—The author agrees with Barthel and von Euler (A., 1923, i, 985) that the formation of lactic acid from dextrose in presence of peptone, described by Schlatter (A., 1922, i, 1096) is due to bacterial contamination. W. O. K.

**Inhibition of Bacterial Growth by Amino-acids.** G. A. WYON and J. W. McLEOD (*J. Hyg.*, 1923, **21**, 376—384).—Amino-acids in appropriate concentrations aid bacterial growth, but in relatively low concentrations they may be inhibitory. Inhibition occurred with ten out of eleven acids studied and with several mixtures rich in amino-acids. The inhibitory concentration varies from 11 to 130 millimols. per litre. The cyclic compounds were inhibitory in the lowest concentrations. Histidine, tyrosine,

tryptophan, and phenylalanine were tested. Of the chain compounds tested, cystine was most inhibitory. *Staphylococcus aureus* was able to split glycine in a high but sub-inhibitory concentration. A polypeptide medium may prove valuable for bacterial growth.

CHEMICAL ABSTRACTS.

**Catalase in Bacteria and its relation to Anaërobiosis.**

A. B. CALLOW (*J. Path. Bact.*, 1923, **26**, 320—325).—Comparative estimations were made of the catalase content of nine anaërobes and twelve aërobes. None of the former, and only streptococci among the latter, produced gas when treated with hydrogen peroxide. Hydrogen peroxide was not detected when anaërobes were grown anaërobically and then subjected to the action of the air. It could not be shown conclusively that anaërobes can grow aërobically in the presence of catalase.

CHEMICAL ABSTRACTS.

**Catalase Production and Sensitiveness to Hydrogen Peroxide among Bacteria: a Scheme of Classification based on these Properties.** J. W. MCLEOD and J. GORDON (*J. Path. Bact.*, 1923, **26**, 326—331).—When the characteristics of sensitiveness to hydrogen peroxide, power of producing catalase, and power of producing hydrogen peroxide are taken into account, bacteria can be roughly divided into four groups: (1) those extremely sensitive to hydrogen peroxide and devoid of catalase (the anaërobes), potential peroxide producers; (2) those moderately sensitive to hydrogen peroxide and devoid of catalase (the peroxide producers); (3) those moderately sensitive to hydrogen peroxide and devoid of catalase, but not peroxide producers; and (4) those sensitive to hydrogen peroxide in varying degrees and producers of catalase (the majority of facultative anaërobes).

CHEMICAL ABSTRACTS.

**Reduction of Sulphites by certain Bacteria in Media containing a Fermentable Carbohydrate and Metallic Salts.**

W. J. WILSON (*J. Hyg.*, 1923, **21**, 392—398).—In media containing sodium sulphite, dextrose, and iron salts, reduction of sulphite to sulphide is effected by *Bacillus typhosus*, *B. enteritidis*, *B. paratyphosus B*, and other members of the Salmonella group, but not by *B. paratyphosus A* and the dysenteriae bacilli.

CHEMICAL ABSTRACTS.

**Toluenated Yeast is not Dead.**

IGOR ASHESHOV and I. GJAJA (*Glas. Acad. Sci. Belgrade*, **105**, 50—57).—In a previous paper (*Compt. rend. Soc. Biol.*, 1922, **86**, 703), it was shown that toluenated yeast consumes considerable quantities of oxygen. In order to determine whether this consumption is due to an oxidation of the dead substance or to the vital functions of the yeast, yeast was toluenated by addition of 2% of toluene. When the toluene was removed by animal charcoal, the yeast regained its activity after incubation for a certain time if transferred to a new substrate. The length of incubation required varied according to the duration of the action of the toluene. If the toluene was absorbed immediately after the toluenisation, eighteen hours' incubation caused the

yeast to regain its activity. After seventy-two hours' contact with toluene, incubation for sixty hours was required. S. S. M.

**Phytochemical Reduction in the *cyclo*Hexane Series.** S. AKAMATSU (*Biochem. Z.*, 1923, **142**, 188—190).—Yeast, actively growing in sugar solutions, reduces inactive 1-methyl*cyclo*hexan-2-one to dextrorotatory 1-methyl*cyclo*hexan-2-ol. J. P.

**Growth of Yeast on a Medium of Wholly Synthetic Origin.** E. I. FULMER, V. E. NELSON, and A. WHITE (*J. Biol. Chem.*, 1923, **57**, 397—399).—Yeast has been subcultured on a wholly synthetic medium. The carbohydrate employed was Loew's methose, which was synthesised from formaldehyde. E. S.

**Relationships between Hydrogen-ion, Hydroxyl-ion, and Salt Concentrations, and the Growth of Seven Moulds.** H. W. JOHNSON (*Iowa State Coll. Research Bull.*, 1923, No. **76**, 307—344).—The known extremes of soil reaction,  $p_H$  3.62—9.68, have little or no inhibiting effect on soil moulds. Seven moulds studied show that the degree of acidity necessary to inhibit growth varies from  $p_H$  1.6 to 3.4, and the degree of alkalinity from  $p_H$  9.0 to 11.2. Salts in order of increasing toxicity are: (1) molecule for molecule. Magnesium sulphate, potassium chloride, magnesium chloride, sodium chloride, calcium chloride, sodium sulphate, sodium carbonate, potassium carbonate; (2) g. per litre. Magnesium sulphate, sodium sulphate, potassium chloride, magnesium chloride, calcium chloride, sodium chloride, potassium carbonate, sodium carbonate. All moulds change the reaction of media in which they grow.

CHEMICAL ABSTRACTS.

**Citric Acid Fermentation.** W. BUTKEWITSCH (*Biochem. Z.*, 1923, **142**, 195—211).—Cultures of *Aspergillus niger* and *Citromyces glaber*, growing in the presence of quinic acid, do not produce citric acid. If calcium carbonate is present, considerable formation of oxalic acid occurs. Sucrose, the hexoses, and glycerol form the best substrates for citric acid fermentation by these fungi, whilst arabinose and mannitol undergo the fermentation to a less extent. Saccharic and gluconic acids do not give rise to citric acid, and are therefore not to be regarded as intermediate stages in the fermentation. Evidence is adduced in favour of the view that the formation of citric acid from the hexoses takes place with intermediate formation of an acid allied to parasaccharinic acid, rather than Euler's view that acetaldehyde is an intermediate. The intermediate acid product is precipitated from the fermentation mixtures by the addition of lead acetate and ammonia. J. P.

**The Fermentation of Dextrose by *Fusarium lini*.** A. K. ANDERSON and J. J. WILLAMAN (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 108—110).—*Fusarium lini*, when grown on dextrose media, produces ethyl alcohol and carbon dioxide as the main by-products of metabolism. Succinic acid was not produced in appreciable amount. In the absence of dextrose, this organism can utilise ethyl alcohol, preferably at a concentration of 2%.

CHEMICAL ABSTRACTS.



**Chemical Composition of the Walls of certain Algæ.** M. E. WURDACK (*Ohio J. Sci.*, 1923, **23**, 181—191).—The cell-walls of representatives of *Vaucheria*, *Cladophora*, *Oedogonium*, *Spirogyra*, *Zygnema*, and *Draparnaldia* are composed of an inner layer of cellulose and an outer layer of pectose or chitin; when the last-named is present, pectose forms a middle layer. In some forms (*Vaucheria*, *Draparnaldia*), the pectose is difficultly permeable to an ammoniacal solution of cupric oxide and a solution of iodine in potassium iodide; in others (*Cladophora glomerata*, *Oedogonium irregulare*), a third layer of chitin is present, and in *Oedogonium crassum amplum* there is a layer of an unidentified substance. Mucilaginous sheaths of the algæ studied are of pectic compounds, of which pectic acid predominates, with pectose in some cases.

CHEMICAL ABSTRACTS.

**Is Gaseous Nitrogen a Product of Seedling Metabolism?** J. DAVIDSON (*Bot. Gaz.*, 1923, **76**, 95—101).—Wheat seedlings and cow pea seedlings were grown in Kjeldahl flasks under sterile and non-sterile conditions. The results indicate that no nitrogen in the gaseous form is lost in the process of germination and in the early life of the seedlings as an inherent function of the metabolic processes.

CHEMICAL ABSTRACTS.

**The Absorption of Ions by Plants.** D. R. HOAGLAND (*Soil Sci.*, 1923, **16**, 225—246).—The results of a comprehensive series of studies on the absorption of ions by barley plants from different solutions are reported. Different ions were absorbed at different rates and the absorption of any one ion was found to be affected by other ions. Thus kations are affected both by kations and anions, and vice versa. For example, potassium is absorbed most rapidly from potassium nitrate, less rapidly from potassium chloride, and least rapidly from potassium sulphate solutions. The proportion of ions absorbed from a solution decreases as their concentration in the solution falls. Ions may be absorbed either more rapidly or less rapidly than water. Thus whilst potassium-, nitrate-, and phosphate-ions may be taken up more rapidly than water, calcium-, magnesium-, and sulphate-ions may be taken up at the same time at a slower rate than water. Attention is directed to the fact that energy exchanges are involved in the process of absorption and that permeability relations alone are inadequate to explain the phenomena of absorption by plants.

G. W. R.

**Phase Reversal in Emulsions and Protoplasm.** W. SEIFRIZ (*Amer. J. Physiol.*, 1923, **66**, 124—139; cf. *Science*, 1923, **57**, 694).—The effects of various electrolytes (sodium hydroxide, sodium chloride, barium hydroxide, barium chloride, and calcium chloride) in causing phase reversal in emulsions of (1) oil in water and (2) water in oil, prepared with various emulsifying agents, were studied. Olive oil emulsions with casein, gliadin, cholesterol, or cephalin in the aqueous phase, form water in oil systems which are reversible with sodium hydroxide. Oil emulsions, in which saponin (senegin, smilacin), gelatose, gum arabic, albumin, lecithin, or plant extract

is the emulsifier, form oil in water systems which are not reversible with barium chloride. The hypothesis of Clowes (A., 1916, i, 583) on the mechanism of permeability changes in the plasma membrane of organisms is based on the behaviour of only one type of emulsion in the presence of certain ions and must be regarded as a purely speculative hypothesis which rests on very uncertain evidence.

CHEMICAL ABSTRACTS.

**Amylase in Plants. III.** K. SJÖBERG (*Biochem. Z.*, 1923, **142**, 274—279).—Following the earlier work of the author on the activity of plant amylases (A., 1923, i, 275), it is shown that an amylase is present in tulip plants, which do not form starch in the dark and very little when exposed to light. It occurs in leaves, sepals, stem, and juice, and is more prominent in the young than in the old plants. Amylase is also present in the roots and more especially in the stem and buds of young specimens of *Pisum sativum*. From the fact that the enzyme is most prominent in actively growing plant-tissues, it is assumed to have a synthetic function possibly in forming cellobiose.  
J. P.

**Analysis of the Jerusalem Artichoke.** A. T. SHOHL (*J. Amer. Chem. Soc.*, 1923, **45**, 2754—2756).—The juice of the Jerusalem artichoke has  $p_H$  5.0. It contains only traces of water-soluble-*B* vitamin. Analysis of the pared tuber (69 % of total weight) gives moisture, 79.0%; total nitrogen, 3.1% (of which 71.5% is water-soluble, and 27.5% present as amino-acids); fat, 0.2%; carbohydrate (inulin), 15.5%; fibre, 0.8%; ash, 1.1%, in close agreement with the results of Strauss (*Berlin. Klin. Woch.*, 1912, **49**, 1213) and of Langworthy (*U.S. Dept. Agric. Bull.*, 1917, **468**). The metabolism of inulin is discussed and a reinvestigation recommended of the use of the Jerusalem artichoke in the treatment of diabetes.  
W. S. N.

**Saponins [of Chestnut Seeds].** A. W. VAN DER HAAR (*Rec. trav. chim.*, 1923, **42**, 1080—1083).—It is shown that the saponin from chestnut seeds, if obtained free from accompanying sucrose, does not give rise, on hydrolysis, to lævulose, as stated by Blau (*Diss. Univ. Zürich*, 1911) and Bosshard (*Diss. Tech. Hochschule Zürich*, 1916). The saponin in question contains 9.8% of water, 1% of ash, and, on hydrolysis, affords: sapogenins, 46.2%; dextrose, 23%; pentose, 4.8%; methylpentose, 4.2%; *d*-galactose, 2.24%; *d*-glycuronic acid, 10% (identified as *d*-glycuronolactone); and acetic acid, 3.4%. Xylose, *d*-mannose, fucose, and galacturonic acid are not products of the hydrolysis.  
E. E. T.

**Influence of Hexamethylenetetramine and Formaldehyde on the Haricot Bean.** E. NICOLAS and G. NICOLAS (*Compt. rend.*, 1923, **177**, 1062—1064).—A continuation and confirmation of previous work (A., 1923, i, 427), using different varieties of haricot beans.  
E. E. T.

## Organic Chemistry.

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### The Lubricant and Asphaltic Hydrocarbons in Petroleum.

C. F. MABERY (*Ind. Eng. Chem.*, 1923, **15**, 1233—1238).—Most crude petroleum begins to show evidence of decomposition at a temperature of 300° even at 20 mm. pressure. In an investigation of the hydrocarbons boiling above this point, applied to samples of crude petroleum of varying origin, separation was therefore effected by means of fractional solution in a mixture of ether and ethyl alcohol. The fractions so obtained were examined as to density, mol. weight (as determined by solution in stearic acid at 50°), and composition by analysis. In all cases, these heavy hydrocarbons fall into one of two classes (*D*) hydrocarbons, lubricants throughout, and (*H*) hydrocarbons of which the heavier are asphaltic. The latter are usually poorer in hydrogen, the series identified through the whole range of samples varying from  $C_nH_{2n-4}$  to  $C_nH_{2n-20}$ . The halogens react normally with these hydrocarbons. The nitro-derivatives of the (*D*) hydrocarbons separate as finely divided crystals, those of (*H*) hydrocarbons as oils when poured into water. These derivatives have much lower mol. weights than the original oils and are nitro-carboxylic acids. All samples of fractions from American petroleum were found to contain carboxylic acids or esters in proportions ranging from traces up to 2%. This probably accounts for irregular variations in the density of succeeding fractions. Iodine number determinations show that only the ring type of unsaturation exists in lubricant hydrocarbons. [Cf. *B.*, Feb.] C. I.

**The Processes of Dehydrogenation in the Presence of Catalysts.** J. K. PFAFF and R. BRUNCK (*Ber.*, 1923, **56**, [B], 2463—2464).—The catalyst is prepared by mixing solutions of sodium aluminate and nickel nitrate and rendering the precipitation complete by passing carbon dioxide to saturation. The paste is mixed with pure, ignited aluminium oxide, filtered, and washed as free as possible from alkali. It is subsequently dried and reduced by hydrogen at 320°. In the presence of this material, benzene is smoothly hydrogenated at 180—200° to hexahydrobenzene, but, unexpectedly, the latter substance is not reconverted into benzene to more than a minimal extent at any temperature below about 500°. Purified lignite tar oil, b. p. 80—150°, is similarly readily saturated with hydrogen at 180—200°, but, under the conditions used in the attempted dehydrogenation of hexahydrobenzene, the product is converted quantitatively into methane. Under similar conditions, a purely aliphatic fraction of American petroleum yields almost entirely methane and leaves a small carbonised deposit on the catalyst; the reaction commences at about 240° and is almost quantitative at 260°.

By means of the nickel catalyst, the aliphatic components can readily be removed as methane from a mixture of aliphatic hydrocarbons and naphthenes. H. W.

**Addition of Nitrogen Trichloride to Unsaturated Hydrocarbons.** I. G. H. COLEMAN and H. P. HOWELLS (*J. Amer. Chem. Soc.*, 1923, 45, 3084—3089; cf. A., 1922, i, 133).—Nitrogen trichloride was added slowly to a solution of  $\Delta^2$ -butene in carbon tetrachloride at  $-10^\circ$ , and after washing and removal of water the  $\beta$ -chloro- $\gamma$ -dichloroaminobutane formed,  $\text{NCl}_2\cdot\text{CHMe}\cdot\text{CHMeCl}$ , was reduced by concentrated hydrochloric acid to  $\beta$ -chloro- $\gamma$ -aminobutane,  $\text{NH}_2\cdot\text{CHMe}\cdot\text{CHMeCl}$ ; the *benzoyl* derivative, colourless needles, m. p.  $105-106^\circ$ , was isolated. Similar reactions with  $\Delta^2$ -butene resulted in the isolation of *r*- $\alpha$ -chloro- $\beta$ -benzamido-butane, slender, silky needles, m. p.  $91-92^\circ$ , which was reduced to *r*- $\beta$ -benzamido-butane, m. p.  $84-85^\circ$ . The latter substance was also prepared from methyl ethyl ketoxime, and it had the same melting point (Pope and Gibson, T., 1912, 101, 1702).  $\beta$ -*p*-Nitrobenzamido-butane obtained from  $\Delta^2$ -butene and from methylethylketoxime melted at  $114.5-115.5^\circ$ . Nitrogen trichloride reacted rapidly with  $\beta$ -methyl- $\Delta^2$ -butene; no amine was produced but amylene dichloride and chloroamylene chloride were formed. F. B.

**Acetylene Condensations.** II. **The Theory of the Formation of Cuprene.** H. P. KAUFMANN and W. MOHNHAUPT (*Ber.*, 1923, 56, [B], 2533—2536).—The conversion of acetylene into cuprene in the presence of copper or copper compounds at  $230-300^\circ$  does not take place in the complete absence of oxygen. The product is not homogeneous, the composition varying between  $(\text{C}_{11}\text{H}_{10})_x$  and  $(\text{C}_{15}\text{H}_{10})_x$ . In addition, small amounts of oily compounds are produced. The colour of the product ranges from pale yellow to dark brown. The authors consider that its formation is due to the production of an intermediate additive compound of acetylene with cuprous or cupric oxide which immediately undergoes pyrogenic decomposition. Possibly the variation in temperature due to the rapid stream of gas plays a distinct part. Since the oxide which is regenerated by decomposition of the acetylide again takes part in the reaction, the proportion of oxygen present (in the case of copper) need not be great. The formation and decomposition of the acetylide explains the peculiar observation that the copper catalyst which originally lies at the bottom of the vessel ultimately becomes distributed throughout the whole reaction chamber. The superiority of copper over other metals as a catalyst is ascribed to the possibility of the simultaneous production of oxide and acetylide. The liberated acetylene must be endowed with particular reactivity, as a consequence of which the reactions which occur are much more profound than those involved in the pyrogenic decomposition of acetylene alone and lead through the most stable forms of combination to the inactive cuprene, the purely aromatic nature of which is thus readily explained (cf. Kaufmann and Schneider, A., 1922, i, 245). H. W.

**Process for Converting Halogen Substitution Products of Hydrocarbons into Hydrocarbons, or other Halogen Substitution Products of Hydrocarbons, containing a Higher Number of Carbon Atoms.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 196272).—The process consists in passing halogen substitution products of hydrocarbons, or mixtures of them, in the presence of water, over a catalyst comprising metals (e.g., platinum) or their compounds (e.g., thorium oxide, zirconium chloride, bismuth oxide, stannic chloride, zinc chloride), or non-metals (e.g., charcoal), carried on porous materials (particularly active charcoal), at an elevated temperature not exceeding 400°. Details are given for the production of ethyl chloride and ethylene from methyl chloride and of ethylidene chloride from a mixture of methyl chloride and methylene chloride. [Cf. *B.*, Feb.]. W. T. K. B.

**Some Constants of Ethyl Chloride.** E. DEISS (*Z. Elektrochem.*, 1923, 29, 586—587).—The ignition temperature of ethyl chloride lies below  $-18.5^{\circ}$ , the lower limit of explosion for mixtures of air and ethyl chloride is found with the mixtures containing 3.6% of ethyl chloride, the upper limit being the mixture containing 11.2%, and the maximum explosion occurs with 6.5% of ethyl chloride. J. F. S.

**Auto-oxidation of Chloroform.** A. M. CLOVER (*J. Amer. Chem. Soc.*, 1923, 45, 3133—3138).—When chloroform was exposed to diffused light it developed acidity and oxidising power. The latter reached a maximum and then decreased, whilst the acidity continued to increase. On dilution with water, the oxidising substance reacted to form hydrogen peroxide. The oxidising substance is probably dichlorocarbon peroxide,  $\text{CO}_2\text{Cl}_2$ . The addition of petroleum, alcohol, phenol, and many other substances inhibits the decomposition of chloroform, but the mechanism of their action remains obscure. Bromoform and methylene chloride also develop oxidising substances on standing. F. B.

**The Synthesis of Higher Members of the Aliphatic Series from Carbon Monoxide.** F. FISCHER and H. TROPSCH (*Ber.*, 1923, 56, [B], 2428—2443).—An examination of the possibility of the conversion of water gas into motor spirit. In the presence of a suitable catalyst, carbon monoxide is reduced by hydrogen to a mixture of alcohols, ketones, aldehydes, etc., which is designated "synthol." It is converted when heated under pressure into a mixture of hydrocarbons, to which the name "synthin" is assigned. In a somewhat similar manner, the direct production of hydrocarbons from mixtures of carbon monoxide and hydrogen has been patented by the Badische Anilin- & Soda-Fabrik (D.R.-P. 293787, 295203, and 295202); the different course of the reaction is possibly due to the fact that technical water gas containing carbon dioxide and an excess of hydrogen over carbon monoxide is used in the experiments now described, whereas in the work of the Badische Anilin- & Soda-Fabrik the carbon monoxide was invariably in excess.

[With W. KRÖNIG.]—Technical water gas is freed as far as possible from compounds of sulphur, compressed at 150 atmospheres and heated at 400–450° in the presence of iron covered with potassium carbonate; the product of the reaction separates into an aqueous and an oily layer in the volume proportion 2 : 1. A marked difference in the components of the two phases is not observed. Each consists of fatty acids, aliphatic aldehydes, ketones, and alcohols; in addition, the oily layer contains esters and hydrocarbons in small amounts. The presence of formic, acetic, propionic, and isobutyric acids is established. Higher fatty acids are also present which have not been identified individually; as judged by equivalent and boiling point, acids of the formula  $C_8H_{16}O_2$  are produced. The presence of propaldehyde, probably *n*-butaldehyde and isobutaldehyde, is established, whereas formaldehyde could not be detected. The ketones comprise acetone, methyl ethyl ketone, diethyl ketone, and methyl *n*-propyl ketone. Methyl, ethyl, and *n*-propyl alcohols are identified in addition to higher homologues. The esters have not been identified. Hydrocarbons are present only in minor amount (about 2%).

The conversion of synthol, b. p. 99–225°, into synthin is effected under pressure at 400–450° in an autoclave in an atmosphere of nitrogen. The liberated gas consists of carbon dioxide (14.5%), hydrocarbons soluble in fuming sulphuric acid (22.7%), oxygen (0.7%), carbon monoxide (14.6%), hydrogen (9.6%), paraffin hydrocarbons (21.8%), and nitrogen (16.1%). The liquid product consists mainly of hydrocarbons which boil over a wider range than the initial material. They are stable towards concentrated sulphuric acid, and therefore saturated. The atomic ratio, C : H, increases from the fractions of lowest to those of highest boiling point. Whereas in the former this ratio is nearly 1 : 2, as is required for the simpler naphthenes, in the latter its value indicates that only saturated hydrocarbons with several condensed ring systems can be present. Possibly, the process consists in the initial conversion of the alcohols by loss of water into olefines which become further subdivided into small portions which unite to form naphthenes.

The theory of the experiments is discussed in detail. It is pointed out that the presence of a hydrogen carrier such as iron, nickel, cobalt, or, possibly, manganese, is essential, in addition to a base or the salt of a base with a weak acid. Apparently the production of oil is favoured by the strength of the base, which, however, by itself (*e.g.*, potassium hydroxide in the presence of pumice) is not sufficient. It appears most probable that the initial product is formaldehyde, which in the absence of bases passes into methane; in the presence of the latter, however, it becomes converted into methyl alcohol, as is established by the production of large amounts of the latter from paraformaldehyde and hydrogen at 400° under 100 atmospheres in the presence of pumice loaded with potassium carbonate. Methyl alcohol is converted by carbon monoxide, either directly or through methyl formate, into acetic acid, the stepwise reduction of which gives

acetaldehyde and ethyl alcohol, whilst its catalytic decomposition gives acetone. An extension of this operation yields propionic acid, propaldehyde, *n*-propyl alcohol, and diethyl ketone. The non-production of members containing more than seven or eight carbon atoms is due to their instability under the experimental conditions. The production of higher alcohols is probably due to loss of water from the simpler members of the series. H. W.

**Alcohols and Hydrocarbons from Beeswax.** GASCARD and G. DAMOY (*Compt. rend.*, 1923, 177, 1442—1443; cf. this vol., i, 8).—The following alcohols (2 and 4 in largest quantity) have been obtained from beeswax, after alkaline hydrolysis: (1) *Neoceryl*,  $C_{25}H_{52}O$ , m. p.  $75.5^{\circ}$ ; (2) *ceryl*,  $C_{27}H_{56}O$ , m. p.  $80^{\circ}$ ; (3) *montanyl*,  $C_{29}H_{60}O$ , m. p.  $84^{\circ}$ ; and (4) *myricyl alcohols*,  $C_{31}H_{64}O$ , m. p.  $87^{\circ}$ . After crystallising the alcohols, the following hydrocarbons were obtained from the mother-liquors: Pentacosane,  $C_{25}H_{52}$ , m. p.  $54-54.5^{\circ}$ ; heptacosane,  $C_{27}H_{56}$ , m. p.  $59.2-59.5^{\circ}$ ; nonacosane,  $C_{29}H_{60}$ , m. p.  $63.5^{\circ}$ , and hentriacontane,  $C_{31}H_{64}$ , m. p.  $68.4-69^{\circ}$ . All the acids, alcohols, and hydrocarbons obtained from beeswax crystallise in hexagonal plates. E. E. T.

**$\Delta^2$ -Pentene- $\gamma$ -ol [Ethyl Allyl Alcohol].** J. BAUDRENHIEU (*Bull. Soc. chim. Belg.*, 1923, 32, 337—339; cf. A., 1922, i, 710; also Delaby, A., 1923, i, 741).—The following physical constants are given: b. p.  $114.2-114.4^{\circ}/753$  mm.,  $d_4^{20}$  0.8373,  $n_D^{20}$  1.4254. Dry hydrogen chloride is absorbed by the alcohol, yielding a mixture of products one of which, believed to be  $CH_2:CH\cdot CH_2EtCl$ , has b. p.  $93-94^{\circ}/759.8$  mm.,  $d_4^{20}$  0.8978,  $n_D^{20}$  1.4254. This substance reacts with potassium acetate with formation of a mixture of isomerides. Hydrogen bromide gives with the alcohol a product, b. p.  $124-131^{\circ}$ , which is very unstable. H. J. E.

**Molecular Conductivity of Potassium Iodide in Epichlorohydrin.** N. A. YAJNIK and B. R. SOBTI (*J. Amer. Chem. Soc.*, 1923, 45, 3138—3139).—The molecular conductivity of potassium iodide in epichlorohydrin was determined by the Kohlrausch method. The results are: mol. volume (litres), 60, 120, 240, 480; specific conductivity 10 mhos, 2.3, 1.3, 0.8, 0.53; mol. conductivity (mhos), 13.8, 15.6, 19.2, 25.4, respectively. F. B.

**Carbohydrates and Polysaccharides. V. Use of Acetylene for the Synthesis of Cyclic Acetals.** H. S. HILL and H. HIBBERT (*J. Amer. Chem. Soc.*, 1923, 45, 3108—3116; cf. A., 1923, i, 439, 753).—The following cyclic acetals were prepared by passing acetylene into a mixture of a polyhydroxy-compound and a small amount of mercuric sulphate with 93% sulphuric acid. Ethylidene trimethylene ether, b. p.  $108-111^{\circ}$ ; ethylidene  $\alpha\beta$ -propylene ether, b. p.  $92^{\circ}$ ; *ethylidene glycerol bromohydrin*, b. p.  $170-182^{\circ}$ ; ethylidene glycerol, b. p.  $189-196^{\circ}$ ; *ethylidene  $\alpha\delta$ -tetramethylene ether*, a colourless liquid, b. p.  $124-127^{\circ}$ ; *ethylidene pinacol*, b. p.  $133-134^{\circ}$ ;  $\beta$ -methylpentane- $\beta\delta$ -diol *ethylidene ether*, b. p.  $139-140^{\circ}$ ; *monoethylidene  $\alpha$ -methyl glucoside*, silky,

colourless crystals, m. p.  $77^{\circ}$ , and ethylidene glucose. The mechanism of the reaction is discussed. F. B.

**Carbohydrates and Polysaccharides. VI. Relative Ease of Formation of Five- and Six-membered Heterocyclic Carbon-Oxygen Configurations.** H. S. HILL and H. HIBBERT (*J. Amer. Chem. Soc.*, 1923, **45**, 3117—3124; cf. preceding abstract).—When one equivalent of acetylene was passed into a mixture of one equivalent of ethylene glycol and one equivalent of trimethylene glycol, the proportion of ethylidene ethylene ether (five-membered ring) to ethylidene trimethylene ether (six-membered ring) was 1 : 2. A similar result was obtained in the case of a mixture of propylene  $\alpha\beta$ -glycol and trimethylene glycol, whilst with a mixture of ethylene glycol and  $\beta$ -methylpentane- $\beta\delta$ -diol the ratio was 1 : 5. Using a mixture of trimethylene glycol and  $\beta$ -methylpentane- $\beta\delta$ -diol, the ratio of the two six-membered ring derivatives was 1 : 2. Thus the six-membered ring compound was formed in preference to the five-membered ring compound, and the presence of methyl groups attached to the glycol carbon atoms favours ring formation. Similar partition experiments with mixtures of glycerol and ethylene glycol led to the conclusion that ethylidene glycerol consists of a mixture of  $\text{CHMe} < \begin{smallmatrix} \text{O} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \\ \text{O} \cdot \text{CH}_2 \end{smallmatrix}$

and  $\text{CHMe} < \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \text{O} \cdot \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{OH}$ , the latter predominating. F. B.

**Carbohydrates and Polysaccharides. VII. The Ease of Formation and Nature of certain Six-, Seven-, and Larger Carbon-Oxygen Cyclic Structures.** H. S. HILL and H. HIBBERT (*J. Amer. Chem. Soc.*, 1923, **45**, 3124—3132; cf. preceding abstract).—The partition of one equivalent of acetylene between one equivalent each of ethylene glycol and tetramethylene glycol shows that the five-membered cyclic acetal is formed three times as readily as the seven-membered compound. Attempts to prepare the cyclic ethylidene derivatives of octa- and deca-methylene glycols resulted in syrupy, odourless acetals with very high and indefinite boiling points. The tendency of atomic chains to assume spiral ring formation is discussed. F. B.

**Preparation of Chloroethylsulphuryl Chloride.** CHEMISCHE FABRIK VORM. WEILER-TER MEER (D.R.-P. 374141; from *Chem. Zentr.*, 1923, iv, 720).—Ethylene chloride is treated with fuming sulphuric acid with or without a catalyst and the resulting *chloroethylsulphuryl chloride*, a colourless, heavy oil with an odour like that of formaldehyde, b. p.  $120\text{--}122^{\circ}/80$  mm., is obtained by first separating through addition of ice-water and then distilling in a vacuum. *Dichlorodiethyl sulphate*, b. p.  $180\text{--}182^{\circ}/60$  mm., is also obtained. G. W. R.

**Noteworthy Behaviour of Organic Sulphur Compounds towards Sodium Arsenite.** A. GUTMANN (*Ber.*, 1923, **56**, [B], 2365—2367).—The mode of combination of sulphur in certain organic (and inorganic) compounds can be distinguished by their



behaviour towards sodium arsenite. Those which convert the arsenite into sodium thioarsenate,  $\text{Na}_3\text{AsSO}_3$ , contain sulphur in the polysulphide form; these also convert cyanide into thiocyanate; those compounds which, through the intermediary action of water, oxidise the arsenite to arsenate, contain sulphur in the persulphide form, corresponding with the peroxide form of oxygen. Di-xanthogen disulphide, diacetyl disulphide, and cupric sulphide all belong to the first class; tin disulphide and ultramarine, however, contain sulphur only in the bivalent form and are not reactive. Diamyl disulphide, diphenyl disulphide, dithio-*N*-dimethylaniline and phenyl ethyl disulphide all oxidise arsenite to arsenate and are reduced to mercaptans; they contain one atom of persulphide sulphur. Methyl trisulphide with sodium arsenite gives both arsenate and thioarsenate, and is reduced to methyl mercaptan; it therefore contains one atom each of polysulphide- and persulphide-sulphur. The free thiocyanogen of Söderbäcks (A., 1920, i, 219) and the phenylthiolthiocyanate of Lecher and Wittwer (A., 1922, i, 641) both contain 1 atom of persulphide sulphur, whilst the disulphur dithiocyanate of the same authors contains 2 atoms of polysulphide and 1 atom of persulphide sulphur. When cupric thiocyanate is heated with sodium arsenite, a green precipitate is first formed which, on boiling, changes into red cuprous oxide, arsenate being formed. In acid solution, white cuprous thiocyanate and arsenate are formed. In this reaction, the formation of cuprous salt is not due to the reducing action of the arsenite; this is oxidised to arsenate by the thiocyanic acid formed when the cupric salt is heated.

E. H. R.

### The Stereoisomerism of Brassidic and Erucic Acids.

D. HOLDE (*Ber.*, 1923, 56, [B], 2405).—A claim of priority in this field against von Auwers (cf. A., 1923, i, 294).

E. H. R.

### A New Unsaturated Fatty Acid in Sperm and Dolphin Oils.

M. TSUJIMOTO (*J. Chem. Ind. Japan*, 1923, 26, 608—620).—By the bromo-ester method of Grün and Janko (*Z. deut. Oel-Fett Ind.*, 1921, 553, 572) and the lead salt-light petroleum method, a new *tetradecenoic acid*,  $\text{C}_{14}\text{H}_{26}\text{O}_2$ , has been isolated from sperm and dolphin oils, the amount being about 3% of the material. The acid was found to be chiefly responsible for the iodine absorption of the lower fractions of the methyl esters. It is a colourless liquid, b. p.  $172^\circ/5$  mm.,  $d_4^{15}$  0.9079,  $n_D^{15}$  1.4566, iodine value 106.8 (*methyl ester*, b. p.  $140^\circ/5$  mm., *barium salt*, a white powder), and gives myristic acid,  $\text{C}_{14}\text{H}_{28}\text{O}_2$ , by reduction with hydrogen in the presence of platinum black, and dihydroxymyristic acid,  $\text{C}_{14}\text{H}_{26}(\text{OH})_2\text{O}_2$ , m. p. 118—119°, by oxidation by Hazura's method. By oxidising with potassium dichromate and sulphuric acid, the acid gave nonoic acid. On treating the acid with ozone in a chloroform solution, an ozonide peroxide,  $\text{C}_{14}\text{H}_{26}\text{O}_2$ , was obtained as a viscid, colourless liquid, the decomposition of which with water gave nonaldehyde, nonoic acid, glutaric acid semialdehyde (?), and glutaric acid. From these facts, it is concluded that the formula is  $\text{CH}_3\cdot[\text{CH}_2]_7\cdot\text{CH}:\text{CH}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$ .

K. K.

**Preparation of the Highly Unsaturated Acids of Fish Oils.**

M. TSUJIMOTO and KANESUKE KIMURA (*J. Chem. Ind. Japan*, 1923, 26, 891—893).—The lithium salt-acetone method of Tsujimoto (A., 1921, i, 78) for the separation of highly unsaturated acids is applicable to the quantitative analysis of the acids, but unsuitable for the preparation of the acids, owing to the need of large amounts of acetone and lithium hydroxide; a modification of the method is therefore proposed for the latter purpose. The fatty acids from fish oil (10 g). are dissolved in acetone (95 c.c.), neutralised with ammonia and mixed with an aqueous solution of the equivalent amount of lithium acetate or chloride, the sulphate not being suitable for the purpose owing to its smaller solubility in water. The amount of water is kept such that the resulting acetone solution is of 95% strength. It is well shaken for thirty minutes and then cooled in ice-water for one hour. Highly unsaturated acids are dissolved, chiefly as ammonium soaps, and the lithium salt acts as the precipitant for less unsaturated acids. The solution is filtered through a dry filter-paper in a cold funnel. After evaporation of the solvent, the residue is treated with a dilute mineral acid and thus highly unsaturated acids are isolated. The yield of the acids by this method is less than that by the peroxide method, but the properties of the products are almost the same. K. K.

**The Decarboxylation of Dimethylpyruvic Acid and its Preparation.** H. K. SEN (*Biochem. Z.*, 1923, 143, 195—200).—Dimethylpyruvic acid ( $\alpha$ -ketoisovaleric acid) was obtained by the following process, used in preference to the method described by Rassow and Bauer (A., 1909, i, 632). Ethyl isopropylacetoacetate was treated with dry ethyl nitrite gas in the presence of sodium ethoxide, and, from the resulting sodium derivative, the oxime of ethyl dimethylpyruvate was obtained and purified by distillation in a vacuum. From the oxime, dissolved in 85% formic acid and treated with nitrosyl sulphuric acid, ethyl dimethylpyruvate together with the free acid was obtained. Hydrolysis of the ester with 5% aqueous potassium hydroxide yielded dimethylpyruvic acid boiling at 76—78°/11 mm. The semicarbazone (prismatic needles) had m. p. 102—103°. Dimethylpyruvic acid in the presence of phosphate buffer mixtures is fermented by preparations of dried yeast to give isobutaldehyde in 50% yield. A 75% yield of the aldehyde is obtained when the fermentation is carried out in the presence of acetate and sodium sulphite. isoButyl alcohol is not formed in detectable amount. J. P.

**Keto-enolic Tautomerism. II. The Combined Application of Chemical Methods to the Estimation of Enols.** H. P. KAUFMANN and G. WOLFF (*Ber.*, 1923, 56, [B], 2521—2526; cf. A., 1922, i, 985; 1923, i, 90).—Fission of the dienolic form of ethyl diacetylsuccinate by ozone at a low temperature gives rise to acetic and oxalic acids, alcohol, and ethyl diketobutyrate. The course of the reaction is explained by assuming that ozonisation occurs at only one double bond, and that the product then suffers fission. The reaction is studied quantitatively by estimating the

oxalic acid produced in the form of calcium oxalate. Fission of the semi-enol by means of ozone occurs in a similar manner, and gives rise to the same products. On the basis of these observations, it is possible to investigate the equilibrium of ethyl diacetylsuccinate dissolved in hexane, carbon tetrachloride, or ether. The proportion of  $\alpha_1\beta$ -ester is determined by the bromine titration method; the colorimetric estimation with ferric chloride gives the sum of  $\alpha$ -ester and  $\alpha_2\beta$ -ester, whereas the fission by ozone gives the sum of all the enols (each of which gives a molecular proportion of oxalic acid). The examples which are cited show that chemical methods in these instances lead to results which cannot be obtained by physical means. The relative proportions of the three enols can be estimated with sufficient exactitude, but there is no process available for estimating directly the proportion of the ketonic form.

Starting from the  $\beta$ -ester, numerous investigations of the equilibria of diacetylsuccinic ester in various solvents have been made. The main difficulty in establishing an exact relationship between the velocity of transformation and the proportion of the enol consists in obtaining absolutely pure solvents free from catalytically active substances. It is, however, certain that equilibrium is established most rapidly, and that the keto-forms predominate in liquids of high dissociating power. Thus in the presence of water the  $\beta$ -variety is remarkably favoured, and all the isomerides are converted into it on contact with water. In nitromethane ( $e=39.4$ ), a small proportion of the  $\alpha_1\beta$ -ester (4.0%), but no other enol, is present. In the series of the alcohols, the  $\alpha_2\beta$ -ester is capable of existence; in addition, the  $\alpha_1\beta$ -compound is present to a considerable extent (42% in ethyl alcohol). In solvents of smaller dissociating power, such as hexane, the relationships are displaced greatly towards the other side. The  $\beta$ -ester is not present in appreciable amount, and the small percentage of ketonic form exists as the  $\gamma$ -ester. The proportion of  $\alpha_1\beta$ -ester recedes, whereas that of the  $\alpha_2\beta$ -compound attains 50%, and the dienolic form is capable of existence. The slight dissociating power of hexane, carbon tetrachloride, and ether influences markedly the rate of transformation of the isomerides. Loss of the enolic hydrogen atom which takes place instantaneously from the dienol, rapidly from the semi-enols in the presence of solvents of higher dielectric constant, becomes so retarded that even the very strongly acidic, dienolic variety is preserved. The primary formation of the  $\alpha_1\beta$ -ester in the establishment of all equilibria is very distinct.

H. W.

**Equilibrium in the System Calcium Oxalate-Dilute Hydrochloric Acid.** E. CARRIÈRE and M. AUMÉRAS (*Compt. rend.*, 1923, 177, 1288—1290).—The equilibrium in the system calcium oxalate-dilute hydrochloric acid has been studied by observing the disappearance of the calcium oxalate precipitate at a certain concentration of acid. Four influences are studied: (1) that of concentration of oxalic acid produced: by plotting concentrations of hydrochloric acid against those of oxalic acid, an almost straight line is obtained; (2) that of temperature: the concentration of

*f*\*

hydrochloric acid is, roughly, proportional to the solubility product of calcium oxalate at different temperatures; (3) that of excess of calcium chloride: the concentrations of hydrochloric acid are approximately proportional to the square root of the concentrations of calcium chloride; (4) that of excess of oxalic acid: the concentrations of hydrochloric acid are roughly proportional to the square root of the concentrations of oxalic acid. E. E. T.

**The Catalytic Bromination of Aliphatic Acid Chlorides.** W. F. GOEBEL (*J. Amer. Chem. Soc.*, 1923, **45**, 2770—2771).— $\alpha$ -Bromoanhydrocamphoronyl chloride (Bredt, A., 1895, i, 242) is prepared as follows. Anhydrocamphoronic acid is warmed with phosphorus pentachloride until the reaction ceases, a small quantity of iron powder is then added, and, while the mixture is heated on the water-bath, bromine is slowly added; the heating is then continued for forty-five minutes, and the mixture allowed to cool. The crude product (yield 75%) is purified by washing with dry ether and then recrystallising from benzene. W. S. N.

**The Supposed Autoxidation of Cysteine.** O. WARBURG and S. SAKUMA (*Pflüger's Archiv*, 1923, **200**, 203—206; from *Chem. Zentr.*, 1923, iii, 1290; cf. A., 1923, i, 11).—The autoxidation of cysteine described by Abderhalden and Wertheimer consists in reality of the oxidation and reduction of a metallic cysteine compound. G. W. R.

**The Oxidation of Hydrocarbons with Special Reference to the Production of Formaldehyde. V. The Slow Oxidation of the Higher Liquid, Saturated Hydrocarbons.** T. S. WHEELER and E. W. BLAIR (*J. Soc. Chem. Ind.*, 1923, **42**, 491—497r).—Experiments on the oxidation of hexane were made, using a method previously described (A., 1923, i, 1175), in which the hydrocarbon mixed with oxygen is passed through a hot tube. The temperatures used were 480°, 520°, 540°, and 590°, the time of heating being 2 sec. The products obtained included higher aldehydes, unsaturated hydrocarbons, formaldehyde, acids in small quantity, carbon monoxide, carbon dioxide, hydrogen at higher temperatures, and water. In presence of excess of oxygen, much of the hexane consumed appears as higher aldehydes, just as with other hydrocarbons, except methane (cf. T., 1923, **123**, 2079). The amount of carbon dioxide formed also increases when more oxygen is used, and as the rate of oxidation of the hexane does not increase as fast as would be expected from the law of mass action, it is clear that surface action is predominant. As the temperature increases, less of the higher aldehyde appears in the product, but more formaldehyde, unsaturated hydrocarbon, carbon monoxide, and carbon dioxide. The unsaturated hydrocarbon at all temperatures is mainly ethylene and the higher aldehydes tend towards acetaldehyde with increasing temperature. No saturated hydrocarbons appear in the products, showing that thermal decomposition of the hexane does not occur appreciably, otherwise methane would appear in quantity. The results are discussed in connexion

with those obtained by other workers, and the probable course of the slow oxidation of hydrocarbons generally is shown diagrammatically.

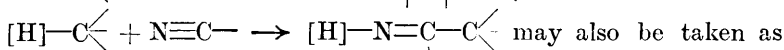
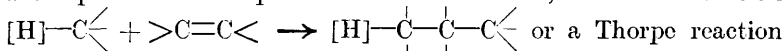
E. H. R.

**Condensation of Aldehydes to Esters by Aluminium Ethoxide.** W. C. CHILD and H. ADKINS (*J. Amer. Chem. Soc.*, 1923, **45**, 3013—3023).—During an investigation on the condensation of acetaldehyde to ethyl acetate, using aluminium ethoxide as catalyst, it was found that the latter existed in two forms. When prepared by the method of Wislicenus, the  $\alpha$ -form only was produced, and this solidified at a little above the ordinary temperature; it was partly converted into the  $\beta$ -form, m. p.  $140^\circ$ , on distillation. The  $\beta$ - was completely converted into the  $\alpha$ -form by heating in a sealed tube at  $275^\circ$  for fifteen hours. Both forms had the same catalytic activity, being more active than Henle's ethoxide (A., 1920, ii, 446). The presence of water in the catalyst or in the aldehyde was detrimental. The effect of the addition of a third substance on the rate of reaction was studied, and the results show that alcohols containing fewer than six carbon atoms are inhibitors, methyl alcohol being the most effective, whilst the chlorides of aluminium, mercury, calcium, and zinc are promoters. The addition of increasing amounts of aluminium chloride was accompanied by increasing yield of ethyl acetate to a certain value; further increase in the amount of promoter caused a decreased production of ester and an increase in the rate of paracetaldehyde formation. The reaction apparently takes place in a homogeneous system and the exclusion of light has no effect. The temperature coefficient of the reaction in xylene solution is approximately 1.30 for a rise of  $10^\circ$  in the vicinity of the ordinary temperature.

F. B.

### The Activation of Hydrogen in Organic Compounds.

E. H. USHERWOOD (*Chemistry and Industry*, 1923, **42**, 1246—1251).—The presence of activated hydrogen in an organic compound may be recognised by a number of properties, among which may be mentioned diad or triad tautomerism, ability to form metallic derivatives, and capacity for alkylation. The ability of a compound to take part in an aldol reaction, a Michael reaction



evidence of the presence of an activated hydrogen atom, indicated above in square brackets. The phenomenon of tautomerism may be regarded as due to the migration of an activated hydrogen atom

within the molecule thus:  $>C[H]-C=O \rightleftharpoons >\underset{|}{C}=CO[H]$ . There is a strong formal resemblance between this reaction and the

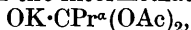
aldol reaction  $>C[H]X + >C:O \rightleftharpoons >CX-\underset{|}{C}-O[H]$ , and this resemblance is intensified by a recent demonstration that the aldol reaction is reversible. Keto-enol tautomerism may therefore be

regarded as an intramolecular aldol reaction. There is a similar analogy between three-carbon tautomerism and the Michael reaction. The structural conditions necessary for the activation of a hydrogen atom to give rise to the above phenomena may be provisionally embraced in two formulæ: (1) The hydrogen atom represented by [H] in the group  $[H]C\equiv X$  is activated no matter whether X is C or N; (2) The hydrogen atom in the group  $[H]C-X=Y$  or  $[H]\equiv C-XY$  is activated no matter whether X is C or N, provided Y is either the electronegative O, N, or S, or is C, which itself is involved in the group  $\equiv C-X=Y$  or  $\equiv C-X\equiv Y$ . The benzene nucleus, considered as a Kekulé individual, forms a special case of the second rule, and it enters into a number of reactions which show that it possesses an activated hydrogen atom. A number of such reactions are discussed, including the addition of benzene to cinnamic acid, the conversion of  $\beta$ -imino- $\gamma$ -cyano- $\alpha$ -phenylpropane into 1:3-naphthalenediamine, and Skraup's quinoline synthesis.

E. H. R.

**Production of Acetone by the Action of Potassium Acetate on Acetic Anhydride.** E. LUCE (*Compt. rend.*, 1923, **177**, 1306—1309).—When an equimolecular mixture of potassium acetate, acetic acid, and acetic anhydride is heated under reflux for thirty hours in a bath kept at 170—180°, some acetone and carbon dioxide are formed. Equimolecular mixtures of potassium acetate and acetic acid, or of acetic anhydride and acetic acid, when similarly treated, give practically no acetone. An equimolecular mixture of potassium acetate (100 g.) and acetic anhydride, however, gives 12.32 g. of carbon dioxide, corresponding with a considerable production of acetone, most of which is lost by polymerisation or evaporation. If the acetone is allowed to distil as fast as it is formed, about 24% of the theoretical quantity (see below) is obtained.

This type of reaction was observed first by Perkin (T., 1886, **49**, 317), whose explanation has now been confirmed. Thus, when a mixture of potassium butyrate and acetic anhydride interacts, acetone and methyl propyl ketone are formed, as would be expected from the decomposition of the intermediate compound,



whereas, if the reaction were due simply to the decomposition of the acid anhydride, acetone alone would result, whilst interaction (with elimination of potassium carbonate) of 2 mols. of alkali salt would only lead to the formation of dipropyl ketone. E. E. T.

**Ketenic Decomposition of Ketones. Keten and Methylketen.** C. D. HURD (*J. Amer. Chem. Soc.*, 1923, **45**, 3095—3101; cf. A., 1911, i, 307).—Acetone vapour was decomposed by contact with a hot platinum wire filament, but the yield of keten was not so good as in the method previously described (A., 1923, i, 1060). Both methyl ethyl ketone and diethyl ketone gave a mixture of methylketen and keten. The presence of keten in the product from diethyl ketone must be due to the decomposition of methylketen.

F. B.

**Oxidation of Carbohydrates.** J. STIEGLITZ (*Proc. Inst. Med. Chicago*, 1916—1917, 1, 41—50).—In the oxidation of dextrose, an intra-atomic phenomenon involving the loss of electrons by the carbon atoms, and essentially like that of an element, the production of an electric current has been observed. The presence of alkalis causes great acceleration, and of acids, retardation; the former condition yields decomposition products more readily oxidised than dextrose itself. There is evidently some fundamental specific factor, probably the oxidising enzymes, having a paramount influence on the physiological processes of oxidation of carbohydrates.

CHEMICAL ABSTRACTS.

**Sources of the Rare Sugars. XI. Preparation of Mannose. XII. Preparation of Inulin.** T. SWANN HARDING (*Sugar*, 1923, 583—585, 636—638).—*Mannose*.—A modification of the method of Hudson and Sawyer (A., 1917, i, 321) is described: Ivory sawdust is mixed with its own weight of sulphuric acid (75%), hydrolysed as directed by Hudson and Sawyer (*loc. cit.*), and barium carbonate added until the reaction is neutral to Congo-red paper. After adding sufficient phosphoric acid to impart a slight acidity, using the same indicator, and also some decolorising carbon, the liquid is filtered. Basic lead acetate is added to the filtrate, which is concentrated to a thin syrup in a vacuum, and treated with twice its volume of alcohol. After further concentration, and the addition of a little glacial acetic acid, crystallisation is readily effected, the mass obtained being diluted with alcohol containing 1% of nitric acid, and the sugar filtered and washed with the acid-alcohol on a Buchner funnel. Lastly, it is dried in a vacuum at the ordinary temperature, ground finely, and the drying continued for twenty-four hours while gradually raising the temperature to 46°, mannose free from acetic acid thus being obtained.

*Inulin*.—A mixture of 1,000 g. of finely ground chicory root and 5 litres of water is boiled for one hour, filtered, and the residue washed with hot water. The filtrate and washings are treated at 40° with basic lead acetate, using a slight excess over that required for the precipitation of the impurities, decolorising carbon is added, the excess of lead thrown down with hydrogen sulphide, and the liquid filtered. After concentrating the filtrate to about 500 c.c., and adding twice its volume of 80% alcohol, the mixture is allowed to remain over-night, when 10—15 per cent. of inulin will deposit. This is dissolved in 1,000 c.c. of 40% alcohol, treated with decolorising carbon, and filtered. Two volumes of 80% alcohol containing 1% of nitric acid are added, the liquid is left over-night at a low temperature, and the inulin obtained dried in a vacuum at about 35° and reprecipitated.

J. P. O.

**Solubility and Insolubility of Starch.** G. MALFITANO and M. CATOIRE (*Compt. rend.*, 1923, 177, 1309—1311).—A 1% aqueous solution of potato starch was obtained (heating not above 80°), the cooled product, consisting of two layers, then being diluted to one-tenth of its original concentration, and the clear portion

evaporated. The gelatinous starch separating did not give a clear solution with boiling water, and on being dried merely swelled when so treated. After washing with water and then with alcohol, the product (containing, like the original material, combined phosphorus, calcium, magnesium, and silicon) resembled cotton, dissolving in water only when heated at 150° with the latter, and being reprecipitated on cooling. On treatment with acids, etc., it gave a product resembling soluble starch.

It is concluded that the solubility of starch depends on the inorganic matter present, starch itself being amylaceous matter combined with phosphates and silicates (of calcium and magnesium).

E. E. T.

### **Starch Paste. I. Relation between the Viscosity of Wheat Starch Paste and the Concentration and Temperature.**

MORIZO YOSHINO (*J. Chem. Ind. Japan*, 1923, **26**, 870—873).—The viscosity was measured by Ostwald's capillary viscosimeter at 20°, 30°, 40°, and 50° for the range of concentration of 0.5—2.5%. The relation between viscosity and concentration is expressed with sufficient accuracy by Arrhenius's formula,  $\log \eta/\eta_0 = \theta C$ , where  $C = 100p/[100 - (n+1)p]$ ,  $p$  being the number of grams of starch in 100 grams of paste and  $n$  the hydration factor. The amount of water absorbed decreases according to the elevation of temperature. The values of  $\theta$  and  $n$  were observed to be as follows: 0.412 and 12.6 at 20°, 0.407 and 10.0 at 30°, 0.407 and 7.6 at 40°, and 0.408 and 5.7 at 50°. When the values of  $p$  become 7.4 at 20°, 9.1 at 30°, 11.6 at 40°, and 14.9 at 50°, the viscosity becomes infinite; that is, the solution changes into a solid. K. K.

**Cellulose. VIII.** K. HESS, W. WELTZIEN, and E. MESSMER (*Annalen*, 1923, **435**, 1—144).—(A) *Cuprammonium-cellulose solutions*, E. MESSMER [and, in part, (FRL.) ELLY JAGLA].—It has already been shown (A., 1921, i, 401) that the copper is present in cellulose-cuprammonium solutions as an optically active complex anion and as (kation) an ammine. The solutions have now been examined further from a mass-action point of view, and the molecular complexity of the dissolved cellulose has been determined. In order to make such a determination trustworthy, the following points had to be proved: (1) Cellulose (in cuprammonium solutions) undergoes no hydrolytic decomposition. This is clearly the case, since the maximum rotation, for a particular concentration, is reached immediately dissolution of cellulose is effected. (2) The rotation is due to a single complex copper compound of high rotatory power. This is shown by the form of the rotation curves (concentration of components of solution against rotation, etc.). Moreover, a maximum rotation is observed when the solution contains 1 atom of copper to 1 mol.  $C_6H_{10}O_5$ . (3) The copper complex is in equilibrium with very weakly rotating cellulose (the latter functioning, in dissolving, as a base). This is shown by other curves, connecting rotation and concentration of copper. A slight excess (1 mol.) of copper is necessary to drive back the dissociation of the complex. When excess of copper is present, addition of



cellulose, within limits, causes a rectilinear rotation-increase curve. (4) The (reacting) copper is used entirely to give the strongly rotating complex. This is shown by studying the effect of sodium hydroxide, which does not increase the rotatory power of the solution (see equation 2 below). (5) The copper dissolves unimolecularly. This is shown by a parallel investigation of dextrosemonoacetone (below).

The above relations are expressed by the equation:  $m\text{Cu} + n(\text{C}_6\text{H}_{10}\text{O}_5)_x \rightleftharpoons \text{Cellulose-copper Complex}$ , and since it has been shown (2, above) that an atom of copper corresponds with  $\text{C}_6\text{H}_{10}\text{O}_5$ , in the given solution,  $m=nx$ .

The formation of a cellulose-cuprammonium solution is expressed by the following equations: (1) In absence of alkali, cellulose is dissolved by cuprammonium hydroxide: (a)  $(\text{C}_6\text{H}_{10}\text{O}_5)_x(\text{solid}) + [\text{Cu}(\text{NH}_3)_4](\text{OH})_2 \rightarrow 2\text{H}_2\text{O} + [\text{C}_6\text{H}_9\text{O}_5]_2[\text{Cu}(\text{NH}_3)_4]$ ; (b) (giving the complex of high rotatory power):  $[\text{C}_6\text{H}_9\text{O}_5]_2[\text{Cu}(\text{NH}_3)_4] + 2[\text{Cu}(\text{NH}_3)_4](\text{OH})_2 \rightleftharpoons [\text{C}_6\text{H}_7\text{O}_5\text{Cu}]_2[\text{Cu}(\text{NH}_3)_4] + 8\text{NH}_3 + 4\text{H}_2\text{O}$ . (2) In presence of alkali (which takes the place of cuprammonium hydroxide):  $\text{Na}[\text{C}_6\text{H}_9\text{O}_5] + [\text{Cu}(\text{NH}_3)_4](\text{OH})_2 \rightleftharpoons [\text{C}_6\text{H}_7\text{O}_5\text{Cu}]\text{Na} + 4\text{NH}_3 + 2\text{H}_2\text{O}$ . The equations (1) and (2) may be summarised thus:  $[\text{C}_6\text{H}_9\text{O}_5]' + [\text{Cu}(\text{NH}_3)_4]'' + 2\text{OH}' \rightleftharpoons [\text{C}_6\text{H}_7\text{O}_5\text{Cu}]' + 4\text{NH}_3 + 2\text{H}_2\text{O}$ . (3) In presence of excess of alkali:  $[\text{C}_6\text{H}_9\text{O}_5]\text{Na} + [\text{C}_6\text{H}_7\text{O}_5\text{Cu}]\text{Na} \rightarrow [\text{C}_6\text{H}_9\text{O}_5\text{Cu}]\text{Na}_2$  (the last formula relating to the copper-sodium-cellulose complex precipitated in presence of excess of alkali).

Since in equation (1) above, the copper has two functions, the investigation of this solution will throw little light on the question at issue. In presence of alkali (2), however, the copper has only one function. If  $\alpha$ =rotatory power of the copper complex,  $a$  and  $b$  are, respectively, the total number of copper atoms and  $\text{C}_6\text{H}_{10}\text{O}_5$  units present in volume  $v$ , and  $x$  is the number of  $\text{C}_6\text{H}_{10}\text{O}_5$  units in the combined cellulose, then, for the interaction of  $m$  atoms of copper and  $n$  molecules of cellulose,  $K$ , the reaction constant, is given by  $K = (a/v - m \cdot \alpha \cdot k)^m (b/xv - n\alpha k)^n / \alpha \cdot k$ . Various values (1 to 4) were taken for  $m$ ,  $n$ , and  $x$ , and  $k$  and  $K$  determined, whence, knowing  $\alpha$  and  $b$ ,  $a$  could be calculated. Approximate agreement between  $a$  (found) and  $a$  (calc.) was only obtained for (1)  $n=m=x=1$ , (2)  $n=m=1$ ,  $x=2$ , (3)  $n=2$ ,  $m=3$ ,  $x=1$ , and (4),  $n=3$ ,  $m=4$ ,  $x=1$ . Of these possibilities, (2), (3), and (4) are excluded on other (experimental) grounds, as is also the possibility of expressing (1) as  $n=m=x=2$  (i.e.,  $2\text{Cu} : \text{C}_{12}\text{H}_{20}\text{O}_{10}$ —i.e., cellobiose) or as  $n=m=x=3$ , and so on.

From the above, it follows that in cuprammonium solutions of cellulose (say, one containing 28 mols. of cellulose, 15 mols. of copper, and 25 mols. of sodium hydroxide), cellulose reacts as if it possessed the molecular formula,  $\text{C}_6\text{H}_{10}\text{O}_5$ . The correctness of this conclusion was established in other ways. Thus, solutions containing  $x$  mols. of cupric hydroxide and  $y$  mols. of cellulose gave the same rotation as solutions containing  $y$  mols. of cupric hydroxide and  $x$  mols. of cellulose.

Experiments were also carried out (cf. A., 1921, i, 401) with cuprammonium solutions of other carbohydrates or their derivatives. Cellobiose had  $[\alpha]_{435.8} +50.6^\circ$ ,  $+50.6^\circ$ , and  $+160.0^\circ$  in aqueous, in ammoniacal sodium hydroxide, and in sodium hydroxide-cuprammonium solutions, respectively. The investigation of the solutions is rendered difficult because of mutarotation, oxidation, etc.  $\alpha$ -Methylglucoside, in the above three solvents, had  $[\alpha]_{435.8} +324^\circ$ ,  $+340^\circ$ , and  $+460^\circ$ . The tendency of the glucoside to form copper complexes is very strong. Although, for this reason, the equilibrium relationship could not be experimentally investigated, clear evidence was obtained that the increased rotation of the cuprammonium solutions was due to a complex, 1 glucoside : 1 copper.  $\beta$ -Methylglucoside, in the above three solvents, had  $[\alpha]_{435.8} -57.4^\circ$ ,  $-53.3^\circ$ , and  $+38.1^\circ$ , respectively. The quantitative study of the cuprammonium solutions of the last three compounds is complicated by the rotation possessed by these compounds. In the case of dextrose monoisopropylidene ether, which had, in the above three solvents,  $[\alpha]_{435.8} -24.8^\circ$ ,  $-31.6^\circ$ , and  $-212.5^\circ$ , respectively, the equilibrium was amenable to experiment, and the existence of the complex, containing  $1\text{Cu} : \text{C}_9\text{H}_{16}\text{O}_6$ , definitely established. Moreover, the molecular weight of the dissolved dextrose monoisopropylidene ether was determined as in the case of cellulose, and also by direct cryoscopic measurement in aqueous solution, when a normal result was obtained. Dextrose monopropylidene ether was found to have m. p.  $160.5\text{--}161^\circ$ ,  $[\alpha]_{\text{D}}^{15} -12.12^\circ$  (cf. Fischer and Rund, A., 1916, i, 363).

Lævoglucosan gives no complex in cuprammonium solutions, the rotation in the latter being the same as that of an aqueous solution.

(B) *The acetylation of cellulose* (W. WELTZIEN [and, in part, R. SINGER, H. JENSEN, and A. REH]).—Whilst dried cotton cellulose does not react with pure, dry, acetyl chloride, cotton cellulose containing 4—5% of moisture, when shaken for four days with eleven times its weight of acetyl chloride at  $17\text{--}20^\circ$ , is converted (92% yield) into crude cellulose triacetate A. If the cooled solution obtained is allowed slowly to lose the hydrogen chloride present, evaporated in a vacuum, the residue treated with chloroform, and the latter evaporated, a solution of the second residue in glacial acetic acid then being precipitated with ether, pure *cellulose triacetate A* is obtained as a pale yellow or colourless powder (60% yield).

If in the original acetylation the conditions are varied, by-products (formed in the above preparation in small quantities), viz., *cellodextrin acetate* and *acetochlorocellobiose*, are obtained in larger quantities, although they are readily separable from cellulose triacetate A. The acetylated celluloses described by Skraup (A., 1906, i, 67) and by Zechmeister (A., 1923, i, 306) are mixtures. (In connexion with the analysis of cellulose acetates, a modification of the Ost and Katayama and the Wenzel method is described, steam vacuum distillation being used. A diagram of the apparatus used is given.)

Cellulose triacetate *A* has m. p. 270—275° (decomp., with brown coloration and frothing), is soluble in chloroform and acetic acid, and insoluble in alcohol or ether. Dissolution is preceded by swelling. Cellulose triacetate *A* has  $[\alpha]_D -16.7^\circ$  in chloroform and  $+4.40^\circ$  in glacial acetic acid. Its solutions in the latter solvent throw little light on its molecular weight, a constant depression being obtained for all solutions containing between 0.03 and 0.3% of the acetate, whilst irregular results are obtained with higher concentrations. The constant depression obtained with low concentrations may be due to the presence of water (cf. Paternò and Salimei, A., 1913, ii, 849). In phenol, cellulose triacetate *A* gives a mol. weight value of 2,380—3,350 (with a specimen obtained in a slightly different manner, 2,030—2,270). Ost's cellulose acetate (in phenol) had a variable mol. weight (2,037—10,133). On treatment with a mixture of acetic and sulphuric acids, Ost's cellulose acetate became more like cellulose triacetate *A*. Thus, whilst originally its product of alkaline hydrolysis was practically insoluble in alkali, after the acetic-sulphuric acid treatment, the hydrolysis product was soluble in alkali.

Cellulose triacetate *A*, on treatment with cold *N*-methyl-alcoholic sodium hydroxide, affords cellulose *A*, readily soluble in 2*N*-sodium hydroxide, the solution affording cellulose *A* on acidification. Cellulose *A* is a white powder with  $[\alpha]_D$  (in 2*N*-NaOH)  $-12.4^\circ$ . It is shown by X-ray analysis to be crystalline, whilst its rotatory power in cuprammonium solutions establishes clearly its structural identity with the original cotton cellulose used. An alkaline solution of cellulose slowly undergoes hydrolysis, reducing properties developing. In the methyl-alcoholic alkaline hydrolysis (above), a little of the reducing substances is formed, and is removed by treating the alkaline solution with ammonia, when pure cellulose *A* is precipitated. In this connexion, it is found that the Schwalbe copper number does not always give trustworthy comparisons of reducing power. A method based on the precipitation of the cellulose to be tested as the sodium-copper derivative (above) is described. Pure cellulose *A* and hydrocellulose (as prepared by Knoevenagel and Busch, A., 1922, i, 636) show no reduction with the improved method, the crude products showing feeble reduction. Ost's cellulose acetate, after acid treatment (as above) was feebly reducing, whilst cellodextrin acetate, and the acetyl derivative obtained by treating cellulose with acetyl chloride at 24—27° were strongly reducing.

By effecting the acetylation of cellulose with acetyl chloride, in presence of acetic anhydride, which decreases the concentration of hydrogen chloride ( $\text{Ac}_2\text{O} + \text{HCl} \rightleftharpoons \text{Ac}\cdot\text{Cl} + \text{Ac}\cdot\text{OH}$ ), a cellulose acetate was obtained which, on hydrolysis, gave a cellulose less soluble in alkali than cellulose *A*.

Cellodextrin acetate is a white, amorphous powder, m. p. 260° (softening at 250°),  $[\alpha]_D^{18} -11.0$  ( $\pm 2.0$ )°,  $[\alpha]_D^{17.5} -12.0$  ( $\pm 1.5$ )°, in chloroform. It is more soluble in solvents than is cellulose triacetate *A*. It gives a molecular weight in acetic acid of 318—1,366, in phenol of 1,260—1,480, in urethane of 1,500—1,540, and

in naphthalene of 1,350—1,470. On hydrolysis with methyl-alcoholic sodium hydroxide, it gives *dextrin* as a white powder, which darkens without melting, reduces Fehling's solution under proper conditions (above), and is converted by acetyl bromide containing hydrogen bromide into acetobromocellobiose, whilst acetic anhydride (and a trace of sulphuric acid) converts the *dextrin* into octa-acetylcellobiose (m. p. 228°).

(C) *Methylation of Cellulose A* [W. WELTZIEN.]—The methylation of cellulose, as effected in presence of alkali (Irvine, T., 1923, 123, 518), gives results of doubtful value, owing to the definite action of alkali on cellulose at the temperature of methylation. Cellulose *A*, on warming with dilute alkali, is so altered that it reduces Fehling's solution, and is no longer precipitated on acidification. Hydrated barium hydroxide has no effect on cellulose *A*, and methylation carried out using this hydroxide and methyl sulphate (at 90—95°) may be assumed to proceed without effecting structural changes. The product obtained in this way was a yellow glass (OMe=30—40%), insoluble in, and unaffected by, alkali, and on further methylation with sodium hydroxide and methyl sulphate (at 80—90°) for three hours gave a product (OMe=42—43%) corresponding with trimethyl cellulose *A*. Further methylation (using silver oxide and methyl iodide or piperidine and methyl sulphate) was impossible. *Trimethyl cellulose A* is a white powder, m. p. 230—245° (softening at 217°), dissolving in cold water and separating on heating this solution, owing to hydrate formation, etc. It has  $[\alpha]_D^{20}$   $-18^\circ$  in water and is inactive in chloroform solution. The freezing-point depression of an aqueous solution slowly decreased on keeping, a result in accordance with the structural similarity of trimethyl cellulose *A* to cellulose *A*. It is concluded that the results obtained by Heuser and von Neuenstein (A., 1923, i, 17) indicate that these authors were dealing with a partly hydrolysed cellulose complex.

(D) *Action of Hydrogen Bromide on Cellulose triacetate A* [K. HESS, W. WELTZIEN, and F. KUNAU.]—Cellulose triacetate *A*, when treated in glacial acetic acid solution with hydrogen bromide, gave acetobromocellobiose (yield, 10—30%). No hexa-acetylbromocellobiose but a little hepta-acetylbromocellobiose was also formed.

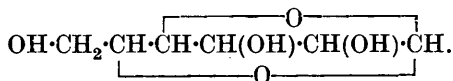
Cellulose triacetate *A* is unaffected by acetyl bromide, but, in presence of hydrogen bromide, a 50% conversion into acetobromocellobiose results. There is also formed a new *acetobromodextrose* (white, amorphous powder, m. p. 60—70° [indef.],  $[\alpha]_D +80^\circ$ ) which does not yield penta-acetyldextrose when treated with silver acetate. The new compound does not depress the freezing point of bromoform, has a normal molecular weight in acetic acid and in phenol, and is (twice) associated in benzene solution. It affords acetobromocellobiose when treated with acetyl bromide containing hydrogen bromide. The acetobromodextrose is readily deacetylated by the method of Fischer and Bergmann (A., 1919, i, 278), whereas acid hydrolysis caused the elimination of bromine, with formation, in very variable yield, of a new substance, *celloglucosan*,  $C_6H_{10}O_5 \cdot H_2O$ , plates, m. p. 107—109°,  $[\alpha]_D +89.31^\circ$ , in

aqueous solution. The molecule of water is firmly attached, and the substance (which is accompanied in its formation by a bromine-free amorphous substance) is not hygroscopic, like some glucosans (below). *Tribenzoylcelloglucosan* has m. p. 126—128°. Cello-glucosan is unaffected by boiling alkali, but affords reducing compounds on acid hydrolysis. It is quantitatively converted by methyl alcohol containing a trace of hydrogen chloride into  $\alpha$ -methyl-glucoside, a fact which is difficult to reconcile with Karrer's suggestion that cellulose is derived from  $\beta$ -glucose (A., 1920, i, 370). Celloglucosan in many respects resembles glucosan (Pictet and Castan, A., 1920, i, 594), but, unlike the latter substance, does not reduce Fehling's solution. The rotation of an aqueous solution of celloglucosan is higher than that of a similar solution of glucosan, but falls to the rotation of the latter if a little hydrochloric acid is added.

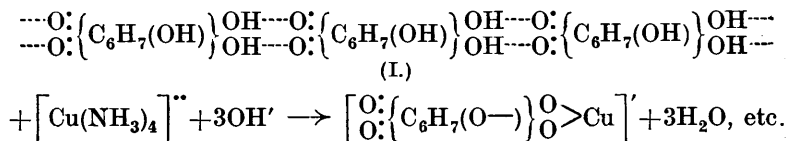
The formation of the new acetobromodextrose, which cannot, like its previously known isomeride, be obtained from cellobiose, proves that cellulose may be converted into derivatives of dextrose without the intermediate formation of cellobiose.

It is concluded (in a comprehensive survey of the whole of the work) that natural (cotton) cellulose is built up from glucose anhydride units, which are associated, not condensed or polymerised. The X-ray diagrams of natural cellulose, and of the cellulose (shown to be a chemical individual) obtained by precipitating cuprammonium solutions, suggest, but do not prove, the identity of these two products. Cellulose and cellulose A give identical values for  $k$  and  $K$  when examined by the above (cuprammonium) method, whilst the hydrolysis product of Ost's cellulose acetate is also shown to be identical, from the same point of view, with cellulose.

If 2 : 3 : 6-trimethylglucose is produced (Irvine, *loc. cit.*) without structural change, cellulose will be :



At variance with this formula, however, are the results of the action of hydrogen bromide on cellulose triacetate A. The authors prefer to write cellulose as I in the scheme below, when its dissolution in cuprammonium solution (which effects saturation of the partial valencies involved in the association of the simple cellulose units) is expressed thus :



Such a formula for cellulose explains its amphoteric character, and its behaviour towards neutral salts such as zinc chloride.

An interesting, but probably misleading, fact is the identity of the heats of combustion of cellulose and of *lævoglucosan*.

Natural cellulose may contain as its crystal unit (cf. X-ray analysis) four  $C_6H_{10}O_5$  residues associated together.

An important result also emerges: cellobiose need no longer be regarded as a degradation product of cellulose, the converse being nearer the truth.

E. E. T.

### Comparative Investigations of Cellulose and Lignin.

F. FISCHER and H. TROPSCH (*Ber.*, 1923, **56**, [B], 2418—2428).—A restatement and extension of the work carried out in the authors' laboratory during recent years.

The hydrogenation of cellulose and lignin by hydriodic acid under pressure does not appear to be suitable to the elucidation of the genetic relationships between the substances, since the course of the change is not obvious and has led to very conflicting results in the hands of various workers.

Cellulose is far more stable than lignin towards aqueous alkali hydroxide under pressure and at elevated temperatures. It is completely dissolved at  $300^\circ$  with production of much carbon dioxide. Lignin, on the other hand, is decomposed by 9.5*N*-potassium hydroxide solution at  $300^\circ$  with production of phenols or phenolcarboxylic acids and adipic acid, and by 10*N* sodium hydroxide solution at  $250^\circ$  with formation of succinic and oxalic acids. Lignin easily becomes autoxidised in the presence of sodium hydroxide, yielding humic acids, non-volatile acids such as succinic, oxalic, and (?) isophthalic, in addition to acetic, formic, and carbonic acids; cellulose is comparatively little attacked. Similar differences are observed in the oxidation of the substances under pressure; it is significant that whereas cellulose yields aliphatic acids, aromatic acids are, in addition, obtained from lignin. The ready nitration of lignin by 5*N* nitric acid is in harmony with a phenolic structure.

The comparative behaviour of cellulose and lignin when subjected to distillation under diminished pressure is described in detail. The yields of coke and tar are widely different with the two compounds. The most significant result, however, appears to be the absence of optically active compounds in the aqueous extracts of lignin tar, whereas under like conditions lævogluconan is obtained from cellulose. It appears therefore improbable that the lignin molecule is composed of polysaccharide components.

H. W.

**Lignin-content of Spruce Wood.** P. KLASON (*Cellulose-chemie*, 1923, **4**, 81—84).—The sulphuric acid method for the determination of lignin is recommended; easy filtration is secured by using a weaker acid than the 72% concentration prescribed by Ost and Wilkening; the washed lignin retains sulphuric acid, but not in the form of a combination. About 1 g. of finely rasped wood is suspended in 50 c.c. of 64% sulphuric acid and allowed to remain over-night. The liquid is diluted and the residue collected on a tared filter, then washed with cold or warm water. The resin and fat are extracted by washing with 50 c.c. of hot alcohol and the lignin is then neutralised with water containing 5 c.c. of *N*/10-potassium hydroxide, washed and dried at  $105^\circ$ .

The correction for ash includes any sulphuric acid not removed in the washing. Calculated on dry substance the values for an eighty-year old spruce stem were: lignin corrected for sulphate, 29.4%; sulphuric acid, 3.6%; resin and fat, 1.1%. The lignin showed on analysis C, 63.97%; H, 5.32%; pentosans, 1.7%. Another stem from the same forest but of one hundred years' growth yielded only 26.6% of lignin. Deposits of "red wood" in the branches contained locally up to 37.1% of lignin. For the direct extraction of fat and resin from wood, ether appears to be the best solvent, free from drawbacks which accompany the use of benzene or alcohol. The benzene extracts always show reactions of lignin, and the alcohol extract, which is indefinite in quantity increasing with the time of extraction, contains very substantial quantities of lignin and carbohydrates in about equal proportions. As a rapid and approximate method for the determination of resin and fat, the washing of the lignin residue after treatment with sulphuric acid may be considered to be satisfactory. J. F. B.

**Chloro-bismuthates.** A. GUTBIER and MANFRED MÜLLER (*Z. anorg. Chem.*, 1923, **128**, 137—152).—By treatment of one molecular proportion of bismuth trichloride with three molecular proportions of the hydrochlorides of organic bases in presence of hydrochloric acid, three new series of compounds have been prepared, viz., *μ*-dichloro-octachloro-dibismuthates,  $[\text{NHR}_3]_4[\text{BiCl}_5]_2$ , of which the dimethylanilinium and diethylanilinium salts are described, *μ*-trichloro-hexachloro-dibismuthates,  $[\text{NH}_3\text{R}]_3[\text{Bi}_2\text{Cl}_9]$ , of which the methylammonium, tetramethylammonium, triethylammonium, tetraethylammonium, *n*-propylammonium, tripropylammonium, *n*-butylammonium, isobutylammonium, and isoamylammonium salts are described, and hexachloro-bismuthates,  $[\text{RNH}_3]_3[\text{BiCl}_6]$ , of which the dimethyl-, trimethyl-, ethyl-, diethyl-, isopropyl-, diisopropyl-, and allyl-ammonium salts, the methyl-, ethyl- and isoamyl-anilinium salts, and the guanidinium, pyridinium,  $\alpha$ -picolinium,  $\beta$ -picolinium, lutidinium, collidinium, quinolinium, and isoquinolinium salts are described. The first and second series may be regarded as hexa-co-ordination compounds by assuming the formulæ given, the two bismuth atoms being linked through two and three chlorine atoms, respectively.

All the compounds are extremely sensitive to changes in environment, and decompose at once in contact with water or moist air.

S. I. L.

**The Derivatives of Hexachloro-antimonic Acid.** A. GUTBIER and W. HAUSMANN (*Z. anorg. Chem.*, 1923, **128**, 153—168).—By combination of antimony pentachloride with alkyl- and aryl-amines in hydrochloric acid solution, a large number of compounds of the general formulæ  $[\text{R}\cdot\text{NH}_3][\text{SbCl}_6]$ ,  $[\text{R}_2\text{NH}_2][\text{SbCl}_6]$ ,  $[\text{R}_3\text{NH}][\text{SbCl}_6]$ , and  $[\text{R}_4\text{N}][\text{SbCl}_6]$ , as well as pyridine and piperidine derivatives, have been prepared. They are moderately stable, crystallising unchanged from hydrochloric acid in colourless, well-formed crystals; they dissolve in water to colourless solutions, which slowly become cloudy, and deposit white precipitates, but

from alcohol solution they may be recovered for the most part unchanged.

The mono-, di-, tri-, and tetra-methylammonium salts, the mono-, di-, tri-, and tetra-ethylammonium salts, the mono-, di-, and tri-propylammonium, isopropyl-, butyl-, isobutyl-, and diisobutylammonium salts, the allyl-, isoamyl-, and benzyl-ammonium salts, the dibenzylethylammonium, ethylenediammonium salts, and the  $\alpha$ -picolinium, collidinium, and piperidinium salts are described.

S. I. L.

**Derivatives of Hexachloro-stannic Acid.** A. GUTBIER, G. KUNZE, and E. GÜHRING (*Z. anorg. Chem.*, 1923, **128**, 169—178).—A series of alkylammonium, arylammonium, and pyridine and quinoline derivatives of the general formula  $X_2[SnCl_6]$  has been prepared. They are generally colourless, and crystallise readily from hydrochloric acid solution. They dissolve readily in water, hydrolysing slowly in the cold; the freshly prepared alcoholic solutions are neutral. Tripropylammonium hexachlorostannate  $[NHPr_3]_2[SnCl_6]$  crystallises in two forms, one bright rose-coloured tablets, the other deep reddish-brown leaflets.

The following compounds are described: the methyl-, dimethyl-, trimethyl-, tetramethyl-, ethyl-, diethyl-, triethyl-, tetraethyl-, normal and isopropyl-, dipropyl-, tripropyl-, normal and isobutyl-, diisobutyl-, triisobutyl-, allyl, and isoamyl-ammonium salts, the ethylene- and propylene-diammonium salts, and the anilinium, pyridinium, collidinium, and quinolinium salts.

S. I. L.

**Röntgenographic Determination of the Structural Formula of Hexamethylenetetramine.** H. W. GONELL and H. MARK (*Z. physikal. Chem.*, 1923, **107**, 181—218).—The crystal structure of hexamethylenetetramine has been investigated by means of X-ray spectra and Laue figures. It is shown that hexamethylenetetramine does not belong to the hexakisoctahedral class,  $O_h$ , as has been assumed from macroscopic examination, but more probably it belongs to the hexakistetrahedral class  $T_d$  or possibly to the tetrahedral pentagonal dodecahedral class  $T$ . The elementary cube has an edge 7.02 Å. long and contains 2 mols. of hexamethylenetetramine. Each nitrogen atom lies between the three nearest carbon atoms in close spherical packing. The shortest distances between neighbouring atoms in the molecule are: N—C=1.48 Å. and C—C=2.58 Å. The lattice is a molecular lattice. The structure thus deduced confirms that found by Duden and Scharff (A., 1896, i, 122) from purely chemical investigation, according to which the molecule is built up of trimethylenetriamine rings. The present work furnishes an example where Röntgenographic investigation enables a decision between possible structural formulæ to be reached when such has not been possible by purely chemical treatment.

J. F. S.

**The Reactivity of Different Amino-acids in the Presence of Blood Charcoal, and of Hydrogen Peroxide.** E. NEGELEIN (*Biochem. Z.*, 1923, **142**, 493—505).—Measurements



have been made of the rate of oxidation in an atmosphere of oxygen, and of the adsorption constants, of various amino-acids in the presence of blood charcoal. The considerable variations found in the former, when equimolecular solutions of the various acids are brought into equilibrium with the adsorbent, are ascribed to differences in the extent of adsorption. In general, primary and secondary amino-acids are much more reactive to oxygen in the presence of charcoal than are the tertiary acids. Closely parallel results are obtained when the rates of oxidation of the amino-acids by activated oxygen (hydrogen peroxide) at  $p_H$  9.2 are measured, the tertiary acids being again much less reactive than the others. The similarity of the two types of oxidation lends support to the views of Warburg, in which the oxidation of amino-acids in the presence of charcoal is ascribed to activated oxygen. J. P.

**The Configuration of Amino-acids. II.** P. KARRER (*Helv. Chim. Acta*, 1923, 6, 957—959).—The conversion of *d*-serine into *l*- $\beta$ -diaminopropionic acid shows that these must have the same configuration. *d*-Serine was converted into its methyl ester, which, by the action of phosphorus pentachloride, was converted into *d*- $\gamma$ -chloro- $\beta$ -aminopropionic acid, as described by Fischer and Raske (A., 1907, i, 900) for the corresponding *l*-compounds. The *d*-chloroaminopropionic acid was converted into *l*-diaminopropionic acid by heating with liquid ammonia. The product contained some racemate, its rotation being  $[\alpha]_D^{18}$   $-18.1^\circ$  instead of  $-24.9^\circ$ . It follows that *l*-serine must have the same configuration as *d*-diaminopropionic acid, which has been shown to correspond with *l*-asparagine and *l*-aspartic acid (A., 1923, i, 660). It therefore follows that the following constituents of natural albumin all have the same configuration: *d*-alanine, *l*-serine, *l*-cystine, *l*-asparagine, and *l*-aspartic acid. It would appear to be a general rule that naturally occurring amino-acids have the same configuration. E. H. R.

**Aliphatic Dialkylaminoalkyl Compounds.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (U.S. Pat. 1429922; from *Chem. Zentr.*, 1923, iv, 591).—Additional data are given for compounds already mentioned (A., 1922, i, 529). Ethyl  $\alpha$ -diethylaminoethylacetoacetate has b. p.  $132-135^\circ/10$  mm., ethyl  $\alpha$ -dimethylaminoethylacetoacetate, b. p.  $124^\circ/12$  mm., ethyl diethylaminobutylacetoacetate, b. p.  $138^\circ/10$  mm. G. W. R.

**The Electro-chemical Preparation of Cyanuric Acid and Allophanic Esters from Formamide.** K. SCHAUM [with H. SCHNEIDER] (*Ber.*, 1923, 56 [B], 2460—2462).—*iso*Cyanuric acid is obtained when formamide is electrolysed between platinum electrodes at a temperature not exceeding  $45^\circ$  with a pressure of 70 volts. A yellow substance, the nature of which has not been elucidated, is obtained as by-product; it is obtained in greater quantity if higher temperatures and current densities are employed. The electrolysis of mixtures of formamide and an alcohol leads to the formation of allophanic esters of which the methyl, ethyl, isopropyl, and isobutyl compounds have been prepared in good

yield. Apparently cyanic acid is formed intermediately either by discharge of a formamide-ion or by anodic oxidation of formamide; the former process appears to predominate when small quantities of water are present, the latter when the quantities are more considerable.

The electrolysis of molten acetamide does not give well-defined products. H. W.

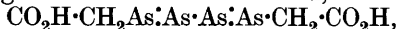
**Crotononitriles.** A. BUELENS (*Bull. Soc. chim. Belg.*, 1923, **32**, 334—337).—Crotononitrile, prepared by three different methods, dehydration of  $\alpha$ -hydroxybutyronitrile and of  $\beta$ -hydroxybutyronitrile and catalytic transformation of ethyl crotonate by Mailhe's method (A., 1920, i, 476), is obtained in each case as a mixture of the two stereoisomerides, that of higher b. p. predominating. In the third case, the author shows that isomerisation occurs during catalysis as the mixture is formed in the same proportions by submitting the isomeride of higher b. p. to the conditions under which catalysis is effected. H. J. E.

**The Vapour Pressure of Hydrocyanic Acid.** RYÔSABURÔ HARA and HEIMA SHINOZAKI (*J. Chem. Ind. Japan*, 1923, **26**, 884—890).—The vapour-pressure curve of hydrocyanic acid has been determined by Smith and Menzies's static isotenoscope method (A., 1910, ii, 1036) within the range of 0—46°. It is believed that the observed values are correct to  $\pm 0.2\%$ . The equation,  $\log P_{mm} = 1836.63/T^{1.05} + 7.5030$ , shows satisfactory agreement with the observations. For obtaining the pressure at any desired temperatures between 0° and 47.5°, the following two values observed were used for the above formula: 519.4 mm. at 15.88° and 1128.4 mm. at 36.68°. The boiling point of the acid was found to be 25.7° instead of 26.5° as generally accepted. Considering the acid as an ideal gas, the heat of vaporisation of the acid was calculated from the Clausius-Clapeyron formula to be 246.4 cal. at 0°, 245.5 cal. at 20°, and 244.5 cal. at 45°. The results are tabulated. K. K.

**Cacodyl Derivatives.** F. A. LEE, C. THING, and W. M. DEHN (*J. Amer. Chem. Soc.*, 1923, **45**, 2996—2998).—Cacodyl, prepared by Bunsen's method, is converted into the chloride, b. p. 109°, which gives the bromide, b. p. 130°, the iodide, b. p. 155—160°, and the cyanide, b. p. 138°, when heated with the molecular proportion of potassium bromide, iodide, and cyanide, respectively. Oxidation of the chloride with moist air gives hydrated cacodyl oxychloride, m. p. 85°. Cacodyl chloride reacts with mercurous and mercuric chlorides, cuprous and cupric chlorides to form additive compounds, which are described. F. B.

**Aliphatic Arseno-compounds. I. Arsenoacetic Acid and Tetra-arsenoacetic Acid.** C. S. PALMER (*J. Amer. Chem. Soc.*, 1923, **45**, 3023—3029).—The barium salt of arsinoacetic acid ( $\text{AsO}_3\text{Ba}\cdot\text{CH}_2\cdot\text{CO}_2$ )<sub>2</sub>Ba was quantitatively produced from chloroacetic acid by reaction with excess of sodium arsenite; the reaction mixture was acidified with acetic acid, the precipitated arsenic trioxide filtered off, and the filtrate added to a solution of barium

chloride. The barium salt was converted into the sodium salt and treatment of the latter with sulphuric acid and sodium hypophosphite gave *arsenoacetic acid*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{As}\cdot\text{As}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , yellow crystals, decomp. above  $200^\circ$ . Simultaneous reduction of one molecular equivalent of arsenic trioxide and two of arsinoacetic acid in the cold gave tetra-arsenoacetic acid,



a vermilion red, crystalline powder, decomp. at  $180^\circ$ . F. B.

**Preparation of Arsinic Acid Derivatives of Aliphatic Carboxylic Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (Aust. Pat. 93325, and Swiss Pat. 97977; from *Chem. Zentr.*, 1923, iv, 721).—Aliphatic halogen carboxylic acids or their derivatives such as amides or esters are treated with arsenious acid, its derivatives, or its salts, in the presence of alkaline reagents. For example, from chloroacetic acid and arsenious oxide *arsinoacetic acid* is obtained as colourless crystals, m. p.  $152^\circ$ . Sodium arsenite and ethyl acetate give *ethyl arsinoacetate*, light yellow leaflets, m. p. about  $95^\circ$ . *Arsinolactic acid* is a viscous, yellow syrup obtained from  $\beta$ -chlorolactic acid and arsenious acid. *Di-arsinoadipic acid*, from dibromoadipic acid, forms colourless crystals, m. p.  $165^\circ$  (decomp.). Phenylarsine oxide and chloroacetic acid give *arsinophenylacetic acid*, m. p.  $145^\circ$  (decomp.). G. W. R.

**Oxidation of Magnesyl [Magnesium Alkyl] Derivatives by Means of Hydrogen Peroxide.** B. ODDO and R. BINAGHI (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 349–353; cf. A., 1922, i, 314).—When oxidised by means of hydrogen peroxide, magnesium *sec.*- and *tert.*-alkyl bromides yield the corresponding alcohols. Similarly, phenols are obtained from magnesium aryl bromides with the exception of magnesium phenyl bromide, and substituted hydroxylamines and per-acids from the products formed by replacing the active hydrogen of primary amines and of the carboxyl group by the grouping MgBr.

Treatment of magnesium phenyl bromide with hydrogen peroxide may give rise to the initial formation of phenol, but the products recognised are phenyl ether, *p*-hydroxyphenyl ether, benzene, diphenyl, and, possibly, phenyl peroxide.

With the other organomagnesium compounds, however, the oxidation proceeds normally and, especially with compounds of the types  $\text{R}_2\text{CH}\cdot\text{MgBr}$  and  $\text{R}_3\text{C}\cdot\text{MgBr}$ , with such regularity in respect to time as to furnish fresh support to the view that only one of the oxygen atoms of hydrogen peroxide is quadrivalent and to strengthen the analogy in behaviour and constitution between the peroxide and formaldehyde (*loc. cit.*). Thus, with hydrogen peroxide,  $\text{CHR}_2\cdot\text{MgBr} \rightarrow \text{CHR}_2\cdot\text{O}(\text{H}_2)\cdot\text{O}\cdot\text{MgBr} \rightarrow \text{CHR}_2\cdot[\text{OH}_2]\cdot\text{OH} \rightarrow \text{CHR}_2\cdot\text{OH}$ , and  $\text{CR}_3\cdot\text{MgBr} \rightarrow \text{CR}_3\cdot\text{O}(\text{H}_2)\cdot\text{O}\cdot\text{MgBr} \rightarrow \text{CR}_3\cdot[\text{OH}_2]\cdot\text{OH} \rightarrow \text{CR}_3\cdot\text{OH}$ , and with formaldehyde,  $\text{CHR}_2\cdot\text{MgBr} \rightarrow \text{CHR}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{MgBr} \rightarrow \text{CHR}_2\cdot\text{CH}_2\cdot\text{OH}$ , and  $\text{CR}_3\cdot\text{MgBr} \rightarrow \text{CR}_3\cdot\text{CH}_2\cdot\text{O}\cdot\text{MgBr} \rightarrow \text{CR}_3\cdot\text{CH}_2\cdot\text{OH}$ .

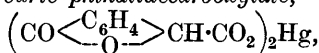
Ethyl hydroperoxide may be regarded as having the aldehydic structure  $\text{O}:\text{OEt}\cdot\text{H}$ , so that, like the aldehydes, it should yield

alcohols of the three series when treated with the three types of magnesium alkyl derivatives. Ethyl peroxide, on the other hand, having the ketonic constitution,  $\text{O}:\text{OEt}_2$ , should yield always secondary and tertiary alcohols.

An outline is given of the experimental results, which are to be published elsewhere.

T. H. P.

**Behaviour of Mercuric Salts of Organic Acids towards Heat.** M. S. KHARASCH and F. W. STAVELEY (*J. Amer. Chem. Soc.*, 1923, 45, 2961—2972); cf. A., 1922, i, 189).—The behaviour of mercuric salts of substituted acetic acids on heating depends on the character of the substituting group. Thus mercuric  $\alpha$ -dimethylpropionate was not decomposed when heated in a vacuum at  $240^\circ$  for twenty minutes or when melted in air, whilst the mercury salts of phenylacetic, diphenylacetic, and triphenylacetic acid gave various products, but none in which the mercury replaces a hydrogen atom attached to the  $\alpha$ -carbon atom. The ease with which the salt loses carbon dioxide is an important factor. When mercuric  $\alpha$ -diethylacetoacetate, m. p.  $103^\circ$ , is heated in a vacuum at  $85^\circ$  carbon dioxide is evolved and mercury bis- $\alpha$ -acetyl- $\alpha$ -ethylpropyl, m. p.  $109^\circ$ , is formed. Treatment of this compound with mercuric chloride gives  $\alpha$ -acetyl- $\alpha$ -ethylpropylmercuric chloride,  $\text{CEt}_2\text{Ac}\cdot\text{HgCl}$ , m. p.  $77^\circ$ . On heating mercuric dimethylacetoacetate in a vacuum at  $90^\circ$ , mercury bis- $\alpha$ -acetyl- $\alpha$ -isopropyl, m. p.  $120^\circ$ , is produced. This gives a mercuric chloride compound, m. p.  $124.5^\circ$ . Mercuric  $\alpha$ -dimethylpropionate, m. p.  $235^\circ$ , did not give off carbon dioxide when heated at  $240^\circ$  in a vacuum. When benzoylacetic acid and mercuric oxide are heated in alcohol solution mercury diphenacyl,  $\text{Hg}(\text{CH}_2\cdot\text{COPh})_2$ , m. p.  $159.5^\circ$ , is formed, and this on treatment with mercuric chloride gives phenacylmercuric chloride, m. p.  $146^\circ$ , which is identical with the substance of known constitution prepared by direct mercuration of acetophenone (A., 1902, i, 849). When benzoylacetic acid and mercuric oxide are heated in chloroform solution, the product is anhydro- $\alpha$ -hydroxymercuribenzoylacetic acid,  $\text{COPh}\cdot\text{CH}\langle\begin{smallmatrix} \text{CO} \\ \text{Hg} \end{smallmatrix}\rangle\text{O}$ , decomp.  $290^\circ$ . On adding a solution of mercuric acetate to a solution of phthalidecarboxylic acid, mercuric phthalidecarboxylate,



is obtained. This reacts with sodium hydroxide to give phthalonic acid and phthalidecarboxylic acid, and has m. p.  $195^\circ$  (decomp.), forming dihydrophthalide, m. p.  $250^\circ$ . Benzoylformic acid in alcohol solution reacted with mercuric oxide to form the mercurous salt which is decomposed by sodium carbonate. The mercuric salt, m. p.  $164^\circ$ , is obtained by adding a solution of mercuric acetate to a solution of benzoylformic acid.

F. B.

**Fixation of Unsaturated Molecules by Metals produced from their Organometallic Derivatives.** A. JOB and R. REICH (*Compt. rend.*, 1923, 177, 1439—1441).—On keeping a solution of

ferrous ethyl iodide (cf. A., 1922, i, 645), metallic iron is deposited as a mirror, ethylene and ethane also being formed. These changes are explained by the following scheme:  $2\text{FeEtI} \rightarrow \text{FeEt}_2 + \text{FeI}_2 \rightarrow 2\text{C}_2\text{H}_4 + \text{FeH}_2 + \text{FeI}_2 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + \text{Fe} + \text{FeI}_2$ , where ferrous hydride reduces ethylene to ethane. This explains why Wanklyn obtained ethylene and ethane from zinc ethyl and ferrous iodide. The iron deposit, which contains traces of ferrous ethyl iodide, is pyrophoric and decomposes water to give hydrogen.

Nickel, cobalt, chromium, and manganese are also produced in active forms from a halide salt and magnesium ethyl bromide, part of the metal being precipitated, the rest remaining in (colloidal) solution. Thus, when an ether-benzene solution of magnesium phenyl bromide is treated, in absence of air, with nickelous chloride, a solution is obtained which (1) rapidly absorbs carbon monoxide, in amount corresponding with the formation of nickel carbonyl,  $\text{Ni(CO)}_4$ ; (2) slowly absorbs, per atom of nickel, 2 mols. of nitric oxide (giving a bluish-green solution); (3) absorbs ethylene (2 mols. for each atom of nickel) to give a reddish-brown solution; (4) absorbs acetylene ( $\text{Ni:3C}_2\text{H}_2$ ); and (5) rapidly absorbs hydrogen ( $2\text{H}_2:\text{Ni}$ ), nickel hydride being precipitated as a black, very reactive powder (cf. Schlenk and Weichselfelder, *Ber.*, 1923, 56, [B], 2230).  
E. E. T.

### Organometallic Compounds. III. Compounds formed between Tin Alkyl Halides and Ammonia and the Amines.

C. A. KRAUS and W. N. GREER (*J. Amer. Chem. Soc.*, 1923, 45, 3078—3083).—Tin trimethyl chloride forms a compound with 1 mol. of aniline, and with 1 mol. of pyridine (m. p.  $37^\circ$ ). Tin trimethyl iodide combines with two equivalents of ammonia, one of which is loosely held, two equivalents of aniline, and one equivalent of pyridine. The compound with pyridine solidifies homogeneously at  $-17^\circ$ . Tin dimethyl dichloride combines with two equivalents of pyridine. Mercury ethyl chloride and mercury amyl chloride each combine with one equivalent of ammonia. Solutions of the metal alkyl halides in amines are fair conductors of electricity, whilst the solutions in neutral solvents are virtually non-conductors. It is suggested that these compounds are of the ammonium type,  
 $\text{C}_6\text{H}_5\cdot\text{N} < \underset{\text{I}}{\text{Sn(CH}_3)_3}$ .  
F. B.

### Organometallic Compounds. IV. Conductivity of Tin Trimethyl Chloride in Mixed Solvents.

C. A. KRAUS and W. N. GREER (*J. Amer. Chem. Soc.*, 1923, 45, 2946—2954; cf. this vol., i, 25).—The electrical conductivity of tin trimethyl chloride in nitrobenzene and acetone solutions on the addition of small amounts of pyridine has been measured. A marked increase in conductivity takes place on the addition of pyridine, and this effect is greater the smaller the amount of pyridine already present. The conductivity of solutions of tin trimethyl chloride in mixtures of 0—100% of acetone and alcohol, nitrobenzene, and pyridine, respectively, has been measured at  $25^\circ$ . The initial conductivity in nitrobenzene is extremely low, indicating that tin trimethyl

chloride is not much ionised in this solvent. The initial conductivity in acetone is markedly higher than in nitrobenzene. Whilst the conductivity in acetone is increased on the addition of alcohol, this increase is much less marked than it is on the addition of pyridine. The results are in keeping with the view that tin trimethyl chloride itself is not a true electrolyte and that its electrolytic properties in solution are due to the formation of compounds of the oxonium and ammonium type, the tin trimethyl group transferring from chlorine to quadrivalent oxygen or quinquivalent nitrogen respectively.

J. F. S.

**The Conditions of Equilibrium and Motion of Molecules in Space.** J. BÖESEKEN (*Ber.*, 1923, **56**, [B], [2411—2414]).—A discussion of the structures of cyclohexane and cycloheptane ring systems, in which a theory previously put forward (Derx, A., 1922, i, 651) is restated. The proof by Schrauth and Görig (A., 1923, i, 1084) that dicyclohexane can exist in three forms is important in this connexion.

E. H. R.

**Ternary System Toluene-Acetone-Water.** J. H. WALTON and J. D. JENKINS (*J. Amer. Chem. Soc.*, 1923, **45**, 2555—2559).—The equilibrium curves for the system toluene-acetone-water have been determined experimentally at 0°, 20°, and 30°. It is shown that temperature has very little effect on the mutual solubility of the three components.

J. F. S.

**Catalytic Condensation of Acetylene with Benzene and its Homologues.** J. S. REICHERT and J. A. NIEUWLAND (*J. Amer. Chem. Soc.*, 1923, **45**, 3090—3091; cf. A., 1923, i, 753).—Diphenylethane, ditolyethane, and dixylylethane were prepared by passing acetylene into benzene, toluene, and xylene, respectively, at 10—20° in the presence of concentrated sulphuric acid and a mercuric salt. Similarly, dimesitylethane was prepared from mesitylene, and ethylidinebisethylbenzene from ethylbenzene.

F. B.

**The Disulphonation of Naphthalene.** H. E. FIERZ-DAVID and A. W. HASLER (*Helv. Chim. Acta*, 1923, **6**, 1133—1146).—An extended account of work already published in brief (Fierz-David, A., 1921, i, 409; 1923, i, 1190). 1 : 5-Naphthalenedisulphonic acid crystallises in well-formed, monoclinic tablets, containing 4H<sub>2</sub>O, losing 2H<sub>2</sub>O in a vacuum at 55°, and the remainder at 125°; m. p. 240—245° (decomp.). It is soluble in 0.98 part of water at 20°, and is not deliquescent. Its salts, with their solubilities in parts of water per part of anhydrous salt, are as follows: Li<sub>2</sub>+2H<sub>2</sub>O, monoclinic; Na<sub>2</sub>+2H<sub>2</sub>O, monoclinic, 9; K<sub>2</sub>+2H<sub>2</sub>O, monoclinic, 15; Rb<sub>2</sub>, Cs<sub>2</sub>, Tl<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub> all anhydrous, monoclinic; Ca+2H<sub>2</sub>O, triclinic, 40; Sr+H<sub>2</sub>O, monoclinic (?), 96; Ba+H<sub>2</sub>O, rhombic, 470; 250 at 100°; Pb+3H<sub>2</sub>O, monoclinic, 82; Mg, (22), Zn (28), Co (46), Ni (73), Cu (21), all with 6H<sub>2</sub>O, form an isomorphous, monoclinic series. The *sulphonamide* forms small needles, m. p. above 310°, and the *sulphanilide* has m. p. 248—249°.

Naphthalene-1 : 6-disulphonic acid crystallises in large, monoclinic, striated prisms with 4H<sub>2</sub>O; it loses water gradually when

heated and melts at  $125^{\circ}$  (decomp.). It is deliquescent in damp air. The *sulphonamide* has m. p.  $297-298^{\circ}$ . The salts and their solubilities are as follows:  $\text{Na}_2 + 7\text{H}_2\text{O}$ , 3;  $\text{K}_2$ , 5;  $(\text{NH}_4)_2 + 2\text{H}_2\text{O}$ , 2;  $\text{Ca} + 4\text{H}_2\text{O}$ , 10;  $\text{Sr} + 5\text{H}_2\text{O}$ , 10;  $\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$ , 16;  $\text{Pb} + 4\text{H}_2\text{O}$ , 12; all the foregoing are rhombic;  $\text{Mg}$ ,  $\text{Zn}$  (3),  $\text{Co}$  (5),  $\text{Ni}$  (5), all with  $6\text{H}_2\text{O}$ , isomorphous, rhombic,  $\text{Cu} + 4\text{H}_2\text{O}$ , 2.

Naphthalene- $\beta$ -sulphonamide can be separated almost quantitatively from the  $\alpha$ -compound or from disulphonamide by dissolving the mixed amides in 20% sodium hydroxide solution and cooling in ice, when the sodium salt of the  $\beta$ -sulphonamide crystallises out. The calcium salt of the 2:6-disulphonic acid can be precipitated quantitatively in the anhydrous form by heating its aqueous solution, alone or mixed with other calcium salts, in a closed vessel at  $130^{\circ}$ .

E. H. R.

**The Diphen succindene Series. V. Colourless and Coloured 9:12-Dialkyl- $\Delta^{9,11}$ -diphen succindadienes.** K. BRAND and F. SCHLÄGER (*Ber.*, 1923, **56**, [B], 2541—2545; cf. A., 1912, i, 960; 1920, i, 486, 487).—An extension of previous work to compounds containing alkyl instead of aryl groups in the 9:12-positions.

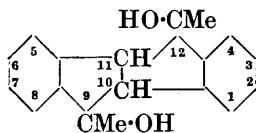
Diphen succindan-9:12-dione is converted by magnesium methyl iodide into 9:12-dimethyldiphen succindan-9:12-diol (annexed formula), colourless needles, m. p.  $170^{\circ}$ .

It is converted by boiling formic and glacial acetic acids into 9:12-dimethyl- $\Delta^{9,11}$ -diphen succindadiene,  $\text{CMe}=\text{C}\cdot\text{C}_6\text{H}_4$ , dark red or yellowish-brown needles, m. p.  $212^{\circ}$ ,

which is hydrogenated in alcoholic solution in the presence of palladised charcoal to 9:12-dimethyldiphen succindane, colourless needles, m. p.  $94^{\circ}$ . 9:12-Diethyldiphen succindan-9:12-diol forms coarse, colourless crystals, m. p.  $102^{\circ}$ . It is transformed by a boiling mixture of formic and glacial acetic acids into 9:12-diethylidene-diphen succindane, slender, colourless needles, m. p.  $199.5^{\circ}$  (which is oxidised by chromic acid to acetaldehyde and diphen succindandione) and 9:12-diethyl- $\Delta^{9,11}$ -diphen succindadiene, red or reddish-brown leaflets, m. p.  $154^{\circ}$  (indefinite). 9:12-Dibenzylidiphen succindan-9:12-diol, small, colourless needles, m. p.  $206^{\circ}$ , is converted by acetic and formic acids into a mixture of coloured 9:12-dibenzyl- $\Delta^{9,11}$ -diphen succindadiene (which could not be isolated in the homogeneous condition) and 9:12-dibenzylidenediphen succindane, colourless needles, m. p.  $255^{\circ}$ ; the latter substance is oxidised by chromic acid to benzoic acid and diphen succindan-9:12-dione, m. p.  $202^{\circ}$ .

H. W.

**The Diphen succindene Series. VI. 9:12-Dinaphthyl Derivatives of the Diphen succindene Series.** K. BRAND and K. TREBING (*Ber.*, 1923, **56**, [B], 2545—2547; cf. preceding abstract).—Diphen succindadiene is transformed by magnesium  $\alpha$ -naphthyl bromide in the presence of ether and benzene into 9:12-di- $\alpha$ -naphthyldiphen succindan-9:12-diol, colourless needles, m. p.  $244^{\circ}$ , which is converted by a boiling mixture of acetic and formic acids



into naphthalene and diphensuccindan-9:12-dione. 9:12-Di- $\beta$ -naphthylidiphensuccindan-9:12-diol, colourless needles, m. p. 286—287°, is transformed under similar conditions into 9:12-di- $\beta$ -naphthyl- $\Delta^{9,11}$ -diphensuccindadiene, reddish-brown leaflets, m. p. 266°. The hydrocarbon is oxidised by chromic acid to o- $\beta$ -naphthoylbenzoic acid, m. p. 168° (cf. Pickles and Weizmann, P., 1905, 20, 201), which is converted by concentrated sulphuric acid into 1:2-naphthanthraquinone, m. p. 168°; it is hydrogenated in the presence of alcohol and palladised charcoal to 9:12-di- $\beta$ -naphthylidiphensuccindane, slender, colourless needles, m. p. 225°.

Magnesium 2-methoxy- $\alpha$ -naphthyl iodide appears to react normally with diphensuccindandione, but the action of water on the product gives naphthyl methyl ether and diphensuccindandione.

H. W.

**Some Colouring Matters Derived from Bidiphenylen-ethylene.** F. KEHRMANN and C. BUFFAT (*Helv. Chim. Acta*, 1923, 6, 955—956).—The red hydrocarbon bidiphenylen-ethylene (A., 1896, i, 565) is readily sulphonated by concentrated sulphuric acid, forming a soluble sulphonic acid having an intense orange colour which dyes wool and silk in the same way as other acid dyes. The hydrocarbon can be nitrated in glacial acetic acid; two dinitro-derivatives were obtained, one forming deep red granules, sparingly soluble in alcohol, m. p. 171°, the other crystallising in orange-red prisms, more soluble in alcohol, m. p. 170°. The nitro-compounds can be reduced to amino-derivatives which form orange-coloured hydrochlorides.

E. H. R.

**2-Nitro- and 2-Amino-cymene.** W. A. DEMONBREUN and R. E. KREMERS (*J. Amer. Pharm. Assoc.*, 1923, 12, 296—300).—For the nitration of cymene, 67 g. is added to an equal weight of sulphuric acid, cooled with ice, and the mixture is stirred until 0° is reached. A cooled mixture of 105 g. of sulphuric acid and 50 g. of nitric acid is then added, drop by drop, with constant stirring, common salt being occasionally mixed with the ice. About six hours are required for the reaction. After being stirred for a further thirty minutes, the mixture is poured into an equal volume of cold water. The oily layer is washed with water and fractionally distilled, the heavier fraction having b. p. 130—135°/14 mm.,  $d^{23}_4$  1.0355,  $n^{23}_D$  1.5290. Reduction by tin or iron and hydrochloric acid gave 2-aminocymene,  $d^{23}_4$  0.9448,  $n^{23}_D$  1.5395 (hydrochloride, m. p. 206—207°; acetyl derivative, m. p. 70—71°).

CHEMICAL ABSTRACTS.

**$\beta$ -Naphthylamine-5:7- and -6:8-disulphonic Acids.** H. E. FIERZ-DAVID and M. BRAUNSCHWEIG (*Helv. Chim. Acta*, 1923, 6, 1146—1151).—A number of salts of these two acids were prepared in the hope of discovering some method of separating the two acids superior to that previously described (Fierz, "Farbenchemie," 2nd ed., p. 43). Although a separation can be effected through the magnesium salts, it offers no advantages.

$\beta$ -Naphthylamine-5:7-disulphonic acid crystallises with 5H<sub>2</sub>O



in well-formed rhombic needles (from hydrochloric acid) or glistening leaflets (from water). It loses its water completely at  $150^{\circ}$ . The following salts are described, with solubilities at  $20^{\circ}$  in g. per 100 g. of saturated solution:  $\text{Na}_2+6\text{H}_2\text{O}$ , felted needles which melt in the hand, 72.2;  $\text{NaH}+4\text{H}_2\text{O}$ , rhombic needles, 7.91;  $\text{K}_2+2\text{H}_2\text{O}$ , rosettes of rhombic needles, 63.9;  $\text{KH}+4\text{H}_2\text{O}$ , short, rhombic prisms, 2.58;  $(\text{NH}_4)_2+3\text{H}_2\text{O}$ , rhombic prisms, 68.1;  $\text{Ca}+4\text{H}_2\text{O}$ , monoclinic prisms, 40.2;  $\text{Sr}+4\text{H}_2\text{O}$ , 29.48,  $\text{Ba}+3\text{H}_2\text{O}$ , 22.7; the following all crystallise in well-formed rhombic needles or prisms:  $\text{Mg}+8\text{H}_2\text{O}$ , 21.09;  $\text{Zn}+8\text{H}_2\text{O}$ , 39.4;  $\text{Co}+8\text{H}_2\text{O}$ , 29.4;  $\text{Pb}+6\text{H}_2\text{O}$ , 48.1;  $\text{Ni}+6\text{H}_2\text{O}$ , 35.5. The solubility of the free acid is 22.97.

$\beta$ -Naphthylamine-6:8-disulphonic acid crystallises with  $4\text{H}_2\text{O}$  in small, monoclinic needles, solubility 9.24 g. per 100 g. of saturated solution at  $20^{\circ}$ . The following salts are described:  $\text{Na}_2+3\text{H}_2\text{O}$ , well-formed prisms, 59.04;  $\text{NaH}+4\text{H}_2\text{O}$ , long, thin needles, 7.46;  $\text{K}_2+2\text{H}_2\text{O}$ , lustrous prisms, 51.6;  $\text{KH}+2\text{H}_2\text{O}$ , long, rhombic prisms, 2.47;  $(\text{NH}_4)_2+2\text{H}_2\text{O}$ , monoclinic, 70.35; the alkaline-earth metal salts are isomorphous, monoclinic, with  $3\text{H}_2\text{O}$ ,  $\text{Ca}$ , 29.1,  $\text{Sr}$ , 20.8,  $\text{Ba}$ , 12.0;  $\text{Mg}+8\text{H}_2\text{O}$ , 8.7,  $\text{Zn}+8\text{H}_2\text{O}$ , 34.5;  $\text{Co}+8\text{H}_2\text{O}$ , 27.96;  $\text{Ni}+6\text{H}_2\text{O}$ , monoclinic prisms, 33.2;  $\text{Pb}+\text{H}_2\text{O}$ , 44.5, aggregates of small needles.

The preparation of the two acids from  $\beta$ -naphthylamine is described in detail.

E. H. R.

**Chloroamidines.** PAUL ROBIN (*Compt. rend.*, 1923, 177, 1304—1306).—Alkali hypochlorites convert amidine hydrochlorides, in aqueous solution, into chloroamidines (cf. Bougault and Robin, A., 1920, i, 568). Thus, benzamidine affords *benzochloroamidine*,  $\text{NH}_2\cdot\text{CPh}\cdot\text{NCl}$  or  $\text{NHCl}\cdot\text{CPh}\cdot\text{NH}$ , colourless, odourless needles, not affected by heating up to  $100^{\circ}$ . It may be crystallised from alcohol, but when heated with this solvent at  $100^{\circ}$ , in a closed tube, affords benzamidine and a volatile chloro-compound. With boiling dilute acids, benzochloroamidine gives chlorine, whilst with aqueous potassium iodide solution, one mol. of the amidine gives 2 atoms of iodine. When heated with water at  $100^{\circ}$  in a closed tube, the chloroamidine affords a mixture of cyaphenin,  $(\text{Ph}\cdot\text{CN})_3$ , benzonitrile, benzoic acid, ammonia, and benzamidine. Benzochloroamidine does not react with antipyrine, but is converted by acetic anhydride, in boiling benzene solution, into an *acetyl* derivative, m. p.  $122^{\circ}$ , in which the chlorine is still reactive towards potassium iodide.

*p*-Tolylchloroamidine and benzylchloroamidine,  $\text{CH}_2\text{Ph}\cdot\text{CN}_2\text{H}_2\text{Cl}$ , melt, respectively, at  $96^{\circ}$  and  $72^{\circ}$ .

E. E. T.

**Preparation of Amidines.** CHEMISCHE FABRIKEN VORM. WEILER TER MEER (D.R.-P. 372842; from *Chem. Zentr.*, 1923, [iv], 661).—Acetanilide, its derivatives, homologues, or analogous compounds, with the exception of arylglycine anilides, are treated with carbonyl chloride in the presence or absence of condensing reagents. The following reaction is typical:  $2\text{NHPh}\cdot\text{COMe}+\text{COCl}_2=\text{HCl}+\text{CO}_2+\text{COMe}\cdot\text{Cl}+\text{NHPh}\cdot\text{CMe}\cdot\text{NPh}$ . The reaction proceeds smoothly

without the formation of by-products. Acetanilide and carbonyl chloride give, as above, diphenylacetamidine hydrochloride. *p*-Acetotoluidide and carbonyl chloride yield *pp'*-ditolylacetamidine, m. p. 122°. *oo'*-Ditolylacetamidine forms flat needles, m. p. 65°. Acetyl compounds of the amines of alkoxyated or halogenated hydrocarbons, or of polynuclear or condensed hydrocarbons may also be used.  $\alpha$ -Dinaphthylacetamidine is crystalline and has m. p. 137°. G. W. R.

**Basic Derivatives of *p*-Aminophenyl Ethyl Ether.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 96389, 96606, and 96607; from *Chem. Zentr.*, 1923, iv, 662—663).—*p*-Acetaminophenol halogenethyl ethers  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{X}$  or their derivatives alkylated in the nucleus, obtained by acting on alkali acetamidophenoxides with ethylene dihalogenides, are allowed to react with secondary aliphatic amines. *p*-Acetamidophenyl  $\beta$ -bromoethyl ether, crystals, m. p. 130°, gives with diethylamine *p*-acetamidophenyl  $\beta$ -diethylaminoethyl ether; the hydrochloride forms small needles, m. p. above 200°. *p*-Acetamidophenyl  $\beta$ -bromoethyl ether gives with piperidine *p*-acetamidophenyl 2-piperidylethyl ether; the hydrochloride forms crystals, m. p. 252°. From 4-acetamido-2-allylphenyl  $\beta$ -chloroethyl ether, crystals, m. p. 60°, and diethylamine, 4-acetamido-2-allylphenyl  $\beta$ -diethylaminoethyl ether, m. p. 70°, is obtained; its hydrochloride is crystalline and has m. p. 149°. G. W. R.

**Methyl Sulphites of Secondary Aromatic Aliphatic Amines.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Aust. Pat. 93319; from *Chem. Zentr.*, 1923, iv, 802; cf. Bockmühl and Windisch, A., 1923, i, 29).—The compounds obtained by earlier patents may also be prepared by *N*-alkylation of the methyl sulphites obtained from primary aromatic amines and a hydrogen sulphite compound of formaldehyde. Examples are given of the preparation of sodium 1-phenyl-2:3-dimethylpyrazole-5-one-4-ethylaminomethyl sulphite and sodium *N*-ethylphenetidine methyl sulphite. G. W. R.

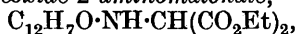
**[Alkali Metal as a Reagent for Weakened Valencies in Organic Compounds.]** K. ZIEGLER and F. THIELMANN (*Ber.*, 1923, 56, [B], 2453).—In their communication on this subject (A., 1923, i, 921), the authors have overlooked the fact that a portion of the work has been described previously by Marcus (*Diss.*, Jena, 1914). H. W.

**The Preparation of  $\beta\beta'$ -Dinaphthyl Ether.** V. M. RODIONOV and S. J. MANZOV (*J. Soc. Chem. Ind.*, 1923, 42, 509—510T).—During the distillation of crude naphthol on the technical scale, the formation of a large proportion of  $\beta\beta'$ -dinaphthyl ether was observed. The cause of this was traced to the presence of inorganic salts, particularly acid salts, during the distillation. When  $\beta$ -naphthol is heated at 200—210° for about ten hours, it is converted entirely into  $\beta\beta'$ -dinaphthyl ether. E. H. R.

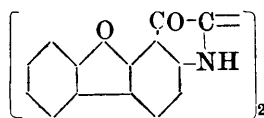
**Substitution Products of Diphenylene Oxide. II.** W. BORSCHÉ and B. SCHACKE (*Ber.*, 1923, **56**, [B], 2498—2508; cf. Borsche and Bothe, A., 1908, i, 528).—An extension of previous work. In consequence of the communication of Mayer and Krieger (A., 1922, i, 746), the compound described previously (*loc. cit.*) as 3-nitrodiphenylene oxide is now considered to be the 2-nitro-derivative.

The nitration of diphenylene oxide in glacial acetic acid solution gives a mixture of 2-nitrodiphenylene oxide and 3(?)*-nitrodiphenylene oxide*, small, yellow needles, m. p. about 110°. The former compound is reduced by sodium and methyl alcohol to 2 : 2'-azoxydiphenylene oxide, pale yellow, matted needles, m. p. 259—260°, and by sodium and boiling amyl alcohol to 2 : 2'-azodiphenylene oxide, m. p. 282°. It is converted by concentrated sulphuric acid into 2-nitrodiphenyleneoxidesulphonic acid,  $\text{NO}_2 \cdot \text{C}_{12}\text{H}_6\text{O} \cdot \text{SO}_3\text{H}$ , which is isolated in the form of its sodium salt, pale yellow needles. The salt is converted by phosphorus pentachloride into 2-nitrodiphenyleneoxidesulphonyl chloride, m. p. about 200° (decomp.), which is transformed by ammonia into the corresponding amide, an amorphous, white powder, m. p. (indefinite) 265° (decomp.). The action of tin and concentrated hydrochloric acid on sodium 2-nitrodiphenyleneoxide-sulphonate yields 2-aminodiphenyleneoxidesulphonic acid, the barium salt of which, colourless leaflets, is described.

2-Aminodiphenylene oxide is converted by ethyl bromomalonate into ethyl diphenyleneoxide-2-aminomalonate,

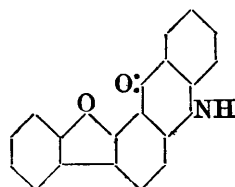


pale yellow needles, m. p. 100°; it is transformed when heated at 240° into ethyl diphenyleneoxideindoxylate,



m. p. 191°, which when fused with alkali hydroxide yields "*bisdiphenyleneoxide-indigo*," a bluish-black powder which remains unchanged below 350°; the annexed formula is assigned to it, but the possibility of the formation of the new ring in the 2 : 3-position is not excluded.

2-Diphenyleneoxide-2'-aminobenzoic acid,  $\text{C}_{12}\text{H}_7\text{O} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , pale yellow needles, m. p. 227°, is obtained by heating *o*-chlorobenzoic acid, 2-aminodiphenylene oxide hydrochloride, potassium carbonate, and copper bronze in the presence of amyl alcohol at 140—150°. It passes when heated with zinc chloride at 240° into 2-anilinodiphenylene oxide,  $\text{C}_{12}\text{H}_7\text{O} \cdot \text{NHPh}$ , colourless leaflets, m. p. 132°; the acid is transformed by the successive action of phosphorus pentachloride and aluminium chloride



into phenylene oxideacridone,  $\text{C}_{19}\text{H}_{11}\text{O}_2\text{N}$ , greenish-yellow leaflets, m. p. above 350° (annexed formula).

2-Diacetamidodiphenylene oxide is converted by nitric acid in glacial acetic acid solution into 3(?)*-nitro-2-diacetamidodiphenylene oxide*, yellow leaflets, m. p. 196—197°, which is hydrolysed by alcohol and fuming hydrochloric acid into 3(?).

*nitro-2-aminodiphenylene oxide*, orange-red needles, m. p. 222°. 2:3(?) *Diaminodiphenylene oxide* forms colourless crystals, m. p. 166° (*hydrochloride*, colourless leaflets); it is characterised as an orthodiamine by its ability to condense with benzil to give the quinoxaline derivative,  $C_{12}H_6O \begin{smallmatrix} & N:CPh \\ & | \\ N:CPh \end{smallmatrix}$ , greenish-yellow needles, m. p. 179°, and with phenanthraquinone to give the compound,  $C_{12}H_6O \begin{smallmatrix} & N:C \cdot C_6H_4 \\ & | \\ N:C \cdot C_6H_4 \end{smallmatrix}$ , yellow needles, m. p. 297°.

The action of aluminium chloride on diphenylene oxide and acetyl chloride in the presence of carbon disulphide leads to the formation of 3-acetyldiphenylene oxide and 3:6(?) *diacetyldiphenylene oxide*, colourless needles, m. p. 140°. *Nitro-3-acetyldiphenylene oxide*, a brown, crystalline powder, m. p. 105°, 3-ethyl-diphenylene oxide, a colourless liquid, b. p. 310°/atmospheric pressure, and *nitro-3-ethyldiphenylene oxide*, yellow needles, m. p. 96°, b. p. 218—226°/15 mm., are described. Diacetyldiphenylene oxide yields a *dioxime*,  $C_{16}H_{14}O_3N_2$ , a colourless, sandy powder, m. p. 250° (decomp.), which is isomerised by phosphorus pentachloride in the presence of ether into *diacetylaminodiphenylene oxide*, colourless leaflets, m. p. 258°, from which *diaminodiphenylene oxide*, slender, colourless needles, m. p. 213°, is obtained. *Diethyldiphenylene oxide*, a colourless, odourless liquid, b. p. 197—199°/20 mm., 334°/750 mm., is prepared by the action of amalgamated zinc and hydrochloric acid on diacetyldiphenylene oxide.

Diphenylene oxide is converted by phthalic anhydride in the presence of nitrobenzene and aluminium chloride into diphenylene-oxidephthalonic acid, m. p. 203—204°, which passes under the influence of anhydrous zinc chloride at 260° into *phthaloyldiphenylene oxide*,  $C_{20}H_{10}O_3$ , greenish-yellow needles, m. p. 258°. The latter substance is reduced by zinc dust and aqueous ammonia to a mixture of *phenyleneoxidedihydroanthranol*,  $C_{20}H_{14}O_2$ , a pale yellow powder, m. p. 169°, and a compound,  $C_{20}H_{12}O$ , yellow leaflets with a green fluorescence, m. p. 311°, the constitution of which has not been elucidated. *Diphthaloyldiphenylene oxide*,  $C_{28}H_{12}O_5$ , crystallises in slender, greenish-yellow needles, m. p. 295°. H. W.

**The Configuration of Cyclic 1:2-Diols.** J. BÖESEKEN (*Ber.*, 1923, 56, [B], 2409—2411).—Methods previously described (cf. Derx, A., 1922, i, 651) have been applied to the determination of the configuration of isomerides of 1-methyl-, 1-phenyl-, and 1-cyclohexyl-cyclohexane-1:2-diols. The 1-methylcyclohexane-1:2-diol, m. p. 67°, obtained by oxidation of 1-methyl- $\Delta^1$ -cyclohexene, is the *cis*-compound (not *trans*, see Nametkin and Jarzev, A., 1923, i, 1081). With potassium hydroxide and boric acid, it forms a crystalline salt,  $C_6H_9Me \cdot O_2 \cdot BOK \cdot 4H_2O$ . The isomeric compound, m. p. 84°, has therefore the *trans*-configuration. *cis*-1-Phenylcyclohexane-1:2-diol is the product, m. p. 95°, obtained by oxidation of 1-phenyl- $\Delta^1$ -cyclohexene with permanganate. It is also the principal product of hydrolysis of 1-phenylcyclohexene 1:2-oxide, but *trans*-1-phenylcyclohexane-1:2-diol is also formed in the reaction product;

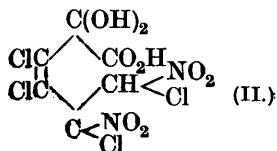
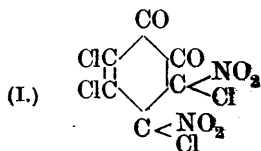
it forms short prisms, m. p.  $98.5^{\circ}$ . It is probably the primary product, but under the experimental conditions isomerises into the *cis*-form (cf. Nametkin and Ivanov, A., 1923, i, 1097). *cis*-1-cyclo-Hexyleyclohexane-1:2-diol, m. p.  $122-123^{\circ}$ , is obtained by oxidation of the corresponding cyclohexene, and the *trans*-isomeride, m. p.  $142^{\circ}$ , by hydration of 1-cyclohexylcyclohexene 1:2-oxide.

E. H. R.

**Action of Nitric Acid and Nitrogen Peroxide on Tetrachloro- and Tetrabromo-pyrocatechol and the Corresponding Quinones.** T. ZINCKE (*Annalen*, 1923, 435, 145-173).—Tetrachloro-*o*-benzoquinone, when treated with nitric acid (*d* 1.4-1.51) gives, according to the concentration of the acid, one of two compounds: A,  $C_6H_4O_5Cl_4$  or B,  $C_6H_4O_8N_2Cl_4$ , which are also produced under similar conditions from tetrachloropyrocatechol. The former (A), colourless needles, m. p.  $95-96^{\circ}$ , is a trihydrate of a tri-keto-compound; when heated, it is converted into trichloro-hydroxy-*p*-benzoquinone, and, on reduction, gives trichloro-hydroxyquinol (cf. [Frl.] Weishaupt, *Dissert.*, Marburg, 1923).

Compound B forms white needles, decomposing at the m. p. ( $114-115^{\circ}$ ) to give water, carbon dioxide, oxides of nitrogen, and the compound,  $C_{10}O_2Cl_8$ , described previously (A., 1909, i, 591; 1912, i, 964). The last compound is formed intermediately on boiling an aqueous solution of B, then decomposing to give perchloroindone. Similarly, on heating a solution of B in alcohol, acetone, or acetic or concentrated sulphuric acids, the compound  $C_{10}O_2Cl_8$  is formed.

Compound B, when treated with alkali, affords a number of decomposition products, depending on the concentration of alkali, etc. Products identified include ammonia, nitrogen, carbon dioxide, and oxalic and nitrous acids. Mainly from this decomposition, and from the fact that compound B is also produced (here not accompanied by A) by treating tetrachloropyrocatechol at  $0^{\circ}$  with liquid nitrogen peroxide, the constitution II is assigned to B, the formation of this substance from tetrachloropyrocatechol proceeding through the corresponding quinone and its nitrogen peroxide additive compound I:



(One  $\text{NO}_2$ -group is probably nitro-, the other nitrite,  $\cdot\text{ONO}$ ).

A low value is obtained for the molecular weight of B when determined cryoscopically in acetic acid owing to the dissociation of the hydrate (II).

Whilst tetrachloro-*o*-benzoquinone does not afford compound (I) (but only tarry products) when treated with nitrogen peroxide,

the constitution (II) assigned to *B* falls into line with the above decomposition in presence of alkali. In this process, chloro-groups and a nitrite group are replaced by hydroxyl, oxalic acid and the compound,  $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OH})_2\cdot\text{CH}(\text{OH})_2$  resulting. Further decomposition affords *s*-dihydroxyethylene, or the isomeric glycollaldehyde, and glyoxylic acid, whence carbon dioxide and more oxalic acid are produced.

When substance *B* is treated with aniline or phenylhydrazine, red or dark-coloured *substances* result, respectively.

Tetrabromo-*o*-benzoquinone behaves unlike the chloroquinone towards nitric acid, white, insoluble *products* being formed. Tetrabromopyrocatechol is, however, converted by nitric acid into a *compound*,  $\text{C}_6\text{H}_4\text{O}_5\text{Br}_4$  (type *A*) which decomposes partly to give a *substance*,  $\text{C}_5\text{O}_2\text{Br}_4$ , m. p. 142—143°. Bromo-compounds corresponding with *B* result when tetrabromopyrocatechol is treated with nitrogen peroxide, no compound of type *A* being produced in this case.

The *bromo*-compound,  $\text{C}_6\text{H}_2\text{O}_7\text{N}_2\text{Br}_4\cdot\text{H}_2\text{O}$  (type *B*), which forms colourless needles, m. p. 113—114° (decomp.), on drying undergoes partial decomposition (the m. p. rising to 126—127°). On keeping, or on warming in solution in glacial acetic, sulphuric, or formic acids, the bromo-compound affords the substance  $\text{C}_{10}\text{O}_2\text{Br}_8$ ; on boiling in aqueous solution, it gives perbromindone; whilst with alkalis the bromo-compound decomposes in a manner similar to that observed with the corresponding chloro-compound (*B*).

When halogenated pyrocatechols are treated with mixed acid ( $\text{HNO}_3$ , 88.9%,  $\text{H}_2\text{SO}_4$ , 9.9%,  $\text{H}_2\text{O}$ , 1.2%), type *A* is produced to a greater extent than when nitric acid alone is used, owing to increased oxidation. The corresponding quinones, when treated with mixed acid, give in the case of the chloro-compound, tarry products, and in that of the bromo-compound, decomposition products of the intermediately-formed *substance*,  $\text{C}_6\text{H}_4\text{O}_5\text{Br}_4$ .

3 : 4 : 6-Trichloro-5-methyl- and 3 : 4 : 5-trichloro-6-methyl-pyrocatechol are converted into compounds of type *B* (but not of type *A*),  $\text{C}_6\text{H}_4\text{O}_8\text{N}_2\text{Cl}_3\text{Me}$ , when treated with nitric acid (*d* 1.45—1.48), or with nitrogen peroxide, indifferent results being obtained using mixed acid.

The *compound*,  $\text{C}_6\text{H}_4\text{MeO}_8\text{N}_2\text{Cl}_3$ , obtained from the 3 : 4 : 6-derivative, forms white needles, m. p. 116—117° (decomp.) (one specimen, m. p. 110—111°), crystallised from dilute hydrochloric acid. After careful drying, the m. p. rises to 126—127°, this m. p. being obtained when the substance is crystallised from nitric acid. The compound, on melting, or, better, on being heated in glacial acetic or sulphuric acid solution, is converted into the substance,  $\text{C}_{10}\text{O}_2\text{Cl}_6\text{Me}_2$  (m. p. 182°), described previously (A., 1897, i, 507). From the decomposition, in presence of alkali, of the compound  $\text{C}_6\text{H}_4\text{MeO}_8\text{N}_2\text{Cl}_3$ , the latter is given the constitution  $\text{NO}_2\cdot\text{CHCl}\cdot\text{CCl}(\text{NO}_2)\cdot\text{CMe}\cdot\text{CCl}\cdot\text{C}(\text{OH})_2\cdot\text{CO}_2\text{H}$ .

The isomeric *compound*,

$\text{NO}_2\cdot\text{CHCl}\cdot\text{CCl}(\text{NO}_2)\cdot\text{CCl}\cdot\text{CMe}\cdot\text{C}(\text{OH})_2\cdot\text{CO}_2\text{H}$ ,  
obtained from 3 : 4 : 5-trichloro-6-methylpyrocatechol, forms

needles, melting at 115—116° (or, after drying, 125—126°) to give the substance  $C_{10}O_2Cl_6Me_2$ , which is more readily obtained by heating the first compound in aqueous, acetic, or sulphuric acid solution, and is identical with a compound (m. p. 175°) previously described (A., 1897, i, 509).

The substance,  $C_{10}O_2Cl_8$ , mentioned above, which is also obtained from the nitric acid decomposition product ( $C_6HO_6N_2Cl_4Me$ ) of tetrachloro-*o*-cresol by warming with concentrated sulphuric acid, has been re-investigated. It was previously stated that it was converted by boiling methyl alcohol into the compound  $C_9Cl_6(OH) \cdot OMe$  (m. p. 138°), which is now written as  $C_{10}O_2Cl_7 \cdot OMe$  (m. p. 136—137°).

The constitution of the compound  $C_{10}O_2Br_8$  (cf. A., 1907, i, 322; 1912, i, 964) is still unsettled, but the possibility of it being a derivative of tetrahydronaphthalene is excluded. The compound, on melting at 207—208°, on heating with glacial acetic acid and sodium acetate, or on heating in nitrobenzene solution, affords perbromindone (m. p. 195—196°), the latter being converted by warm aniline into the anilide,  $C_9OBr_5 \cdot NHPh$ , scarlet leaflets, m. p. 224° (decomp.).

E. E. T.

**The Constitution of Weselsky and Benedict's Dinitroquinol Methyl Ether.** F. KEHRMANN and G. JEQUIER (*Helv. Chim. Acta*, 1923, 6, 949—951).—The constitution of this ether given by Reverdin and de Luc (A., 1911, i, 965), who concluded that it is 3:5-dinitro-4-hydroxyanisole, has been confirmed by the preparation of the isomeric ether. The silver salt of 3:5-dinitroquinol 1-acetate reacts with methyl iodide to give 2:6-dinitro-4-acetoxyanisole, small, yellow crystals, m. p. 63°, which when hydrolysed gives 2:6-dinitro-4-hydroxyanisole, yellow crystals, m. p. 149°. The dinitroquinol monoacetate used for the preparation was obtained by nitration of quinol diacetate (see following abstract).

E. H. R.

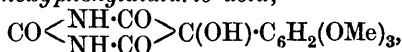
**The Action of Nitric Acid on Quinol Diacetate.** F. KEHRMANN and W. KLOPFENSTEIN (*Helv. Chim. Acta*, 1923, 6, 952—954).—Nitration of quinol diacetate with fuming nitric acid below 10° gives, not 3:5-dinitroquinol diacetate, as stated by Nietzki and Preusser (A., 1887, 574), but 3:5-dinitroquinol 1-monoacetate, yellow tablets, m. p. 94°. Acetylation of this with acetic anhydride gives 3:5-dinitroquinol diacetate, colourless needles, m. p. 134°. More careful nitration of quinol diacetate at 0° gives 3-nitroquinol 1-acetate, lemon-yellow needles, m. p. 84°. This can be acetylated to 3-nitroquinol diacetate, colourless needles, m. p. 80°. It is evident that nitration of quinol diacetate cannot proceed without elimination of one acetyl group.

E. H. R.

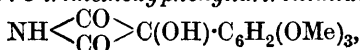
**Some Condensation Products of Hydroxyquinol Trimethyl Ether.** T. SZÉKI (*Ber.*, 1923, 56, [B], 2464—2468).—Hydroxyquinol trimethyl ether condenses with acetone in glacial acetic acid solution in the presence of concentrated sulphuric acid to give

2 : 4 : 5 : 2' : 4' : 5'-*hexamethoxydiphenylisophorone* [1 : 5 : 5-trimethyl-3 : 3-bis-2' : 4' : 5'-trimethoxyphenyl- $\Delta^1$ -cyclohexene] (annexed formula) colourless needles, m. p. 207°, which is converted by bromine in glacial acetic acid solution into the bromo-derivative,  $C_{27}H_{36}O_6Br_2$ , colourless, lustrous crystals, m. p. 119°; as by-product of the condensation, 2 : 4 : 5-trimethoxybenzenesulphonic acid, colourless needles, m. p. 115°, is obtained, the sodium salt of which is described.

The action of hydrogen chloride on a solution of 2 : 4 : 5-trimethoxybenzene and alloxan in alcohol leads to the production of 2 : 4 : 5-trimethoxyphenyldialuric acid,



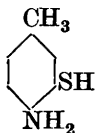
small, colourless needles, m. p. 248—249° (decomp.). It is converted by acetic anhydride and sulphuric acid monohydrate into the corresponding *acetate*, decomp. 270—292°, and is decomposed by boiling *N/5* sodium hydroxide solution into ammonia, carbon dioxide, and 2 : 4 : 5-trimethoxyphenyltartronimide,



colourless, microscopic leaflets, m. p. 220—221°. 2 : 4 : 5-Tri-methoxyphenacyldialuric acid, slender, colourless crystals, m. p. 245° (decomp.) after darkening at 220°, is prepared from 2 : 4 : 5-trimethoxyacetophenone and alloxan.

Benzhydrol is converted by 2 : 4 : 5-trimethoxybenzene in alcoholic solution in the presence of hydrogen chloride into 2 : 4 : 5-trimethoxytriphenylmethane,  $C_6H_2(OMe)_3 \cdot CHPh_2$ , colourless needles, m. p. 117°. In a similar manner, 2 : 4 : 5'-tetramethoxydiphenylcarbinol and 2 : 4 : 5-trimethoxybenzene yield 2 : 4 : 5 : 2' : 4' : 5' : 4'-heptamethoxytriphenylmethane, slender, colourless needles, m. p. 162°, whereas 2 : 4 : 5-trimethoxyphenyl- $\alpha$ -naphthylcarbinol and 2 : 4 : 5-trimethoxybenzene give 2 : 4 : 5 : 2' : 4' : 5'-hexamethoxydiphenyl- $\alpha$ -naphthylmethane, slender, colourless needles, m. p. 198°. H. W.

**Action of Sulphur on *p*-Toluidine in the Presence of Litharge.** Thio-*p*-toluidine, its Constitution and some of its Derivatives. M. T. BOGERT and M. R. MANDELBAUM (*J. Amer. Chem. Soc.*, 1923, **45**, 3045—3055).—The formation of thio-*p*-toluidine by heating *p*-toluidine with sulphur at 140° in the presence of litharge takes place through the mercaptan (annexed formula) which reacts with a nuclear hydrogen atom of unchanged *p*-toluidine. A small proportion of the mercaptan was oxidised to dithio-*p*-toluidine, m. p. 88.5°, acetyl derivative, m. p. 213°. The sulphide produced by de-amination of thio-*p*-toluidine was identical with di-*m*-tolyl sulphide synthesised from *m*-iodotoluene and sodium *m*-tolyl sulphide. The respective sulphones and a mixture of them melted at 94°. In the absence of litharge and





at 180—220°, the intermediate mercaptan reacted with the methyl group of unchanged *p*-toluidine to give dehydrothio-*p*-toluidine. The authors failed to convert thio-*p*-toluidine into dehydrothio-*p*-toluidine. The former gave a *diacetyl* derivative, m. p. 165° (corr.), which was oxidised to *bis*-2-acetamido-5-carboxyphenylsulphone, m. p. above 360°. The latter was de-acetylated and the resulting *bis*-2-amino-5-carboxyphenylsulphone melted above 360° (decomp.); the *methyl* ester forms thin, square, colourless tablets, m. p. 234° (corr.), the *ethyl* ester forms yellow, transparent prisms, m. p. 206° (corr.).  
F. B.

**Formation of Liquid Crystals of Mixtures of Cholesterol and Cetyl Alcohol.** A. MŁODZIEJOWSKI (*Z. Physik*, 1923, 20, 317—342).—The conditions necessary for the production of liquid crystals of mixtures of cholesterol and cetyl alcohol and the approximate character of the equilibrium diagram relating to the phases of mixtures of these substances have been determined. Cholesterol exists in two solid enantiomorphic modifications, the transformation temperature associated with which is about 43°. Liquid cetyl alcohol on cooling deposits needle-shaped crystals at about 50°. Crystallisation is accompanied by the separation of an amorphous solid phase characterised by the presence of lenticular masses. The transformation from liquid to solid is reversible. Liquid crystals of mixtures of cholesterol and cetyl alcohol may be either homogeneous or may exhibit a spherulitic or myelin structure characterised by the presence of rod-like, biscuit- or worm-shaped masses in a state of agitation. Of these two varieties of liquid crystals, the homogeneous variety is the more stable. Cetyl alcohol is practically insoluble in this modification. The liquid crystals are probably composed of equal molecular proportions of the two components, and on heating are reversibly converted into solid crystals provided the concentrations of the components are within certain limits. They form an eutectic mixture with cetyl alcohol.  
J. S. G. T.

**Preparation of Nucleus-substituted Hydroxyl Derivatives of  $\beta$ -Amino- $\alpha$ -hydroxy- $\alpha$ -arylethanes and  $\beta$ -Amino- $\alpha$ -bisaryl-ethanes.** O. HINSBERG (D.R.-P. 373286; from *Chem. Zentr.*, 1923, iv, 662; cf. A., 1923, i, 923).—Phenols, naphthols, or their substitution products are allowed to react with aminoacetal or its *N*-mono- or di-alkylated derivatives in the presence of hydrochloric acid under pressure. For example, with equimolecular proportions of phenol and aminoacetal, in the presence of hydrochloric acid under pressure at 100°, the following reaction takes place:  $\text{PhOH} + \text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2 + \text{HCl} + \text{H}_2\text{O} =$   
 $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{NH}_2 \cdot \text{HCl} + 2\text{EtOH}.$

$\alpha$ -*p*-Hydroxyphenyl- $\beta$ -aminoethanol thereby obtained has m. p. above 250°; the *hydrochloride* has m. p. 172° (decomp.). Phenol (2 mols.) and aminoacetal (1 mol.) give  $\beta$ -amino- $\alpha$ -bis(*p*-hydroxyphenyl)ethane, which has m. p. 105°. Pyrocatechol and methylaminoacetal yield *o*-dihydroxyphenylethanolmethylamine (adrenaline). *p*-Cresol and aminoacetal give  $\beta$ -amino- $\alpha$ -hydroxy- $\alpha$ -1-

*hydroxy-4-methylphenylethane*, an unstable compound which gives a *hydrochloride* with m. p.  $120^{\circ}$  (decomp.). G. W. R.

**Naphthenic Acid. III. Naphthenic Acids from Kubiki Kerosene Distillate.** Y. TANAKA and S. NAGAI (*J. Chem. Ind. Japan*, 1923, **26**, 1115—1123; cf. *ibid.*, 1923, **26**, 309; A., 1923, i, 464).—A crude mixture of acid substances was obtained by acidifying a waste lye obtained in the refining of kerosene distillate from crude oil produced at Kubiki. Crude naphthenic acids ( $d_4^{15}$  0.9647,  $n_D^{15}$  1.4790, and acid value 202.8) were then obtained by three methods. About 86% of the crude acids distilled at  $140\text{--}210^{\circ}/8.9\text{--}9$  mm. The lower distillates contained some phenolic compounds, and the fractions above  $200^{\circ}$  showed lower specific gravities than the preceding ones. The acid was converted into methyl esters,  $d_4^{15}$  0.9368,  $n_D^{15}$  1.4663, about 83% of which distilled at  $120\text{--}180^{\circ}/8.9\text{--}9$  mm., and the fractions above  $170^{\circ}$  gave decreasing specific gravities. A mixture of pure naphthenic acids ( $d_4^{15}$  0.9587,  $n_D^{15}$  1.4707, and acid value 244.5) was obtained by saponifying the mixed esters, about 90% of which distilled at  $150\text{--}210^{\circ}/8.9\text{--}9$  mm. The higher fractions above  $200^{\circ}$  showed again lower specific gravities than the preceding ones. The mixed naphthenic acids and their distillates of Kubiki origin have much smaller specific gravities than those of Kurokawa origin, which indicates the presence of isomerides having low specific gravities in the former. K. K.

**Normal Ammonium Salts of some Organic Acids and their Substitution Derivatives. VIII.** L. McMASTER and P. K. PRATTE (*J. Amer. Chem. Soc.*, 1923, **45**, 2999—3001).—A description of normal ammonium salts of organic acids prepared by the method previously described (A., 1918, i, 263). The solubilities of the normal ammonium salts of the following acids are expressed in g. of salt per hundred g. of water, methyl alcohol, and ethyl alcohol in the order named. Phenoxyacetic acid 13.03, 3.97, 0.44, *p*-nitrophenylacetic acid 7.41, 15.14, 1.82, *o*-iodobenzoic acid 67.11, 184.10, 63.37, *o*-methoxybenzoic acid 38.25, 17.85, 4.82, 2 : 4-dinitrobenzoic acid 62.70, 21.39, 3.85, 5-nitrosalicylic acid 4.43, 4.41, 1.96, naphthalene-1-sulphonic acid 45.91, 34.45, 9.22, naphthalene-2-sulphonic acid 11.71, 8.33, 2.53, 2 : 5-dichlorobenzenesulphonic acid, 11.30, 20.15, 2.59, 6-chloro-3-nitrobenzenesulphonic acid 4.72, 2.76, 0.96. F. B.

**3 : 5-Dinitrobenzoates of Phenols.** R. C. BROWN and R. E. KREMERS (*J. Amer. Pharm. Assoc.*, 1922, **11**, 607—608).—3 : 5-Dinitrobenzoic esters of phenol (m. p.  $145\text{--}146^{\circ}$ ), *o*-cresol ( $133\text{--}134^{\circ}$ ), *m*-cresol ( $160\text{--}162^{\circ}$ ), *p*-cresol ( $180\text{--}182^{\circ}$ ), guaiacol ( $138\text{--}139^{\circ}$ ), carvacrol ( $76\text{--}77^{\circ}$ ), and thymol ( $102\text{--}103^{\circ}$ ) were prepared as a means of identification of the phenols.

CHEMICAL ABSTRACTS.

**Proteinogenous Amino-alcohols and Cholines. III.** P. KARRER, E. HORLACHER, F. LOCHER, and M. GIESLER (*Helv. Chim. Acta*, 1923, **6**, 905—919; cf. A., 1922, i, 813).—*N*-Dimethyl-leucinol

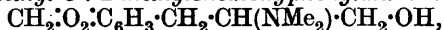
[ $\beta$ -dimethylaminoisohexylalcohol] (cf. A., 1921, i, 228) condenses with *p*-nitrobenzoyl chloride in chloroform solution to give *p*-nitrobenzoyl-*N*-dimethyl-leucinol. This can be reduced to *p*-aminobenzoyl-*N*-dimethyl-leucinol, which, in the form of its hydrochloride, is a very powerful local anæsthetic. The corresponding *N*-diethyl, *N*-dipropyl, and *N*-pentamethylene [piperidino] compounds are likewise powerful local anæsthetics. Of the four, the *N*-diethyl compound is the most powerful, being eight times as active as novocaine and at the same time less poisonous than cocaine.

*p*-Nitrobenzoyl-*N*-dimethyl-leucinol hydrochloride,



forms yellow needles, m. p.  $149.5^\circ$ . It is reduced by hydrogen in the presence of platinum black to *p*-aminobenzoyl-*N*-dimethyl-leucinol hydrochloride, bright yellow needles, m. p.  $196^\circ$ . *N*-Diethyl-leucine ethyl ester is prepared by condensing racemic  $\alpha$ -bromoisohexoic acid with diethylamine and esterifying; it forms a pale yellow oil, b. p.  $204\text{--}208^\circ/720$  mm. It is reduced by sodium and alcohol to *N*-diethyl-leucinol, a colourless oil, b. p.  $208\text{--}211^\circ$ . *p*-Nitrobenzoyl-*N*-diethyl-leucinol hydrochloride forms pale yellow needles, m. p. about  $163^\circ$  (depending on the rate of heating). *p*-Aminobenzoyl-*N*-diethyl-leucinol hydrochloride forms white leaflets, m. p.  $191^\circ$ . *N*-Pentamethyleneleucine ethyl ester [ethyl  $\alpha$ -piperidinoisohexoate], from  $\alpha$ -bromoisohexoic acid and piperidine, forms an oil, b. p.  $248\text{--}255^\circ/726$  mm.; by reduction, it gives *N*-pentamethyleneleucinol [ $\beta$ -piperidinoisohexyl alcohol], b. p.  $250\text{--}252^\circ$ . The *p*-nitrobenzoate hydrochloride crystallises in nodular aggregates of thin prisms, m. p.  $156^\circ$ , and the *p*-aminobenzoate hydrochloride crystallises similarly.

The synthesis of 3:4-methylenedihydroxyphenylalaninecholine iodide was accomplished as follows. Piperonyl bromide was obtained by the action of hydrogen bromide on piperonyl alcohol; it crystallises in needles, and does not form a compound with magnesium in ether solution. It condenses with ethyl malonate, by means of sodium in alcoholic solution, forming ethyl piperonylmalonate,  $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2$ , a yellow, viscous oil, b. p.  $200\text{--}220^\circ/15$  mm., which when hydrolysed gives piperonylmalonic acid, m. p.  $156^\circ$ . This was brominated to bromopiperonylmalonic acid,  $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CB}(\text{CO}_2\text{Et})_2$ , m. p.  $147\text{--}148^\circ$  (decomp.), which when heated at  $120\text{--}130^\circ$  loses carbon dioxide, forming  $\alpha$ -bromopiperonylacetic acid. The latter was not isolated, but was heated directly with dimethylamine at  $100^\circ$ ; the *N*-dimethyl-3:4-methylenedioxyphenylalanine formed was not isolated but treated with alcohol and hydrochloric acid, forming the ethyl ester, a viscous, yellow oil, b. p.  $200^\circ/14$  mm. This was reduced with sodium and alcohol forming *N*-dimethyl-3:4-methylenedioxyphenylalaninol,

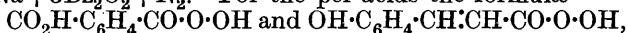


b. p.  $180^\circ/14$  mm.; the hydrochloride crystallises in white leaflets, m. p.  $165^\circ$ . When the alaninol is treated with excess of methyl iodide in alcohol solution, 3:4-methylenedioxyphenylalaninecholine iodide [ $\beta$ -dimethylamino- $\gamma$ -piperonylpropyl alcohol methiodide], m. p.  $184^\circ$ , is formed. The following palmitic and stearic

acid esters of proteinogenous cholines are described: *p-methoxy-phenylalanine methiodide stearate*, bunches of needles, sinters from 98°, m. p. 195°; the corresponding *palmitate*, similar crystals, m. p. 138—141°; *alanine methiodide stearate*, silky leaflets, m. p. 210—212°; *palmitate*, white needles, m. p. 203—210°; *alanine methochloride stearate*, hygroscopic needles, m. p. 202—205°, and *palmitate*, m. p. 202—205°.

E. H. R.

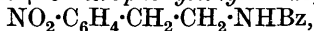
**Effect of Silver Nitrate and Alkali Nitrates on Aromatic Anhydrides.** C. V. GHEORGHIU (*Ann. Sci. Univ. Jassy*, 1923, ii, 308—309; from *Chem. Zentr.*, 1923, iii, 1155).—Benzoic anhydride when heated with silver nitrate explodes with evolution of gas, development of the odour of nitrobenzene, and formation of silver. Phthalic anhydride and coumarin behave in a similar way. The alkali nitrates can also act like silver nitrate. The author supposes that benzoyl peroxide or perbenzoic acid, the salts of which are explosive, may be formed, e.g.,  $4\text{Bz}_2\text{O} + 2\text{NaNO}_3 = 2\text{BzONa} + 3\text{Bz}_2\text{O}_2 + \text{N}_2$ . For the per-acids the formulæ



respectively, are given. Nitrobenzene is probably formed by nitration of benzoyl peroxide.

G. W. R.

**o-Nitrophenylpropionic Acid.** A. JAENISCH (*Ber.*, 1923, 56, [B], 2448—2450).—An improved method is described for the conversion of o-nitrobenzylmalonic ester into β-o-nitrophenylpropionic acid, m. p. 115°; the *silver, lead, copper, mercury, barium, calcium* (+2H<sub>2</sub>O), and *zinc* (+2H<sub>2</sub>O) salts are described. The *methyl ester* is a liquid, b. p. 171—172°/12 mm. β-o-Nitrophenylpropionyl chloride, needles, m. p. 43° (prepared from the acid and phosphorus pentachloride) is transformed by ammonia into the corresponding *amide*, colourless plates and needles, m. p. 121—122°, which is converted by Hofmann's method into the *bromoamide*, C<sub>8</sub>H<sub>5</sub>O<sub>3</sub>N<sub>2</sub>Br, yellow needles, m. p. 136—137°, and thence into β-o-nitrophenylethylamine, NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CH<sub>2</sub>·NH<sub>2</sub>, a liquid, b. p. 147°/13 mm. (*hydrochloride*, plates, m. p. 174·5°; *picrate*, m. p. 148·5°). Benzo-β-o-nitrophenylethylamide,



crystallises in stellar aggregates, m. p. 98°; it is reduced by phosphorus and hydriodic acid to benzo-β-o-aminophenylethylamide, leaflets, m. p. 135° (the *hydriodide* is described). β-o-Nitrophenylethylphthalimide, NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CH<sub>2</sub>·N:C<sub>8</sub>H<sub>4</sub>O<sub>2</sub>, needles, m. p. 120—121°, β-o-aminophenylethylphthalimide, needles, m. p. 163°, β-o-nitrophenylethylsuccinimide, needles, m. p. 116°, and β-o-aminophenylethylsuccinimide, needles, m. p. 141°, are described. Reduction of β-o-nitrophenylethylamine by phosphorus and hydriodic acid yields β-o-aminophenylethylamine [*di-hydroiodide*, yellow needles and leaflets, m. p. (indefinite) 260°; *dihydrochloride*, softening at 184°; *picrate*, m. p. 142—143°; *benzoyl derivative*, m. p. 139—140°].

ω-o-Nitrobenzylacetophenone, stellar aggregates, m. p. 68—69°, prepared from o-nitrobenzylacetyl chloride, benzene, and aluminium chloride is reduced by phosphorus and hydriodic acid to 2-phenyl-

quinoline, m. p.  $81^{\circ}$ .  $\alpha$ -Keto- $\gamma$ -o-nitrophenyl- $\alpha$ -anisylpropane, pale yellow rodlets, m. p.  $59^{\circ}$ , and 2-anisylquinoline, leaflets, m. p.  $123.5^{\circ}$ , are described. Similarly, the reduction of ethyl o-nitrobenzylmethylacetoacetate, a liquid, yields 2:3-dimethylquinoline, m. p.  $64.5^{\circ}$ , and not a dihydro-derivative.

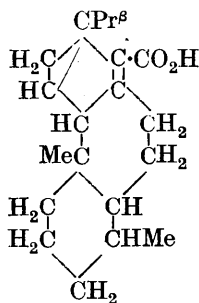
$\beta$ -o-Nitrophenylpropionitrile, prepared from the amide and thionyl chloride, m. p.  $41-42^{\circ}$ , is reduced by stannous chloride and hydrochloric acid to 2-aminoquinoline hydrochloride.

$\alpha$ -Bromo- $\beta$ -o-nitrophenylpropionic acid, rhombohedra, m. p.  $115-116^{\circ}$ , is prepared by the action of bromine and phosphorus on the parent acid or by heating bromo-o-nitrobenzylmalonic acid, prisms, m. p.  $143^{\circ}$  (decomp.).  $\alpha$ -Hydroxy- $\beta$ -o-nitrophenylpropionic acid, rectangular plates, m. p.  $103^{\circ}$ , is prepared from the bromo-acid and silver nitrate solution; it is decomposed by sodium hydroxide solution with production of o-nitrotoluene. H. W.

#### $\alpha\alpha\beta$ -Triphenylpropionic Acid and some of its Derivatives.

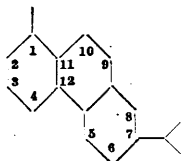
[MME] P. RAMART (*Compt. rend.*, 1924, 178, 93-96).—Benzyl diphenylacetate (needles, m. p.  $35^{\circ}$ , b. p.  $205-207^{\circ}/2$  mm.), from diphenylacetyl chloride and benzyl alcohol, when treated successively with sodamide and benzyl chloride, affords benzyl  $\alpha\alpha\beta$ -triphenylpropionate (prisms, m. p.  $85^{\circ}$ , b. p.  $270-275^{\circ}/2$  mm.). The latter, on hydrolysis, affords  $\alpha\alpha\beta$ -triphenylpropionic acid (prisms, m. p.  $132^{\circ}$ ; amide, needles, m. p.  $111^{\circ}$ ). The nitrile (m. p.  $126^{\circ}$ ) is formed from benzyl chloride and sodio-diphenylacetoneitrile, or from phosphoric oxide and the amide (above). Neure (A., 1889, 597) obtained the nitrile, but was mistaken with regard to the constitution of his acid of m. p.  $162^{\circ}$  (cf. Bistrzycki and Mauron, A., 1910, i, 845). E. E. T.

**Higher Terpene Compounds. XVI. The Carbon Framework of Abietic Acid and Dehydrogenating Disruption in the Abietic Acid Series.** L. RUZICKA, H. SCHINZ, and J. MEYER (*Helv. Chim. Acta*, 1923, 6, 1077-1096).—The annexed constitutional formula for abietic acid (pinabietic acid) put forward by Virtanen (A., 1921, i, 669) does not conform with the principle,



which has been found general for the sesquiterpenes, that the carbon framework must be divisible into isoprene residues. This formula was based partly on the observation that the hydrocarbon abietin,  $C_{19}H_{28}$ , when oxidised with manganese dioxide and sulphuric acid, gives trimellitic acid. Hence it is argued that abietin must contain a benzene ring and that the corresponding ring in abietic acid must contain the double bond and the bridging ring (or, as is now known to be the case, the two double bonds) as well as the carboxyl group. A study of the oxidation of abietin, abietene, methylabietin, and abietic acid leads to the conclusion that Virtanen's reasoning is incorrect. Methylabietin, which, according to Virtanen, should also contain a benzene ring, is com-

pletely oxidised by cold aqueous permanganate to acids, and by oxidation with manganese dioxide and sulphuric acid it gives trimellitic acid, as also does abietic acid. It is concluded, therefore, that the carboxyl group cannot be in the same ring as the isopropyl group, and as the 9 and 10 positions are excluded (see annexed diagram and A., 1922, i, 829), the only remaining positions are 2, 3, and 4. The remaining methyl group may be in position 11, or possibly in 12, but only if the carboxyl is in 2.



Oxidation of abietic acid and its related compounds with manganese dioxide and 57% sulphuric acid leads to a mixture of benzene polycarboxylic acids, some of which are formed normally from the carbon framework of the oxidised substance, some indirectly. Trimellitic acid and mellophanic acid (which is confirmed to be the 1:2:3:4-tetracarboxylic acid, cf. Bamford and Simon, T., 1910, 97, 1904) are probably formed normally, and are obtained from abietene (mixed with abietin), abietic acid, and methylabietin. Pyromellitic acid and benzenepentacarboxylic acid are obtained from abietic acid, their formation being possibly due to polymerisation of the abietic acid at a double bond. A number of methods in which this may occur are discussed. Retenequinone and methylretenequinone are oxidised to mellitic acid, whilst the former also gives pyromellitic acid. Dihydroabietene is oxidised to mellophanic acid without formation of any trimellitic acid, and the same is the case when methylabietin is oxidised first with cold permanganate and then boiled with manganese dioxide and sulphuric acid.

The mechanism of the oxidation of the above compounds with manganese dioxide and sulphuric acid consists first in dehydrogenation of the individual hydroaromatic rings followed by disruption to benzenecarboxylic acids. The process is referred to as "dehydrogenating disruption." The different benzenepolycarboxylic acids are best separated by fractional distillation of their methyl esters, which crystallise readily.

The reduction of ethyl abietate by Bouveault's method to abietenol, which still contains one unsaturated bond, indicates that there is no double bond in the ring containing the carboxyl group (A., 1922, i, 829). The exact position of the double bonds in abietic acid remains uncertain.

E. H. R.

**Higher Terpene Compounds. XVII. The Gentle Action of Potassium Permanganate on Abietic Acid.** L. RUZICKA and J. MEYER (*Helv. Chim. Acta*, 1923, 6, 1097—1108).—To obtain a crystalline product by the oxidation of abietic acid with potassium permanganate, great care is required. The oxidation is carried out in potassium hydroxide solution, using 2 to 3 atoms of available oxygen per mol., and at a high dilution. After fifteen hours, the manganese dioxide is filtered off and unoxidised abietic acid precipitated by a current of carbon dioxide. When part of the oxidation product has started to precipitate, the solution is filtered and the main product precipitated with acetic acid. The precipi-

tate is filtered, dried, and digested with a little methyl alcohol, which leaves a crystalline residue, about 3—8% of the weight of the abietic acid taken, m. p. 106°. This is separable by fractional precipitation into an unknown substance,  $C_{18}H_{32}O_7$ , m. p. 154°, and a *dihydroxyabietic acid*,  $C_{20}H_{30}O_2(OH)_2$ , m. p. 152°, which gives a *diacetyl* derivative, m. p. 163° (decomp.), and a possibly stereoisomeric diacetyl compound, m. p. 240°. On separate occasions the oxidation took different courses, giving products of m. p. 135° and 360°.

E. H. R.

**The Resolution of *dl*-Tyrosine into its Two Optically Active Components.** E. ABDERHALDEN and H. SICKEL (*Z. physiol. Chem.*, 1923, 131, 277—280).—Formyl-*dl*-tyrosine, obtained from tyrosine by boiling with formic acid for three hours, has been separated into its components by recrystallisation from hot water containing four equivalents of brucine. The *brucine* salt of formyl-*d*-tyrosine which crystallises out forms four- or six-sided leaflets, which decompose at 145°. Formyl-*d*-tyrosine is obtained from this salt on decomposing it with alkali. Hydrolysis of formyl-*d*-tyrosine with 10% hydrochloric acid yields *d*-tyrosine,  $[\alpha]_D^{25} + 8.7^\circ$ . The corresponding *l*-salt was not obtained pure from the mother-liquors. The best preparation gave  $[\alpha]_D^{25} - 6.2^\circ$ .

W. O. K.

**Dichlorotyrosine** [ $\alpha$ -Amino- $\beta$ -3 : 5-dichloro-4-hydroxyphenylpropionic Acid]. CHEMISCHE FABRIK FLORA (Swiss Pat. 99453; from *Chem. Zentr.*, 1923, iv, 828).—A suspension of tyrosine in acetic acid is treated with chlorine. *Dichlorotyrosine hydrochloride* separates out from which the free base may be obtained in crystalline form. It is optically active.

G. W. R.

**Preparation of Dibromotyrosine** [ $\alpha$ -Amino- $\beta$ -3 : 5-dibromo-4-hydroxyphenylpropionic Acid]. CHEMISCHE FABRIK FLORA (Swiss Pat. 95300; from *Chem. Zentr.*, 1923, iv, 663).—A suspension of tyrosine in acetic acid is treated with bromine; from the products of reaction,  $\alpha$ -amino- $\beta$ -3 : 5-dibromo-4-hydroxyphenylpropionic acid is obtained. It is crystalline and optically active.

G. W. R.

**Derivatives of  $\alpha$ -Naphthol-2-carboxylic Acid.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (D.R.-P. 373736; from *Chem. Zentr.*, 1923, iv, 593).—Additional to Brit. Pat. 195513. 4 : 4'-Dihydroxydinaphthylketone-3 : 3'-dicarboxylic acid is a powder decomposing at 259°.  $\alpha$ -Naphthol-2 : 4-dicarboxylic acid decomposes at about 286°.

G. W. R.

**$\alpha$ -Naphthol-4-carboxylanilide.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 99280; from *Chem. Zentr.*, 1923, iv, 829).—An ester of  $\alpha$ -naphthol-4-carboxylic acid, for example, methyl  $\alpha$ -naphthol-4-carboxylate, is heated with aniline.  $\alpha$ -Naphthol-4-carboxylanilide thus obtained is crystalline and has m. p. 203°.

G. W. R.

**The Constitution of Sparassol.** E. WEDEKIND and K. FLEISCHER (*Ber.*, 1923, **56**, [B], 2556—2563; cf. Falck, *ibid.*, 2555).—The substance is shown to be methyl 4-hydroxy-2-methoxy-o-toluate.

Sparassol,  $C_{10}H_{12}O_4$ , crystallises from methyl or ethyl alcohol in needles, m. p. 67—68°. It contains two methoxyl groups, is saturated, and does not possess a ketonic or a reactive methylene group. Its aromatic nature is established by the isolation of methyl 3(?)5-nitro-4-hydroxy-2-methoxy-o-toluate, yellow needles m. p. 168—169°, and methyl 3:5-dinitro-4-hydroxy-2-methoxy-o-toluate, small, pale yellow needles, m. p. 150°. The presence of a phenolic hydroxyl group in sparassol is established by its solubility in alkali hydroxide, but not in alkali carbonate, and by the formation of methyl 4-acetoxy-2-methoxy-o-toluate, small, hexagonal plates, m. p. 63—64°, and of methyl 2:4-dimethoxy-o-toluate, rhombic plates, m. p. 42—43·5°; the isolation of 4-hydroxy-2-methoxy-o-toluic acid, m. p. 165—166° (decomp.) after slight previous softening, as by-product of the action of methyl sulphate and potassium hydroxide on sparassol indicates the presence of the carbomethoxy-group. When treated with fuming hydrochloric acid under pressure, sparassol yields orcinol. A comparison of the properties of sparassol and the corresponding carboxylic acid with those of the known orcinolcarboxylic acids and their methylated derivatives excludes the possibility that the constitution of sparassol is other than methyl 4-hydroxy-2-methoxy-o-toluate.

It is established that the amount of benzenoid compounds in the culture medium is insufficient to account for the production of sparassol; an example is therefore afforded of the conversion of an aliphatic compound (sugar) into an aromatic substance by a biochemical method. H. W.

**Preparation of Aryl Hydroxynaphthyl Ketones.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (D.R.-P. 378908, 378909, and Swiss Pat. 98559; from *Chem. Zentr.*, 1923, iv, 593—594).— $\beta$ -Naphthol or negatively substituted derivatives of  $\alpha$ - or  $\beta$ -naphthol are treated with aryl trichlorides with or without addition of diluents or condensing reagents in the absence of alkali hydroxides. The carboxylic acids and sulphonic acids of 4-hydroxynaphthalene-1-arylketens are heated at high temperatures, preferably in suspension or in the presence of diluents. 1-Hydroxynaphthalene-2-carboxylic acid when heated with benzotrichloride at 100—120° until evolution of hydrogen chloride has ceased, or at 15° in the presence of strong sulphuric acid, gives 4-hydroxy-1-benzoylnaphthalene-3-carboxylic acid, small needles, m. p. 205°. On heating the latter compound under pressure with strong sulphuric acid, phenyl 4-hydroxy- $\alpha$ -naphthyl ketone is obtained, m. p. 164—165°. 4-Hydroxy-1-o-chlorobenzoylnaphthalene-3-carboxylic acid, from 1-hydroxynaphthalene-2-carboxylic acid and o-chlorobenzotrichloride, has m. p. 213°. 1-Chloro-4'-hydroxy-2:1'-dinaphthyl-ketone-3'-carboxylic acid, from 1-hydroxynaphthalene-2-carboxylic acid and 1-chloro-2-naphthotrichloride, has m. p. 210—211°. The following com-



pounds are also mentioned: *phenyl 2-hydroxy- $\alpha$ -naphthyl ketone*, m. p. 175°, from  $\beta$ -naphthol and benzotrichloride; *2-hydroxy-1-benzoylnaphthalene-3-carboxylic acid*, from 2-hydroxynaphthalene-3-carboxylic acid and benzotrichloride; *phenyl 5-chloro-4-hydroxy- $\alpha$ -naphthyl ketone*, m. p. 121°, from 8-chloro-1-hydroxynaphthalene and benzotrichloride; *4-hydroxy-1-benzoylnaphthalene-3-sulphonic acid*, a white powder giving phenyl 4-hydroxy- $\alpha$ -naphthyl ketone by elimination of the sulphonic acid group, from 1-hydroxynaphthalene-2-sulphonic acid and benzotrichloride; *4-hydroxy-1-benzoylnaphthalene-5-sulphonic acid*; *1-hydroxy-2-benzoylnaphthalene-4-sulphonic acid*; *1-hydroxy-2-benzoylnaphthalene-5-sulphonic acid*. By heating the above-mentioned carboxylic acids or sulphonic acids with 5% sulphuric acid under pressure at 180–190°, or in the presence of dimethylaniline at 150°, the carboxylic acid or sulphonic acid groups are eliminated. Examples are given of the preparation by this reaction of *phenyl 4-hydroxy- $\alpha$ -naphthyl ketone*, 1-chloro-4'-hydroxy-2 : 1'-dinaphthyl ketone, crystals, m. p. 213°, and 4 : 4'-di-hydroxy-1 : 1'-dinaphthyl ketone.

G. W. R.

**3-Methoxynaphthalene-2-ketocarboxylic Acid.** W. DILTHEY and G. LIPPS (*Ber.*, 1923, 56, [B], 2443–2445).—3-Acetyl-2-methoxynaphthalene condenses with benzaldehyde in the presence of alcoholic sodium ethoxide to give 2-cinnamoyl-3-methoxynaphthalene,  $C_6H_4$   $\begin{matrix} <CH:C\cdot OMe \\ CH:C\cdot CO\cdot CH:CHPh \end{matrix}$ , deep yellow leaflets, m. p. 87°, which is oxidised by potassium permanganate in the presence of

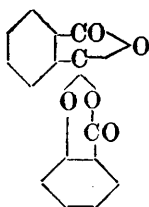
pyridine to 3-methoxy-2-naphthoylformic acid,  $C_6H_4$   $\begin{matrix} <CH:C\cdot OMe \\ CH:C\cdot CO\cdot CO_2H \end{matrix}$ , pale greenish-yellow crystals, m. p. 162–163° (decomp.). The presence of the carbonyl group in the latter acid could not be established in the usual manner, but it is shown that the gas evolved when it is melted consists of approximately equal volumes of carbon monoxide and carbon dioxide. Attempts to oxidise it to 3-methoxynaphthalene-2-carboxylic acid were unsuccessful, the substance being either unchanged or transformed into  $\beta$ -naphthyl methyl ether. During the preparation of the acid, a second acid, colourless, rhombohedral crystals, m. p. 142–143°, is also obtained, the constitution of which has not been elucidated.

The following substances are also described: 1-cinnamoyl-4-ethoxynaphthalene, yellow needles or almost colourless leaflets, m. p. 85°; 2-methoxycinnamoyl-3-methoxynaphthalene, yellow needles, m. p. 99–100°; 1-methoxycinnamoyl-4-ethoxynaphthalene, greenish-yellow needles, m. p. 110–111°; 2-o-chlorocinnamoyl-3-methoxynaphthalene, pale yellow needles, m. p. 121°; 1-o-chlorocinnamoyl-4-ethoxynaphthalene, pale yellow needles, m. p. 97–98°.

H. W.

**Substituted Salicylic Acids. III. The Reaction of  $\gamma$ -Dicarboxyl Chlorides with Sodium Salicylate.** H. P. KAUFMANN and H. VOSS (*Ber.*, 1923, 56, [B], 2508–2514; cf. A., 1922, i, 252; 1923, i, 795).—The condensation of *s-o*-phthaloyl chloride with sodium or disodium salicylate with the production of salicylic

phthalidylidene ether ester (annexed formula) has caused the authors to examine the action with other  $\gamma$ -dicarboxyl chlorides. The problem is intimately connected with the transformation of symmetrical into unsymmetrical acid chlorides and the production of unsymmetrically constituted derivatives from the former.

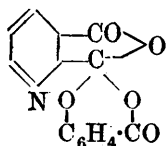


*s*-Tetrachlorophthaloyl chloride reacts with disodium salicylate in the presence of benzene to give *salicylic tetrachlorophthalidylidene ether ester*, colourless crystals, m. p.  $199^{\circ}$ , which is stable towards cold sodium carbonate solution, but is hydrolysed when warmed. *as*-Tetrachlorophthaloyl chloride, prepared by the action of aluminium chloride on the symmetrical chloride at  $150^{\circ}$  (cf. Ott, A., 1912, i, 828) long, lustrous needles, m. p.  $137^{\circ}$ , is more stable than *as*-phthaloyl chloride, and is only partly transformed into the symmetrical variety when distilled.

*s*- $\Delta^{2,6}$ -Dihydrophthaloyl chloride, a pale yellow liquid, b. p.  $122^{\circ}/13$  mm., gives with sodium salicylate in the presence of ether *salicylic  $\Delta^{2,6}$ -dihydrophthalidylidene ether ester*, colourless crystals, m. p.  $165^{\circ}$ ; *as*- $\Delta^{2,6}$ -dihydrophthaloyl chloride forms pale yellow crystals, m. p.  $131^{\circ}$ .

*s*- $\Delta^2$ -Tetrahydrophthaloyl chloride, a pale yellow liquid, b. p.  $129^{\circ}/14$  mm., is readily converted into *salicylic  $\Delta^2$ -tetrahydrophthalidylidene ether ester*, a colourless substance, m. p. (indefinite)  $105^{\circ}$  (decomp.). The conversion of the symmetrical into the unsymmetrical chloride could not be effected.

Pyridine-2 : 3-dicarboxyl chloride and sodium salicylate in the presence of boiling benzene give *salicylic pyridine-phthalidylidene ether ester* (annexed formula), m. p.  $168^{\circ}$ .



Succinyl chloride and sodium salicylate yield *salicylic succinidylidene ether ester* which exists in two isomeric forms, colourless needles, m. p.  $176^{\circ}$  when rapidly heated, and m. p.  $192^{\circ}$ ; the former compound passes into the latter when it is boiled with glacial acetic acid. The isomerism probably depends on keto-enolic desmotropy.

*Salicylic maleinidylidene ether ester*, m. p.  $204^{\circ}$ , is prepared with the aid of fumaroyl chloride. It dissolves in cold sodium carbonate solution, from which it is precipitated unchanged by acetic acid. The unusual solubility is attributed to the wandering of a hydrogen atom, although the mobility of hydrogen attached to a doubly bound carbon atom is surprising.

[With W. DÄHNERT.]— $\alpha\beta$ -Dibromomaleinyl chloride reacts with sodium salicylate in the presence of ether to give *salicylic  $\alpha\beta$ -dibromomaleinidylidene ether ester*, needles, m. p.  $160^{\circ}$ , which does not dissolve in cold sodium carbonate solution. H. W.

**The Diphenic Acid and the Fluorenone Series.** I. H. W. UNDERWOOD, jun., and E. L. KOCHMANN (*J. Amer. Chem. Soc.*, 1923, 45, 3071—3077).—Diphenic anhydride and phenol react in the

presence of fuming stannic chloride and from the product phenoldiphenein, colourless, rhombic crystals, m. p. 250—251°, and an amorphous powder were isolated. The former dissolved in sodium hydroxide to a yellow solution, whilst the latter gave a deep red colour. The reaction between resorcinol and the anhydride in the presence of zinc chloride gave resorcinol-diphenein, colourless crystals, m. p. 178—179°, soluble in sodium hydroxide without fluorescence, and an amorphous powder which gave strong fluorescence when dissolved in dilute sodium hydroxide (T., 1923, **123**, 225). No definite substance was isolated from the product of reaction between diphenic anhydride and pyrogallol in the presence of stannic chloride. Diphenic anhydride was converted into its isomeride diphenylene-ketone-4-carboxylic acid on heating with stannous chloride or zinc chloride, and the reverse change was accomplished by heating the ketone acid with acetic anhydride and glacial acetic acid. The ketone acid reacted with phenol and resorcinol to give amorphous substances identical with those obtained in the reactions described above. Fluorenone reacted with phenol and resorcinol to give similar products. None of these products appear to possess quinoid structure.

F. B.

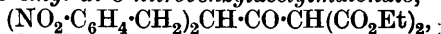
F. B.

**Certain Cyclic and Fatty-aromatic Bases from Di-*o*-nitrobenzyl-acetoacetic and -malonic Esters.** S. GABRIEL and REINHOLD WOLTER (*Ber.*, 1923, **56**, [B], 2445—2448).—Ethyl di-*o*-nitrobenzylacetoacetate is reduced by stannous chloride in

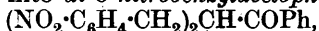
the presence of glacial acetic and fuming hydrochloric acids to the *substance* (annexed formula), colourless needles, m. p. 184° after softening at 178°, which is transformed by boiling hydriodic acid into non-homogeneous

**3-*o*-aminobenzyl-2-methylquinoline** (see below).

Ethyl di-*o*-nitrobenzylmalonate is conveniently transformed into di-*o*-nitrobenzylacetic acid, m. p. 149°, by treatment with somewhat diluted sulphuric acid at 180–185°. Di-*o*-nitrobenzylacetyl chloride, prepared from the acid and phosphorus pentachloride, m. p. 91–92°, is converted by ethyl sodiomalonate in the presence of benzene into ethyl di-*o*-nitrobenzylacetylmalonate,



colourless, rhombic leaflets, m. p. 80° after softening at 77°, from which *di*-o-nitrobenzylacetone,  $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH})_2\text{CH} \cdot \text{COMe}$ , prisms, m. p. 89—89.5°, is prepared by the action of boiling hydrochloric acid. The ketone is reduced by phosphorus and hydriodic acid to 3-o-aminobenzyl-2-methylquinoline (see above), flat needles or oblong plates, m. p. 166—167°, which yields a crystalline *dihydroiodide* and *dihydrochloride*. The base is converted by phthalic anhydride into the substance,  $\text{C}_{25}\text{H}_{18}\text{O}_2\text{N}_2$ , m. p. 127—128°, and by benzaldehyde into the *benzylidene* derivative, m. p. 170—171°. *Di*-o-nitrobenzylacetylchloride is converted by benzene and aluminium chloride into *di*-o-nitrobenzylacetophenone,





disregarded. The phenolic ester, m. p.  $158^{\circ}$ , is isomerised by treatment with methyl-alcoholic hydrogen chloride to the methoxy-acid, m. p.  $165^{\circ}$ . *Methyl  $\beta$ -2-methoxy-1:4-naphthaquinonyl-3-acrylate*,  $\text{OMe}\cdot\text{C}_{10}\text{H}_4\text{O}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ , MeOH, pale yellow needles, m. p.  $130$ – $131^{\circ}$  (decomp.), is prepared by the action of a large excess of boiling methyl iodide on the di-silver salt of the hydroxy-acid; the firmness with which the molecule of methyl alcohol is retained suggests that it is attached to a carbonyl group in the form of a semi-acetal. The hydroxy- and methoxy-acids are only very slowly acted on by bromine dissolved in chloroform, whereas the phenolic ester, m. p.  $158^{\circ}$ , absorbs two atomic proportions of the halogen, one of which is subsequently lost in the form of hydrogen bromide. The hydroxy-acid and the phenolic ester give reddish-brown or orange-yellow solutions in hot sodium hydroxide solution, which rapidly become dark blue and from which a dark violet acid is precipitated by dilute sulphuric acid; this acid has not been obtained in the homogeneous crystalline form, but there can be little doubt that it is a chromanone derivative,  $\text{C}_6\text{H}_4\begin{smallmatrix} < \text{CO}\cdot\text{C}-\text{O}\cdot\text{CH}\cdot\text{CO}_2\text{H} \\ \text{CO}\cdot\text{C}\cdot\text{CO}\cdot\text{CH}_2 \end{smallmatrix}$ . The phenolic ester, unlike the hydroxy- or methoxy-acid, is converted rapidly at the atmospheric temperature by ammonia into a bluish-black compound, to which the constitution  $\text{C}_6\text{H}_4\begin{smallmatrix} < \text{CO}\cdot\text{C}\cdot\text{NH}\cdot\text{CH}\cdot\text{CO}_2\text{Me} \\ \text{CO}\cdot\text{C}\cdot\text{CO}\cdot\text{CH}_2 \end{smallmatrix}$  is assigned.

Reduction of di-potassium  $\beta$ -2-hydroxy-1:4-naphthaquinonyl-3-acrylate by sodium hyposulphite in aqueous solution leads to the production of  $\beta$ -1:2:4-trihydroxy-3-naphthoylacrylic acid, yellow needles, m. p.  $208^{\circ}$ .  
H. W.

**Bile Acids.** X. M. SCHENCK (*Z. physiol. Chem.*, 1923, **131**, 269–276).—(1) Deoxycholic acid, when heated with alcoholic ammonia in a sealed tube at about  $220^{\circ}$  yields the amide,  $\text{C}_{24}\text{H}_{41}\text{O}_3\text{N}$ , m. p.  $186^{\circ}$ , which crystallises from a mixture of alcohol and water in needles containing  $3\text{H}_2\text{O}$ . (2) Biloidanic acid, obtained from bilianic acid purified by means of a new method through the dioxime, has the formula  $\text{C}_{22}\text{H}_{32}\text{O}_{12}$ . From isobilianic acid, when oxidised by 32–35% nitric acid, there is obtained in small yield a *triketo-tricarboxylic acid*,  $\text{C}_{24}\text{H}_{32}\text{O}_9$ , fine, six-sided, rectilinear plates which froth and turn brown at  $230$ – $235^{\circ}$ .  
W. O. K.

**Preparation of Deoxycholic Acid.** J. D. RIEDEL, AKT.-GES. (D.R.-P. 374367; from *Chem. Zentr.*, 1923, iv, 726).—Dihydroxy-cholenic acid is hydrogenated in the presence of catalysts. Deoxycholic acid is obtained from the products by way of the crystalline acetic acid-deoxycholic acid compound, m. p.  $141^{\circ}$ .

G. W. R.

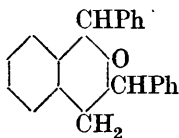
**Preparation of an Unsaturated Bile Acid.** J. D. RIEDEL, AKT.-GES. (D.R.-P. 374366; from *Chem. Zentr.*, 1923, iii, 726; cf. A., 1922, i, 1160).—In variation of an earlier patent, dihydroxy-cholenic acid, m. p.  $260^{\circ}$ , is treated with bromine and alkaline

reagents. For example, dihydroxycholenic acid is treated with bromine in methyl-alcoholic solution. From the products, after boiling with an alkali hydroxide, a substance, apparently *dihydroxy-choladienic acid*, is obtained, m. p. 245—247°. G. W. R.

**Preparation of Benzaldehyde.** THE BARRETT CO. (Brit. Pat. 189091).—The catalytic action of the oxides of various metals on toluene, in the vapour phase and in the presence of a gas containing oxygen (e.g., air, oxygen, ozone), is found to differ considerably. Thus, vanadium oxide gives benzoic acid, benzaldehyde, maleic acid, and a measurable amount of the products of complete combustion; the oxides of molybdenum, tantalum, tungsten, and zirconium give relatively high yields of benzaldehyde and a relatively low degree of combustion; the oxides of uranium, manganese, copper, nickel, chromium, and thorium give relatively high yields of benzaldehyde together with relatively high degrees of combustion; the oxides of cobalt and cerium give relatively low yields of benzaldehyde and relatively high degrees of combustion, whilst the oxides of titanium, bismuth, and tin give relatively low yields of benzaldehyde and relatively low degrees of combustion. Greatly increased yields of benzaldehyde, accompanied by low degrees of combustion, are obtained by using as catalyst mixtures of the above oxides, provided that at least one of these oxides is that of a metal of the fifth or sixth periodic group. Particularly efficient is a mixture of oxides of uranium and molybdenum (approximately in the proportion of from three to thirteen of the former to one of the latter), or of oxides of molybdenum, uranium, and copper. In preparing these oxides, the best results are obtained by starting from a solution of the metals in organic acids. The temperature of the catalyst should be between about 300° and 700°. W. T. K. B.

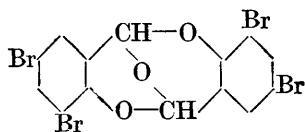
**Organomagnesium Derivatives. III.** A. GARCÍA BANÚS and L. MEDRANO (*Anal. Fis. Quím.*, 1923, **21**, 436—463; cf. García Banús and Vila, A., 1922, i, 734).—A study of the reaction between benzaldehyde and magnesium benzyl halides. On adding benzaldehyde (1 mol.) to magnesium benzyl iodide (1 mol.) in ethereal solution, the reaction proceeds normally, yielding phenyl-*o*-tolylcarbinol, whilst, when magnesium benzyl bromide is used, phenylbenzylcarbinol, crystals, m. p. 62—65°, is formed. In the inverse reaction, where magnesium benzyl bromide is added to benzaldehyde in ethereal solution, stilbene, phenylbenzylcarbinol, and diphenylisochroman, m. p. 90—95°, are formed. Using an excess of benzaldehyde with magnesium benzyl chloride, phenylbenzylcarbinol is formed by reaction in the cold. When the reaction is carried out with boiling in a reflux apparatus, the reaction proceeds differently. From the products of the reaction, dibenzoylphenylmethane, m. p. 144—146°, stilbene, deoxybenzoin, benzylidenedeoxybenzoin, m. p. 101—102°, and isobenzylidenedeoxybenzoin, m. p. 86°, are obtained, but no diphenylisochroman. Magnesium benzyl iodide gives with an excess of benzaldehyde amongst other products, dibenzoylphenylmethane and a small quantity of diphenylisochroman. The

formation of diphenylisochroman is held to be conditioned by the presence of excess of benzaldehyde. When heated with hydrochloric and acetic acids, diphenylisochroman gives diphenylindene. From this and from the fact that a hydroxyl group was shown to be absent, the annexed formula is suggested for diphenylisochroman. From the formation of diphenylisochroman from benzaldehyde and magnesium benzyl bromide, the presence of a conjugated double bond in the latter compound is indicated.



G. W. R.

**Quinonemethides [Methylenequinones] and Pseudophenol-halogenides.** II. H. LINDEMANN and H. FORTH (*Annalen*, 1923, 435, 219—232).—An attempt has been made to prepare o-quinonemethides (cf. A., 1923, i, 686).



3:5-Dibromosalicylaldehyde is converted by thionyl chloride into a colourless *anhydro*-compound (m. p. 243°) (annexed formula). The tri- and mono-acetates of the aldehyde have m. p. 99—100° and 71°, respectively (Simonis and Wenzel, A., 1900, i, 496, give 103° and 90°, respectively). 3:5-Dibromo-2-methoxybenzaldehyde with phosphorus pentachloride gives the corresponding benzylidene *chloride* (needles, m. p. 76°), from which a quinonemethide cannot be obtained. 3:5-Dibromo-2-hydroxybenzylidene *chloride*, from phosphorus pentachloride and the corresponding aldehyde (in presence of benzene), forms needles, m. p. 97°. It is rapidly reconverted into the aldehyde when treated with warm alcohol or acetic acid, a cold solution in these solvents, when treated with water, becoming first orange (possibly owing to formation of quinonechloromethide) and then yellow (aldehyde). In the preparation of the last-named chloride, a *polymeride* of 3:5-dibromo-1:2-benzoquinone-1-chloromethide, m. p. 220—225°, is also formed.

3:5-Dibromosalicylaldehyde, with phosphorus pentabromide, gives, together with some *anhydro*-compound (m. p. 243°, above), the corresponding *bromide* (needles, m. p. 99°), the latter (or the corresponding chloride) giving an *acetyl* derivative (m. p. 113—114°) and an *anil*, red needles, m. p. 105°, and *imine*.

2-Hydroxy-4:6-dimethylbenzaldehyde, on bromination in presence of sodium acetate and acetic acid, affords the 3:5-dibromo-derivative, yellow needles, m. p. 190—191° (the *anil*, red needles, has m. p. 180—181°). The dibromo-aldehyde, which is unaffected by thionyl chloride, is converted by phosphorus pentachloride (in presence of phosphorus oxychloride) into the *anhydro*-derivative (m. p. above 300°) or (in presence of benzene) into the corresponding benzylidene *chloride* (needles, m. p. 114—115°), the latter, with aqueous alkali, giving first a transient orange colour (quinone-methide?) and then the yellow colour of the aldehyde.

3:5-Dibromo-2-hydroxy-4-methoxybenzaldehyde (pale yellow needles, m. p. 97—98°; *triacetate*, m. p. 98°, *monoacetate*, m. p. 78°)

gives an *anil* (yellow needles, m. p. 105°) and an *imine* (m. p. 206°), the corresponding benzylidene *chloride* having m. p. 99°.

3 : 5-Dibromo-4-hydroxy-2-methoxybenzaldehyde has m. p. 170—171° (*triacetate*, m. p. 124°; *anil*, m. p. 185°), the corresponding benzylidene *bromide* having m. p. 111°. The latter, with aqueous alkali or ammonia gives successively a yellow, blue, and yellow colour, whilst, with sodium acetate solution, 3 : 5-dibromo-2-methoxy-1 : 4-benzoquinone-1-bromomethide is formed (yellow needles, m. p. 78—79°). The latter, when treated with water, gives the original aldehyde. The corresponding benzylidene *chloride* has m. p. 81° and affords the *chloromethide*, m. p. 98—100°.

2-Hydroxy-1-naphthaldehyde could not be converted into any derivatives of the type under discussion. E. E. T.

**Compound of Cinnamaldehyde with Amylene.** NEVENKA ALUJEVICH (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 292—294).—Exposure to the action of light in a glass tube of a mixture of cinnamaldehyde with excess of amylene results in the formation of an oily additive *compound*,  $C_{14}H_{18}O$ , which has the normal molecular weight in freezing benzene or acetic acid, but was not found capable of purification. The compound unites with bromine, yielding a brown *dibromide*, and gives benzoic acid when oxidised by means of permanganate. Reduction of the compound by means of hydriodic acid yields a small proportion of a product not yet identified, and treatment with phosphoric oxide gives a crystalline *compound*, m. p. 125°, also unidentified. T. H. P.

**4 : 6-Dinitroisophthalaldehyde.** W. BORSCHKE (*Ber.*, 1923, 56, [B], 2357—2359).—It was shown previously (A., 1912, i, 180) that both methyl groups of 4 : 6-dinitro-*m*-xylene react with benzaldehyde to give 4 : 6-dinitro-1 : 3-distyrylbenzene. It is now found that the 4 : 6-dinitro-*m*-xylene does not react with nitrous acid to form the expected dialdoxime, but does react with *p*-nitrosodimethylaniline, in alcoholic solution in presence of sodium carbonate, to give 4 : 6-dinitroisophthalaldehyde-bis-*p*-dimethylaminoanil,

$C_6H_2(CH:N \cdot C_6H_4 \cdot NMe_2)_2(NO_2)_2$ , a black, crystalline powder, m. p. 208°. This is readily hydrolysed by nitric acid in benzene suspension to 4 : 6-dinitroisophthalaldehyde,  $C_6H_4(CHO)_2(NO_2)_2$ , pale yellow needles, m. p. 132°. This gives a *dioxime*, bright yellow needles, m. p. 184°, and a *bisphenylhydrazone*, black needles, m. p. 251°. From benzene solution in sunlight, the aldehyde is gradually precipitated in the form of yellow needles, m. p. 185—186°, apparently of 4 : 6-dinitrosoisophthalic acid. 4 : 6-Dinitro-*m*-xylene also reacts with mercuric chloride in presence of sodium ethoxide to form 4 : 6-dinitroisophthalylidenetetramercuriodioxide,  $C_8H_4O_6N_2Hg_4$ , a heavy, yellow powder. E. H. R.

**Electrolytic Oxidation of isoEugenol.** A. LOWRY and C. M. MOORE (*Trans. Amer. Electrochem. Soc.*, 1922, 42, 273—284).—The authors have investigated a process for the production of vanillin by the electrolytic oxidation of *isoeugenol*, described in the German patent (D.R.-P. 92007). Experiments carried out with sodium



hydroxide or sulphuric acid as electrolyte gave in every case negative results. Vanillin itself is found to be readily oxidised electrolytically, and even if formed by the electrolytic oxidation it would be immediately converted into other products. Hence it is concluded that if vanillin is produced by the electrolytic oxidation, a totally different condition must prevail from that described in the patent.

J. F. S.

### Acetyl Derivative of Deoxybenzoin (Tautomeric Form).

C. V. GHEORGHIU (*Ann. Scient. Univ. Jassy*, 1923, **11**, 307—308; from *Chem. Zentr.*, 1923, iii, 1159).—By treatment of deoxybenzoin with acetic acid and zinc chloride, a crystalline precipitate, m. p. 102—106°, held to be the *acetyl* derivative in the enol form,



is obtained. On hydrolysis, however, it does not give the corresponding alcohol, but deoxybenzoin.

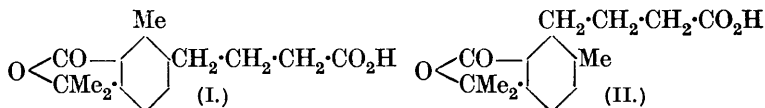
G. W. R.

### Electrolytic Reduction of Oximes. I. Benzoinoxime.

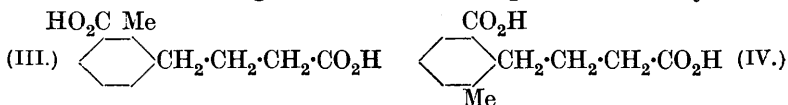
MASAYOSHI ISHIBASHI (*Mem. Coll. Sci. Kyoto*, 1923, **7**, 39—44).—Benzoinoxime is only partly reduced electrolytically in acid solution. A part is hydrolysed before electrolytic reduction occurs, and the benzoin resulting from the hydrolysis is reduced to form hydrobenzoin, benzoinpinacone, and deoxybenzoinpinacone. Optimal conditions for the preparation of the amine require that the electrolysis be conducted at 19° to 20° with a current density of about 0.3 amp. per sq. cm., and that a cathode of tin or lead be employed. The concentration of sulphuric acid in the catholyte should not exceed 5%. In alkaline or neutral solution no appreciable electrolytic reduction or hydrolysis of benzoinoxime is observed.

J. S. G. T.

**Picrotin Ketone and Picrotinic Acid.** F. ANGELICO and F. MONFORTE (*Gazzetta*, 1923, **53**, 800—807; cf. A., 1909, i, 318; 1910, i, 404, 576).—The failure of the action of sodium hypobromite on picrotin ketone to yield bromoform and that of the action of iodine and potassium hydroxide to give iodoform render doubtful Horrmann and Bischof's suggestion that the molecule of this ketone contains the grouping  $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$  (A., 1922, i, 161). Fusion with potassium hydroxide of picrotinic acid, for which formula (I) or (II) may be assumed, yields, besides products of profound decomposition, a

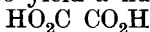


dicarboxylic acid,  $\text{C}_{12}\text{H}_{14}\text{O}_4$ , m. p. 132°, of constitution (III) or (IV). On the other hand, gradual oxidation of picrotinic acid yields a



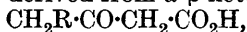
series of acids of the formulæ  $\text{C}_{15}\text{H}_{16}\text{O}_6$ ,  $\text{C}_{13}\text{H}_{12}\text{O}_6$ , and  $\text{C}_{13}\text{H}_{12}\text{O}_7$ , all

of which give acetone when fused with potassium hydroxide, and hence contain the phthalide grouping intact (A., 1910, i, 404). From its formula the acid  $C_{15}H_{16}O_6$ , known as picrotinphthaldicarboxylic acid, evidently contains a carboxyl group in place of the methyl group of picrotinic acid, so that its possible constitutions follow from formulæ (I) and (II). Since, when fused with potassium hydroxide, picrotinic acid loses only acetone and gives a dibasic acid, picrotinphthaldicarboxylic acid should, under similar conditions, yield a tribasic acid. A crystalline acid, m. p. about  $153^\circ$ , is indeed obtained in this way, but in quantity insufficient for analysis; since, however, it condenses with resorcinol in presence of sulphuric acid, to yield a fluorescent compound, it is probable



that its formula is  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ , and that picrotinic acid is represented by formula (I).

Horrmann (A., 1916, i, 828) suggests that picrotin ketone and picrotinic acid may be derived from a  $\beta$ -ketonic acid,



which cannot be isolated, possibly owing to the readiness with which it loses carbon dioxide. Neither picrotin nor picrotoxinin has, however, yet yielded an oxime, and the authors find that the action of amyl nitrite on picrotin in presence of sodium ethoxide gives principally two nitrogen-free acids.

*Oximinopicrotin ketone*,  $C_{14}H_{15}O_3N$ , m. p.  $215^\circ$  (decomp.), is readily convertible into the *dioxime*,  $C_{14}H_{14}O_4N_2$ , which crystallises in minute needles, m. p.  $232^\circ$  (decomp.).

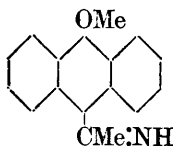
The *acid*,  $C_{11}H_{14}O_5$  or  $C_{13}H_{16}O_6$ , obtained by treating picrotin with amyl nitrite and sodium ethoxide, forms minute crystals, m. p.  $330^\circ$ , and sublimes at the melting point, giving vapours which irritate the mucus. When heated with fused potassium hydroxide, it yields acetone, and with sulphuric acid and resorcinol it forms a fluorescein. It is accompanied by another *acid*, which contains C 54.29% and H 7.58%, and forms silky, white needles, m. p.  $95^\circ$ .

T. H. P.

**Anomalous Splitting of Ketimides.** F. KROLLPFELFFER (Ber., 1923, 56, [B], 2360—2365).—The ketimides obtained by condensing anthranol methyl ether with nitriles are not, as was to be expected, hydrolysed by dilute acids to the corresponding ketones, but are decomposed into anthrone. Thus 10-methoxy-9-anthrylmethyl-ketimide decomposes with formation of methyl alcohol, acetic acid, and anthrone. The ketone, 10-methoxy-9-anthrylmethyl ketone, is only obtained in small yield by boiling an aqueous solution of the hydrochloride of the ketimide; the ketone itself is readily hydrolysed to anthrone. The phenyl derivative, 10-methoxy-9-anthryl-phenyl-ketimide, is much more stable than the methyl compound; it is only hydrolysed by boiling concentrated hydrochloric acid, giving anthrone and benzoic acid. The *N*-methyl derivative of this ketimide is likewise hydrolysed by boiling concentrated hydrochloric acid, forming anthrone, methylamine, and

benzoic acid. The readiness with which the acyl residue is removed in the anthryl ketones appears to be influenced by the  $\mu$ -methoxy group, for  $\mu$ -anthryl phenyl ketone is not hydrolysed by hot hydrochloric acid in acetic acid solution, although with warm concentrated sulphuric acid it gives anthracenesulphonic acid and benzoic acid.

**10-Methoxy-9-anthryl-methyl-ketimide** (annexed formula) is obtained by mixing anthranol methyl ether and acetonitrile with aluminium chloride and passing a current of dry hydrochloric acid through the cooled mixture; it forms a pale yellow, crystalline powder, m. p. 145—146°. **10-Methoxy-9-anthryl methyl ketone** forms pale yellow, glistening, square leaflets, m. p. 182—183°. **10-Methoxy-9-anthryl-phenyl-ketimide** forms stout, yellowish-green crystals, m. p. 147—148°; its *hydrochloride* forms an orange, crystalline precipitate. **10-Methoxy-9-anthryl-phenyl-N-methyl-ketimide** is obtained by methylating the ketimide with methyl sulphate; it forms pale yellow needles, m. p. 127°. E. H. R.



**2 : 3-Diaminoanthraquinone.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 98312; from *Chem. Zentr.*, 1923, iv, 829).—3-Bromo-2-aminoanthraquinone is treated with aqueous or ethyl-alcoholic ammonia in the presence or absence of catalysts at 170—190° under pressure. **2 : 3-Diaminoanthraquinone** thus obtained is crystalline. G. W. R.

**Derivatives of  $\beta$ -Methylantraquinone. III. The Synthesis of *Frangula Emodin*.** R. EDER and C. WIDMER (*Helv. Chim. Acta*, 1923, 6, 966—981).—It is known that emodin is a trihydroxy- $\beta$ -methylantraquinone, and it is highly probable that two of the hydroxyl groups are in the 1 : 8-positions and the methyl group in the 3-position as in chrysophanic acid. It is also probable that the third hydroxyl is in a  $\beta$ -position and not adjacent to an  $\alpha$ -hydroxyl group. These probabilities have now been confirmed by synthesis and the constitution of emodin established as 1 : 6 : 8-trihydroxy-3-methylantraquinone. The synthesis was accomplished in a manner similar to that of chrysophanic acid (*A.*, 1923, i, 688), starting from 3 : 5-dinitrophthalic acid and *m*-cresol. **3 : 5-Dinitrophthalic anhydride** is formed by boiling the acid with acetic anhydride; it crystallises in white, stout, hygroscopic needles, m. p. 163—164°. It condenses with *m*-cresol in presence of aluminium chloride to give **3 : 5-dinitro-o-3'-hydroxy-p-toluoylbenzoic acid**, greenish-yellow leaflets, m. p. 236—237°. This compound is very sensitive to alkalis, forming a compound,  $C_{15}H_{11}O_6N$ , white needles, m. p. 251—252° (decomp.). It corresponds in composition with a nitrohydroxytoluoylbenzoic acid, but could not be identified as such a compound. It can be reduced to an *amino*-compound, yellow needles, m. p. 305—306° (decomp.). **3 : 5-Dinitro-o-3'-hydroxy-p-toluoylbenzoic acid** is reduced by ferrous sulphate and ammonia to **3 : 5-diamino-o-3'-hydroxy-p-toluoylbenzoic acid**, pale

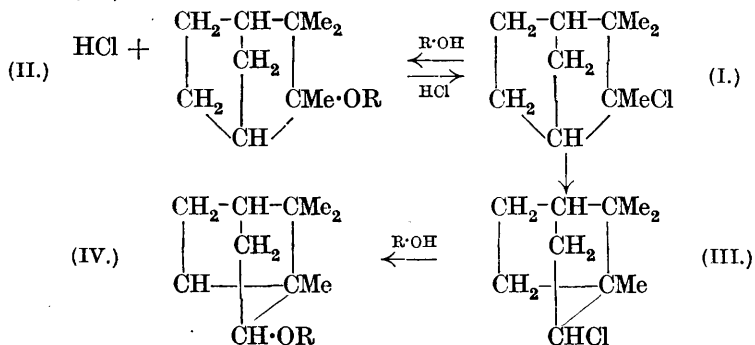
yellow needles, m. p. 233—234°. When heated in concentrated sulphuric acid at 160—170°, this is converted into 6:8-diamino-1-hydroxy-3-methylantraquinone, stout, red needles, m. p. 306—307°. This compound is soluble in alkalis, separating as a salt on cooling; in concentrated sulphuric acid, it dissolves with a yellow colour. It can be tetrazotised in concentrated sulphuric acid solution, and when the solution is heated on the water-bath it decomposes forming 1:6:8-trihydroxy-3-methylantraquinone, orange needles, m. p. 256°, identical with emodin. It was not possible to condense 3:5-dinitro-*o*-3'-hydroxy-*p*-toluoylbenzoic acid to an anthraquinone derivative. E. H. R.

**1:8-Dihydroxy-3-methylantraquinone.** R. EDER (Swiss Pats. 95614 and 95947; from *Chem. Zentr.*, 1923, iv, 664).—1:8-Dihydroxy-3-methylantraquinone may be prepared from  $\alpha$ -nitrophthalic acid (Eder and Widmer, A., 1922, i, 260) and also by condensation of  $\alpha$ -aminoacetylphthalic acid with *m*-cresol in the presence of aluminium chloride to 3-amino-*o*-2'-hydroxy-*p*-toluoylbenzoic acid, from which 1:8-dihydroxy-3-methylantraquinone is obtained by way of the diazo-compound, or by heating with strong sulphuric acid at 150°, whereby 8-amino-1-hydroxy-3-methylantraquinone, reddish-brown needles, m. p. 237—238°, is obtained. The latter, by diazotisation and boiling, yields the 1:8-dihydroxy-compound. G. W. R.

**Intramolecular Displacements of Atoms. I. Addition of Alcohols to Camphene.** H. MEERWEIN and L. GÉRARD (*Annalen*, 1923, 435, 174—189).—Semmler (A., 1901, i, 90), by treating camphene with alcohols in presence of sulphuric acid, obtained, as he supposed, *isobornyl* ethers, which are similarly obtainable from *isoborneol*. A precise proof of the constitution of the ethers is now given for the first time. *isoBornyl* methyl ether is formed by the interaction of camphene, methyl alcohol, and sulphuric acid, or by that of methyl iodide and sodium bornylxide, and is quite distinct from the methyl ether of camphene hydrate, obtained from the potassium derivative of camphene hydrate and methyl iodide.

The results recorded previously (A., 1920, i, 855) in connexion with the action of alcohols on camphene hydrochloride have an interesting sequel. If a solution of camphene hydrochloride in an alcohol is kept at 20°, the concentration of free hydrogen chloride (cf. A., 1922, ii, 751), initially high, slowly falls to a minimum (after several days) and then slowly rises to 100% of that present originally. These phenomena are due to the following processes: (1) Reversible interaction of camphene hydrochloride (I) and alcohol to give hydrogen chloride and an ether (II). This inter-conversion is entirely analogous to that of triphenylchloromethane and triphenylcarbinyl ethers (a little of II decomposes into camphene and alcohol). (2) Isomerisation of unchanged camphene hydrochloride into *isobornyl* chloride (III). As a result of this, the change II  $\rightarrow$  I is promoted, until no more ether remains.

(3) Interaction of *isobornyl* chloride with alcohol to give *isobornyl* ethers (IV) :



This scheme was suggested by the results of a determination (against time) of the relative proportions of free hydrogen chloride, *isobornyl* chloride, and camphene hydrochloride in such a system, starting with camphene hydrochloride and an alcohol. With methyl alcohol, a maximum content of *isobornyl* chloride is present at the time corresponding with the above minimum concentration of hydrogen chloride. Proof of the explanation given is afforded in the following :

If an ethereal solution of camphene hydrochloride is slowly added to a methyl-alcoholic suspension of anhydrous potassium carbonate, so that the solution never becomes acidic, camphene hydrate methyl ether is obtained (in 50% yield), identical with the product from the action of methyl iodide on the potassium derivative of camphene hydrate (this preparation being effected in xylene suspension, unchanged camphene being finally removed by means of ozone). *Camphene hydrate methyl ether* has m. p. 12–14°, b. p. 201.5°, or 88.5–89°/17 mm.,  $d_4^{20}$  0.9477–0.9481, and  $n_D^{20}$  1.47153 (mean constants of the two samples obtained). Active camphene,  $[\alpha]_D^{25} +50.75^\circ$  when converted, through the hydrochloride into the ether, gives the latter with  $[\alpha]_D^{25} -12.71^\circ$ . When shaken with a solution containing potassium ferrocyanide and hydrochloric acid, the methyl ether affords an *additive* compound,  $3\text{C}_{10}\text{H}_{17}\text{OMe} \cdot \text{H}_4\text{Fe}(\text{CN})_6$ .

Whilst *camphene hydrate ethyl ether* could not be obtained from camphene hydrate, it is readily obtained (although in small yield, because of its sensitivity to acids) from camphene hydrochloride, potassium carbonate, and ethyl alcohol, and forms a colourless oil (b. p. 93°/17 mm.,  $d_4^{20}$  0.9350), decomposing at 200° into camphene and alcohol.

If camphene hydrochloride is allowed to remain in methyl-alcoholic solution for about fourteen days at 30°, or until the concentration of free hydrogen chloride no longer increases, *isobornyl* methyl ether results; if the above active camphene is used, the resulting ether has  $[\alpha]_D^{25} -23.4^\circ$ . Semmler's method, using active camphene, gives the ether with  $[\alpha]_D^{25} -14.82^\circ$ , a rotation decreased

by prolonging the action of the methyl-alcoholic sulphuric acid. (This preparation depends on the initial formation of camphene hydrate sulphuric ester, which changes into the *isobornyl* ester, this with alcohol giving the ether. The rate of conversion of camphene hydrate esters into *isobornyl* ethers is greater with sulphuric and aromatic sulphonic esters than with halogen esters.) Similarly, the ether was obtained from sodium bornoxide and methyl iodide, the mean physical constants of the various products being: b. p. 191—191.5°, 78°/17 mm. or 80°/19 mm.,  $d_4^{20}$  0.9250—0.9277,  $n_D^{20}$  1.46252—1.46282. The unstable additive compounds described by Bertram and Walbaum (A., 1894, i, 204) could not be obtained. It was found that *isobornyl* methyl ether was readily converted by hydrogen bromide into *isobornyl* bromide, hydrogen chloride acting similarly, but more slowly.

When treated with hydrochloric acid and potassium ferrocyanide, the ether gives an *additive* compound,  $3C_{10}H_{17}OMe \cdot H_4Fe(CN)_6$ , decomposing at 170°, whilst on heating with anhydrous zinc chloride it gives camphene and methyl alcohol, stannic chloride effecting the same change more slowly, whilst other metallic chlorides are without action.

*isoBornyl* methyl ether is also formed by warming camphene hydrate methyl ether with methyl-alcoholic hydrogen chloride, or by treating *isobornyl* chloride with methyl alcohol. Camphene hydrate methyl ether is rapidly decomposed, whereas *isobornyl* methyl ether is unaffected, by glacial acetic acid at 80°. The camphene produced (through the first-formed camphene hydrate acetate) is readily estimated by titration with perbenzoic acid so that mixtures of the two ethers may readily be analysed.

Camphene hydrate ethyl ether affords camphene even when shaken for a few hours with 1% sulphuric acid, the methyl ether being practically unaffected by the latter. The methyl ether is rapidly converted by traces of zinc, stannic, aluminium, ferric, and mercuric chlorides or antimony pentachloride into camphene and methyl alcohol (cf. *isobornyl* methyl ether), whilst hydrogen chloride and bromide decompose both hydrate ethers to give camphene hydrochloride (hydrobromide), this passing rapidly into *isobornyl* chloride (bromide).  
E. E. T.

[Intramolecular Displacements of Atoms.] II. Camphor dichloride. [2 : 2-Dichlorocamphane]. H. MEERWEIN and R. WORTMANN (*Annalen*, 1923, 435, 190—206).—The conversion:  $CMe_3 \cdot CHMe \cdot OAcyl \rightleftharpoons CMe_3(OAcyl) \cdot CHMe_2$  may be regarded as a result of ionisation, followed by intra-ionic rearrangement,  $(CMe_3 \cdot CHMe) \overset{+}{O} \cdot \overset{-}{Acyl} \rightleftharpoons (CMe_2 \cdot CHMe_2) \overset{+}{O} \cdot \overset{-}{Acyl}$ , free radicals not being involved. The ordinary pinacone-pinacolin change may, similarly, be written:

$(CMe_2 \cdot CMe_2 \cdot OAcyl) \overset{+}{O} \cdot \overset{-}{Acyl} \rightarrow (CMe_3 \cdot CMe \cdot OAcyl) \overset{+}{O} \cdot \overset{-}{Acyl}$ ,  
the reverse change not occurring, owing to the instability of pinacolin esters other than those with halogen acids. Pinacolin dichloride [ $\gamma$ -dichloro- $\beta$ - $\beta$ -dimethylbutane] and pinacone dichloride

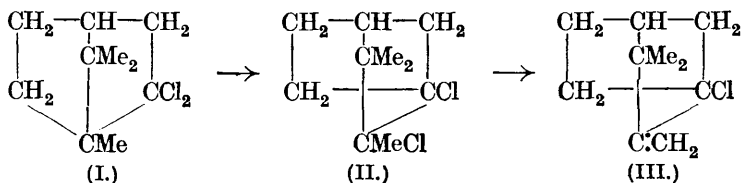
[ $\beta$ -dichloro- $\beta$ -dimethylbutane] cannot be interconverted, but if the vapours of the first substance be passed over barium chloride, heated at 400—450°, a little  $\beta$ -dimethylbutadiene results, probably owing to the intermediate formation of pinacone dichloride.

Greater powers of isomerisation would be expected from 2 : 2-dichlorocamphane, which possesses a similar structure to pinacolin dichloride. The substance described as dichlorocamphane by previous authors (*e.g.*, Bredt, A., 1901, i, 217; Marsh and Gardner, T., 1897, 71, 290; Marsh and Hartridge, T., 1898, 73, 852) is now shown to be a mixture of substances. If, however, a mixture of camphor (200 g.), phosphorus trichloride (170 g.), and pure phosphorus pentachloride (294 g.) is left at 0° for a month, pure  $\alpha$ -camphor dichloride (2 : 2-dichlorocamphane) (I) is obtained, m. p. 146—148° (decomp.). Occasional preparations fail, and it is always necessary to test the product by studying its interaction with sodium ethoxide (boiling alcoholic solution) or with methyl alcohol (at 50°), which proceeds in a characteristic manner.

When heated with a mixture of phenol and potassium acetate, 2 : 2-dichlorocamphane affords  $\alpha$ -chlorocamphene (III) (colourless, setting point about 20°, b. p. 193—197°), this, on reduction with sodium and alcohol affording camphene (setting point 44·5°, b. p. 156·5—158°), and on ozonolysis giving  $\alpha$ -chlorocamphenilone. The latter compound (in which CO replaces the hemi-cyclic CH<sub>2</sub> group in III) has setting point, 14·5°, b. p. 116—118°/18 mm., gives a semicarbazone, m. p. 206—207° (mixed with a little  $\beta$ -chlorocamphenilone semicarbazone?) and an oxime, m. p. 210—211°.

Pinacolin dichloride with phenol and potassium acetate gives  $\beta$ -chloro- $\gamma$ -dimethyl- $\Delta^a$ -butene, no intramolecular change occurring.

The conversion of 2 : 2-dichlorocamphane into  $\alpha$ -chlorocamphene occurs according to the scheme :

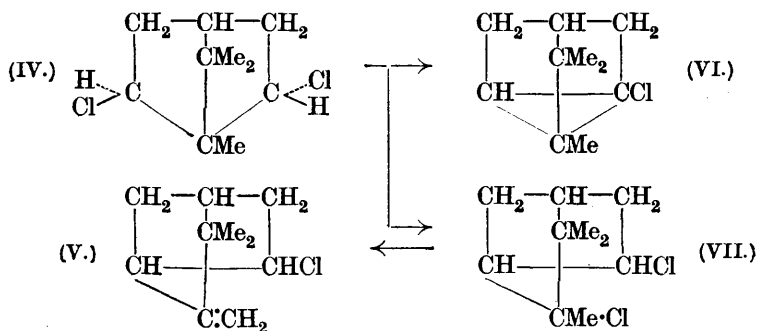


the intermediate  $\alpha$ -chlorocamphene hydrochloride (II) being obtainable by combining  $\alpha$ -chlorocamphene and hydrogen chloride. This hydrochloride is less easily decomposed than camphene hydrochloride, but is completely decomposed by methyl alcohol at 50° in half an hour. This shows that the dichlorocamphane of previous authors contained, at most, traces of  $\alpha$ -chlorocamphene hydrochloride.

The isomerism between pinacolin dichloride and pinacone dichloride is now seen to be similar to that between dichlorocamphane and  $\alpha$ -chlorocamphene hydrochloride :  $\text{CMe}_3 \cdot \text{CMeCl}_2 \longrightarrow \text{CMe}_2\text{Cl} \cdot \text{CMe}_2\text{Cl}$ , so that the present work affords a first confirmation of the authors' views with regard to the pinacolin change (above). Moreover, 2 : 2-dichlorocamphane may undergo the retrograde

change. If, in its preparation, the temperature is allowed to rise, or if impure phosphorus pentachloride is used, an isomeride,  $\beta$ -camphor dichloride (colourless crystals, m. p. 178—179°), is the main product. This substance is easily distinguished from its  $\alpha$ -isomeride by its much smaller rate of reaction with 0.2*N* sodium ethoxide (or methyl alcohol), and is best prepared by treating  $\alpha$ -camphor dichloride, in toluene solution, with stannic chloride until the product no longer reacts rapidly with sodium ethoxide (or methyl alcohol).

On reduction,  $\beta$ -camphor dichloride affords camphane, and, on warming with phenol and potassium acetate, gives a mixture of  $\beta$ -chlorocamphene (V) and chlorotricyclene (VI), as was proved by the fact that this mixture, on reduction with sodium and alcohol, afforded tricyclene and camphene. The latter, but not tricyclene, is oxidised by ozone, and the mixture can thus be identified. Again, the mixture of  $\beta$ -chlorocamphene and chlorotricyclene, on treating with ozone, gave a mixture of chlorotricyclene (m. p. 134—135°, b. p. 194—196°) and  $\beta$ -chlorocamphenilone, needles, m. p. 162—163° (semicarbazone, m. p. 244—245°).  $\beta$ -Camphor dichloride is therefore *trans*-2 : 6-dichlorocamphane (IV), the above reactions being expressed :



$\beta$ -Chlorocamphene hydrochloride (VI) may be obtained from  $\beta$ -chlorocamphene and hydrogen chloride.

The conversion of  $\alpha$ - into  $\beta$ -camphor dichloride is effected under conditions causing the change of camphene hydrochloride into isobornyl chloride. The conversion is rapid in phenol solution, but very slow in most solvents, unless stannic chloride or antimony pentachloride is present. The dielectric constant of the solvent is of far greater influence than the nature of the catalyst, the change being very slow in light petroleum, more rapid in benzene, and still more rapid in the ionising solvents, chlorobenzene and nitrobenzene. The case is evidently one of the intra-ionic isomerisation of esters, no tricyclene compounds being necessarily involved. Into the same class of change may be put the relationships (hitherto unexplained) between fenchyl alcohol,  $\alpha$ -fenchene hydrate, isofenchyl alcohol, and  $\beta$ -fenchene hydrate (these relationships being shown schematically in the paper).

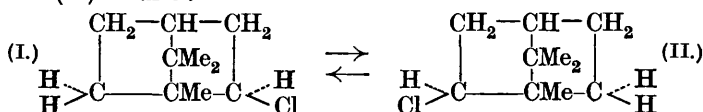
E. E. T.



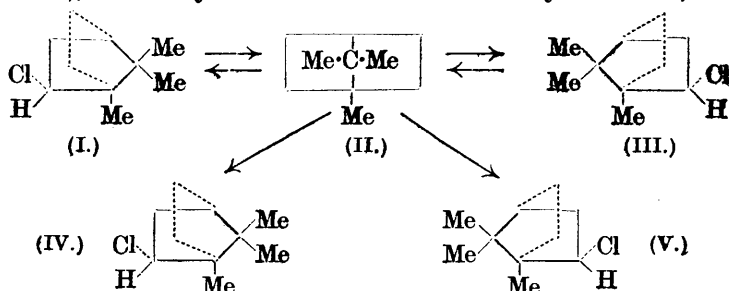
[Intramolecular Displacements of Atoms.] III. Racemisation Phenomena in the Camphor Series. H. MEERWEIN and F. MONTFORT (*Annalen*, 1923, 435, 207—218).—Optically active *isobornyl* esters undergo racemisation under conditions specially favouring the rapid conversion of camphene hydrate esters into *isobornyl* esters (A., 1922, ii, 751). *isobornyl* chloride undergoes complete racemisation in three hours in cresol solution at 20°. In most solvents, racemisation is too slow to follow, and the use of catalysts is to be avoided, owing to their tendency to form additive compounds with the solvent, with resulting decay of activity. To overcome this difficulty, the velocity of racemisation has been measured in cresol, and in mixtures of this solvent with nitromethane, nitrobenzene, bromobenzene, chlorobenzene, ethyl bromide, benzene, light petroleum, benzonitrile, anisole, acetonitrile, and ether. It is found that, except in the cases of acetonitrile, benzonitrile, and anisole, which form additive compounds with cresol, the order of solvents from the point of view of decreasing racemisation velocities is the same as that of the velocity of conversion of camphene hydrochloride into *isobornyl* chloride (*loc. cit.*), which in turn is (approximately) the order of decreasing dielectric constants. In the three cases where additive compounds are formed, the velocity constant tends to decrease. If, however, the solvent-mixture is left for some time before use, a good constant is obtained, somewhat smaller than that otherwise observed.

The parallelism between the two above types of change suggests that the racemisation change, like that of camphene hydrochloride into *isobornyl* chloride, is due to ionisation; two alternative schemes are suggested for the actual mechanism of the former change:

(1) By analogy to the behaviour of  $\alpha$ -camphor dichloride (this vol., i, 188), the chlorine atom in *d-isobornyl* chloride (I) may be assumed to wander from position 2 to position 6, when *l-isobornyl* chloride (II) results:



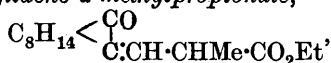
(2) The second suggested scheme is self-explanatory (I to V being, respectively, *d-isobornyl* chloride, the *isobornyl*-ion (plane formula), *l-isobornyl* chloride and *d-* and *l-bornyl* chlorides):



This would account for the observed formation of bornyl chloride during the racemisation of isobornyl chloride (*loc. cit.*). E. E. T.

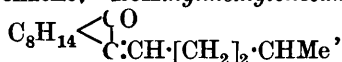
**The Rotation-dispersion of some Homologous Methylene-camphor Derivatives.** H. RUPE and C. COURVOISIER (*Helv. Chim. Acta*, 1923, 6, 1049—1071).—The method described by Rupe and Burckhardt for the synthesis of  $\beta$ -camphorylidene-propionic acid from chloromethylenecamphor and ethyl sodioacetoacetate (A., 1917, i, 141) is a general one, and has now been used for the synthesis of a number of homologous acids, from chloromethylenecamphor and ethyl alkylacetoacetates. Since the acids readily lose carbon dioxide when heated, giving alkylmethylenecamphors, a general method is provided for the synthesis of these compounds. It was found that the optical rotations of these alkylidenecamphors changed when the substances were repeatedly distilled. This phenomenon is to be attributed to *cis-trans*-isomerism, and in the case of ethylmethylenecamphor it is probable that at least one isomeride was obtained in the pure form. This isomeric change during distillation accounts for the different values for the optical rotation of methylmethylenecamphor recorded by different observers. The rotations of the compounds described were measured for four different wave-lengths, and all showed normal rotation-dispersion.

*Ethyl  $\beta$ -camphorylidene- $\alpha$ -methylpropionate,*

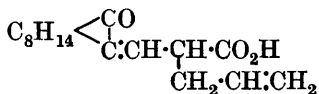


obtained from chloromethylenecamphor and ethyl methylacetoacetate by the action of sodium ethoxide, distils at 164—167°/12 mm. It is hydrolysed by boiling in a mixture of glacial acetic acid and fuming hydrochloric acid. The free  $\beta$ -camphorylidene- $\alpha$ -methylpropionic acid is purified through its calcium salt and by distillation. It forms an oil which crystallises slowly in bunches of needles, m. p. 109—110°. It decomposes at 160°, giving a quantitative yield of *ethylmethylenecamphor* (*n*-propylidenecamphor), b. p. 113—116°,  $[\alpha]_D^{20} +149.81^\circ$ ,  $d_4^{20}$  0.9497 (prepared from non-crystalline acid), or  $[\alpha]_D^{30} +73.26^\circ$ ,  $d_4^{30}$  0.9533 (from the crystalline acid). The latter product partly crystallised in white needles, m. p. 41—43°, giving in benzene  $[\alpha]_D^{20} +22.67^\circ$ ,  $[\alpha]_F/[\alpha]_C$  2.16°. The crystalline product is probably a pure isomeride, but whether *cis* or *trans* it is impossible to say. *Ethyl  $\beta$ -camphorylidene- $\alpha$ -ethylpropionate*, from ethyl ethylacetoacetate and chloromethylenecamphor, is a pale yellow, bitter liquid, b. p. 169°/12 mm. The free acid forms silky, white needles, m. p. 118°; the calcium salt forms bunches of short, white needles. The free acid begins to decompose at 125°, giving a quantitative yield of *n*-butylidenecamphor, b. p. 130—131°/12 mm.,  $[\alpha]_D^{20} +94.58^\circ$ ,  $d_4^{20}$  0.9389,  $[\alpha]_F/[\alpha]_C$  2.36. *Ethyl  $\beta$ -camphorylidene- $\alpha$ -propylpropionate*, from ethyl *n*-propylacetoacetate and chloromethylene camphor, has b. p. 176—179°/9.5 mm.; the free acid has m. p. 95—96°. *n*-Valerylidenecamphor has b. p. 139—141°/12 mm.,  $[\alpha]_D^{20} +116.48^\circ$ ,  $d_4^{20}$  0.9332,  $[\alpha]_F/[\alpha]_C$  2.36. The condensation of ethyl sodioisopropylacetoacetate with chloromethylenecamphor

was unsatisfactory, but ethyl sodiobutylacetoacetate condensed normally, forming *ethyl β-camphorylidene-α-n-butylpropionate*, a yellow oil, b. p. 191—193°/11 mm.; the free acid can be crystallised with difficulty in white needles, m. p. 76°. The acid decomposes at 170°, giving *n-hexylidenecamphor*, b. p. 147—149°/13 mm.,  $[\alpha]_D^{20} + 141.13^\circ$ ,  $d_4^{20}$  0.9252,  $[\alpha]_F/[\alpha]_D$  2.37. *Ethyl β-camphorylidene-α-isobutylpropionate* is a viscous, pale yellow oil, b. p. 183—185°/10 mm.; the free acid forms white needles, m. p. 97—98°; it has  $[\alpha]_D^{20} + 108.74^\circ$  in benzene. *isoAmylmethylenecamphor*,



is a viscous oil, b. p. 144—146°/12 mm.,  $[\alpha]_D^{20} + 133.84^\circ$ ,  $d_4^{20}$  0.9202,  $[\alpha]_F/[\alpha]_D$  2.35. *β-Camphorylidene-α-allylpropionic acid* (annexed formula) has m. p. 95°; its *ethyl* ester is a mobile oil, b. p. 183—185°/11 mm. The acid loses carbon dioxide normally when heated, giving



*α-camphorylidene-Δ<sup>5</sup>-pentene*, a pale yellow, mobile oil having an odour of camphor and garlic, b. p. 136—137°/11 mm.,  $[\alpha]_D^{20} + 144.23^\circ$ ,  $d_4^{20}$  0.9475,  $[\alpha]_F/[\alpha]_D$  2.37. *β-Camphorylidene-α-benzylpropionic acid* forms white, silky crystals, m. p. 127°; the *ethyl* ester is a pale yellow, viscous oil, b. p. 226—228°/12 mm.; the *sodium* salt is very sparingly soluble. Distillation of the acid gives *phenylpropylidenecamphor*, a pale yellow, viscous oil, b. p. 204—206°,  $[\alpha]_D^{20} + 126.92^\circ$ ,  $d_4^{20}$  1.0104,  $[\alpha]_F/[\alpha]_D$  2.36. *Camphorylidene-methylsuccinic acid*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{CO} \\ \diagdown \end{array} \text{C} : \text{CH} \cdot \underset{\text{CH}_2 \cdot \text{CO}_2\text{H}}{\underset{|}{\text{CH}}} \cdot \text{CO}_2\text{H}$ , crystallises in bunches

of small, white needles, m. p. 158°; the *ethyl* ester is a yellow, viscous oil, b. p. 219—222°/12 mm. Distillation of the dicarboxylic acid at 190—215°/12 mm. gives *γ-camphorylidenebutyric acid*, a viscous, yellow oil, b. p. 210—213°/10 mm.,  $[\alpha]_D^{20} + 32.31^\circ$ , in benzene,  $d_4^{20}$  0.9078.

In the course of the work, a number of by-products were obtained. In several cases, the *cis*-form of dicamphoethandiene (A., 1919, i, 335) was isolated from the reaction product. Another class of by-product resulted from the fact that the *β*-camphorylidenepropionic acid and its derivatives form sodium derivatives which can react with a second molecule of chloromethylenecamphor, forming dicamphorylidene derivatives. The following compounds of this type were identified. *Ethyl di(camphorylidenemethyl)-propionate*,  $(\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{CO} \\ \diagdown \end{array} \text{C} : \text{CH})_2 : \text{CMe} \cdot \text{CO}_2\text{Et}$ , m. p. 118°; *ethyl di(camphorylidenemethyl)-n-butyrate*, m. p. 161°; *ethyl di(camphorylidenemethyl)-n-valerate*, m. p. 175°; *ethyl di(camphorylidenemethyl)allylacetate*, m. p. 148°, and *ethyl di(camphorylidenemethyl)succinate*, m. p. 105°.

E. H. R.

#### Action of Ferric Chloride on Hydroxymethylenecamphor.

H. RUPE and M. SCHÄRER (*Helv. Chim. Acta*, 1923, 6, 1072—1076).—When hydroxymethylenecamphor is boiled for some hours in alcoholic solution with ferric chloride, *α*-chlorocamphor is formed;

in the same manner, ferric bromide gives  $\alpha$ -bromocamphor. To explain the reaction, it may be assumed that hydrochloric acid combines with the hydroxymethylenecamphor, forming hydroxymethylchlorocamphor, which reacts with water, forming chlorocamphor and formic acid. Prolonged action of ferric chloride on hydroxymethylenecamphor results in the formation of camphoric anhydride, probably with camphorquinone as an intermediate stage.

E. H. R.

### Preparation of Menthyl Diethylaminoethylcarbamate.

SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 99625; from *Chem. Zentr.*, 1923, iv, 829).—Menthyl halogen formates are treated with at least the molecular quantity of diethylethylenediamine,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_2$ . *Menthyl diethylaminoethylcarbamate*, thus prepared from an ethereal solution of menthyl chloroformate and an aqueous solution of diethylethylenediamine, with agitation and cooling, is an oil having b. p.  $142^\circ/0.015$  mm.

G. W. R.

### The Action of Phenylhydrazine on Pinene Nitrosochloride.

R. E. KREMERS (*J. Amer. Pharm. Assoc.*, 1922, **11**, 604—606).—Phenylhydrazine and pinene nitrosochloride, when allowed to react in 95% ethyl alcohol, yielded phenylhydrazine hydrochloride, an unidentified substance, yellow crystals, m. p.  $147$ — $148^\circ$ , and a substance,  $\text{C}_{16}\text{H}_{21}\text{N}_2$ , faintly yellow, hard prisms, m. p.  $148$ — $150^\circ$ .

CHEMICAL ABSTRACTS.

**Stick-lac.** A. TSCHIRCH and F. LÜDY, jun. (*Helv. Chim. Acta*, 1923, **6**, 994—1008; cf. Tschirch and Farner, A., 1899, i, 446).—A systematic investigation has been made of Indian stick-lac, the resin formed by a species of louse, *Tachardia lacca*, parasitic on certain trees in the East. The aqueous extract contains one of the dyes present in the stick-lac; this is precipitated by lead acetate as a violet lake. The filtrate contains dextrose and lævulose, besides albumin; the ash from the evaporated filtrate contains nitrogen, sulphur, potassium, and calcium. The lac appears to contain invert-sugar, probably formed enzymatically by the insect from the sucrose of the tree. The red dye, laccaic acid, is obtained from the lead acetate precipitate by extraction with alcohol containing hydrochloric acid; it crystallises in stout, red prisms. Dimroth and Goldschmidt (A., 1913, i, 981) failed to prove that the dye is an anthraquinone derivative; this has now been done by distillation with zinc dust. In dilute alcohol, laccaic acid shows absorption bands at  $\lambda$  0.545—0.520  $\mu$  and 0.510—0.488  $\mu$ . Since the dye is formed in the *Tachardia* by a yeast-like organism, it is interesting to find that its absorption bands are very similar to those shown by the colouring matters from red yeasts and bacteria. In concentrated sulphuric acid, laccaic acid dissolves with a carmine-red colour, showing the bands  $\lambda$  0.590—0.560  $\mu$ , 0.540—0.520  $\mu$ , and 0.505—0.490  $\mu$ , and in sodium hydroxide solution its colour is reddish-violet with the three bands  $\lambda$  0.610—0.575  $\mu$ , 0.555—0.533  $\mu$ , and 0.510—0.490  $\mu$ . The dye is a good indicator, the change from yellow (acid) to violet (alkali) being sharp. Alkaline solutions of the dye are unstable. Dyeings on silk and wool from an acid bath

are very fast to light. The constitution of the dye is as yet unknown. Although it is probably a glucoside, no sugar could be obtained from it by hydrolysis. Extraction of the residue from the aqueous extraction of the stick-lac with cold alcohol removes the resin, the perfume, and a second dye, erythrolaccin. The alcoholic extract is poured into dilute hydrochloric acid and the precipitate filtered off, dried, and extracted with ether. The ethereal extract is evaporated, and from the residual resinous oil the erythrolaccin crystallises in yellow leaflets. The crystals can be freed from resin by means of chloroform. The dye can be sublimed, forming red, felted crystals. Its yellow solution in an ether-alcohol mixture has a band at  $\lambda$  0.510—0.485  $\mu$ ; with sodium hydroxide, there are two bands, at  $\lambda$  0.615—0.590  $\mu$  and 0.572—0.548  $\mu$ . The bluish-violet solution in concentrated sulphuric acid shows four bands at  $\lambda$  0.680—0.640  $\mu$ , 0.610—0.590  $\mu$ , 0.560—0.540  $\mu$ , and 0.525—0.500  $\mu$ . It forms a *tetra-acetyl* derivative, green, oblique tablets, and is probably a *tetrahydroxymethylanthraquinone*. From an alkaline solution of the resins, after separation of the erythrolaccin, ether extracts the perfume, which crystallises in tablets having the characteristic shellac odour. The portion of the resins soluble in ether contains, besides aleuritic acid, shown by Harries and Nagel to be a trihydroxypalmitic acid (A., 1922, i, 522), a *monohydroxypalmitic acid*, m. p. 76.5—77°, and probably other fatty acids. These are probably present as lactides. The resin insoluble in ether is soluble in hot alcohol, and can also be hydrolysed, giving aleuritic acid. *Ethyl aleurate* crystallises in long needles, m. p. 57—58°. The residue from the stick-lac, when extracted with boiling alcohol, gives a wax crystallising in colourless leaflets, m. p. 82°, from which, by hydrolysis, an alcohol, *tachardiacerol*,  $C_{24}H_{50}O$ , m. p. 81—82°, and an *acid*, m. p. 74—76°, were obtained. The remainder of the wax was extracted by boiling benzene; this fraction has been examined by Gascard (A., 1914, i, 1045). After these extractions, the residue of the stick-lac consists only of the skeleton of the *Tachardia* with a little adsorbed laccaic acid.

E. H. R.

**Scission of Potassium Atractylate.** F. ANGELICO and F. MONFORTE (*Gazzetta*, 1923, 53, 808—812; cf. A., 1907, ii, 122; 1910, i, 403).—Potassium atractylate, the glucoside of *Atractylis gummifera*, or either of its decomposition products, *atractyliretin* and *atractyligenin*, serves as an excellent colour reagent for aromatic hydroxy-aldehydes in general. The reagent is treated first with a little concentrated sulphuric acid and, after a few minutes, with a drop of an aqueous solution of the hydroxy-aldehyde; a red coloration similar to that of rosolic acid is obtained, the exact tint varying somewhat with the aldehyde employed.

Estimation of the sulphur and potassium present in, and of the valeric acid and dextrose formed on hydrolysis of, a sample of potassium atractylate gives results in agreement with the formula  $C_{30}H_{52}O_{18}S_2K_2$ . Atractyligenin,  $C_{14}H_{22}O_4$ , obtained by hydrolysing the glucoside and afterwards acidifying the liquid, forms

white crystals, m. p.  $168^{\circ}$ , and does not reduce Fehling's solution. Atractyliretin, prepared by prolonged boiling of the glucoside with normal sulphuric acid, is obtained as a white compound which hardens when it is triturated with water and then forms a white powder, m. p. about  $190^{\circ}$  (decomp.); like the isomeric atractyligenin, it exhibits acid properties and does not react with hydroxylamine or phenylhydrazine.

T. H. P.

**Loganin or Meliatin?** M. BRIDEL (*Bull. Soc. Chim. biol.*, 1923, 5, 801—805).—The work of Rosenthaler recently has shown that the glucoside loganin, originally described by Dunstan and Short (A., 1885, 395), is a mixture of meliatin (A., 1910, i, 692) and another substance not identified. The name loganin has therefore no longer any significance.

C. R. H.

**The Saponins of the Sarsaparilla Root.** H. P. KAUFMANN and C. FUCHS (*Ber.*, 1923, 56, [B], 2527—2533).—An investigation of the saponins of sarsaparilla root imported from Honduras in 1918; the date of harvesting is uncertain.

The ash contains the following substances expressed as percentages of the dried root:  $\text{SiO}_2$ , 1.25;  $\text{Al}_2\text{O}_3$ , 0.79;  $\text{CaO}$ , 0.57;  $\text{MgO}$ , 0.50;  $\text{K}_2\text{O}$ , 1.51;  $\text{Cl}$ , 0.46.

The finely divided root is extracted successively with chloroform, light petroleum, benzene, ether, anhydrous alcohol, and aqueous alcohol (50%). The light petroleum extract contains cetyl alcohol. The saponins are isolated as a form soluble in absolute alcohol (saponin A) and an insoluble form (saponin B). Saponin A is purified by dialysis against running water, whereby it is obtained as a fawn-coloured powder which cannot be caused to crystallise. The presence of considerable amounts of dextrose in the sarsaparilla root considered in conjunction with the ready hydrolysis of the saponins by acids justifies the conclusion that the primary crystalline glucosides are partly changed by fermentative fission to amorphous, secondary glucosides; the contradictory results of previous investigations are probably due to the use of fresh or stored material. Saponin B is similarly purified by dialysis, which, however, does not remove a considerable content of aluminium, magnesium, and calcium, which are probably present in combination with galacturonic acid. These can be eliminated by solution of saponin B in alkali and precipitation with acid. The purified material then closely resembles saponin A. The composition of the products varies somewhat in different preparations; it appears that a loosely combined saccharide component is removed during the protracted extraction.

The saponins are hydrolysed by sulphuric acid (3—5%), whereby possibly galacturonic acid, glucose, pentoses, and methylpentoses are obtained. The presence of galactose, arabinose, or rhamnose could not be established. The sapogenin is freed from dark coloured impurities by solution in alcohol and precipitation with sodium ethoxide, whereby ultimately sarsapogenin,  $\text{C}_{26}\text{H}_{42}\text{O}_5 \cdot \text{H}_2\text{O}$ , slender, colourless needles, m. p.  $183^{\circ}$  (corr.),  $[\alpha]_D^{25} -58.68^{\circ}$  in absolute methyl alcohol, is isolated; the substance is identical with that

obtained by Power and Solway (T., 1914, 105, 201) from Jamaica sarsaparilla. The substance contains one hydroxyl group, since it yields a monoacetate, colourless needles, m. p. 127°,  $[\alpha]_D^{18} - 57.1^\circ$  when dissolved in chloroform (Power and Solway, *loc. cit.*, give m. p. 137°). The acetyl compound is hydrolysed by barium hydroxide to a substance,  $C_{26}H_{42}O_3 \cdot H_2O$ , m. p. 122°; possibly racemisation or intramolecular transformation takes place. The *monobenzoyl* derivative forms colourless crystals, m. p. 124°. The presence of a carboxyl, carbonyl, alkyloxy-, or lactonic group could not be established in the usual manner. The remaining two oxygen atoms must therefore be present in the molecule as a stable bridge. Distillation with zinc dust and treatment of the distillate with steam gives a diterpene,  $C_{10}H_{16}$ , b. p. 204—206°/748 mm., (slight decomp.). H. W.

**The Influence of Oxalic Acid on the Formation of Aniline-black.** J. PICCARD (*Helv. Chim. Acta*, 1923, 6, 1029—1032).—The oxidation of a solution of aniline hydrochloride by sodium dichromate is accelerated about forty times by the addition of a small quantity of oxalic acid to the solution. The mechanism of the accelerating action has not been elucidated. The printing of Aniline-black on cotton or silk is facilitated by impregnating the material with aniline oxalate. [Cf. B., 91.]; E. H. R.

**Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. IV. Reduction of Furfuraldehyde and its Derivatives.** W. E. KAUFMANN and R. ADAMS (*J. Amer. Chem. Soc.*, 1923, 45, 3029—3044; cf. A., 1922, ii, 558; 1923, ii, 310, 773).—When furfuraldehyde in alcoholic solution was reduced with hydrogen under 1—2 atm. pressure in the presence of platinum black, the first molecular equivalent of hydrogen absorbed gave a quantitative yield of furfuryl alcohol. The latter then reacted with hydrogen in four different ways to produce tetrahydrofurfuryl alcohol, *n*-amyl alcohol, pentane- $\alpha$ -diol, and *pentane- $\alpha\beta$ -diol*. The last-named substance,  $CH_2Me \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$ , boiled at 210.5—211.5°/751 mm.,  $n_D^{19} 1.4412$ ,  $d_{20}^{20} 0.9802$ . Its *diacetate* boiled at 219—220°/748 mm.,  $n_D^{19} 1.4202$ ,  $d_{20}^{20} 1.0148$ . The catalyst made from spectroscopically pure chloroplatinic acid was very inefficient and the addition of ferrous chloride increased the rate of reduction to a maximum beyond which the rate decreased rapidly. This decrease in the case of the reduction of the aldehyde group was much less than that of the subsequent reduction of the ethylene double bonds. After the absorption of each molecular equivalent of hydrogen the catalyst was reactivated by shaking with air or oxygen. Pyromucic acid gave tetrahydropyromucic acid, m. p. 21°, and ethyl pyromucate gave ethyl tetrahydropyromucate, b. p. 82°/11 mm.,  $\beta$ -furylacrylic acid gave  $\beta$ -tetrahydrofurylpropionic acid, b. p. 135—137°/4 mm., furoin gave  $\alpha\beta$ -dihydroxy- $\alpha\beta$ -ditetrahydrofuryl-ethane,  $C_4H_7O \cdot CH(OH) \cdot CH(OH) \cdot C_4H_7O$ , furfurylideneacetone gave  $\alpha$ -tetrahydrofurylbutan- $\gamma$ -one and  $\alpha$ -tetrahydrofurylbutan- $\gamma$ -ol, b. p. 93—94°/2 mm., furfurylideneacetophenone gave  $\gamma$ -phenyl-

tetrahydrofurylpropan- $\gamma$ -one, b. p. 153—154°/2 mm., and  $\gamma$ -phenyl-tetrahydrofurylpropan- $\gamma$ -ol, b. p. 167—168°/2 mm. F. B.

**Hydroxymethylfurfuraldehyde from Cellulose and its Derivatives.** E. HEUSER and W. SCHOTT (*Cellulosechemie*, 1923, 4, 85—89).—The hydroxymethylfurfuraldehyde which is formed on heating cellulose with 5% oxalic acid solution in an autoclave at 180° for half an hour has been shown to be identical with the isomeric modification described by Kiermayer. The following derivatives were prepared for this identification: Semicarbazone, m. p. 235—236°; phenylhydrazone, m. p. 140°; anhydride, m. p. 112°; *anti*-aldoxime, m. p. 76°; *syn*-aldoxime, m. p. 106°. The normal modification prepared by Erdmann from bromomethylfurfuraldehyde (from lævulose) gave a semicarbazone melting at 216°. This modification is converted into the isomeride by heating with 0.3% oxalic acid in a sealed tube. The hydroxymethylfurfuraldehyde is extracted from the filtered digestion liquor by shaking with ethyl acetate. The quantity of the aldehyde increases with the degree of hydrolysis of the cellulose; thus normal cotton yielded 15.36% of dextrose and only 0.82% of the aldehyde, viscose cellulose gave 63.21% of dextrose and 5.16% of the aldehyde, whilst hydrocellulose prepared from viscose according to the prescription of Knoevenagel and Busch yielded 68.47% of dextrose and 10.84% of hydroxymethylfurfuraldehyde. The presence of the aldehyde does not interfere with the estimation of the dextrose by the fermentation method. J. F. B.

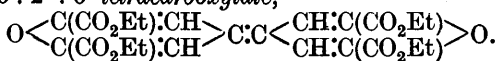
**Preparation of Chromans.** L. CLAISEN (D.R.-P. 374142; from *Chem. Zentr.*, 1923, iv, 725; cf. Claisen and Tietze, A., 1921, i, 263—264).—Phenols are treated with butadienes in the presence of acid condensing reagents. Phenol and isoprene give 2:2-dimethylchroman. *p*-Cresol and isoprene give 2:2:6-trimethylchroman, a colourless oil with a strong odour, b. p. 244—244.5°;  $d_{15}^{25}$  0.9920. *p*-Cresol and  $\beta\gamma$ -dimethylbutadiene give 2:2:3:6-tetramethylchroman, an oil, b. p. 257—258°;  $d_{15}^{25}$  0.9813. *m*-Xylenol and  $\beta\gamma$ -dimethylbutadiene give a pentamethylchroman, b. p. 263—265°. G. W. R.

**The Reduction of Chrysin.** J. PICCARD and E. OPPENHEIM (*Helv. Chim. Acta*, 1923, 6, 1009—1011).—Chrysin is reduced by magnesium in glacial acetic acid solution, forming a compound which is probably the hydrol of chrysin,  $C_{15}H_{12}O_4$ . It forms an amorphous, red powder, m. p. 210—226°, soluble in concentrated sulphuric acid and in alkalis with a yellow colour. It does not appear to be analogous to the violet substance obtained by Baeyer and Piccard by the reduction of dimethylpyrone (A., 1911, i, 901). E. H. R.

**Dipyrroles.** F. ARNDT and P. NACHTWEY (*Ber.*, 1923, 56, [B], 2406—2409).—When ethyl acetonedioxalate or ethyl chelidonate is boiled in benzene solution with phosphorus pentasulphide, a com-



pound is formed probably having the constitution *ethyl 4:4'-dipyrylene-2:6:2':6'-tetracarboxylate*,



It forms slender, cinnamon to carmine-red needles, m. p. 203—204°. In concentrated sulphuric acid, it dissolves with a deep red colour, changing slowly to deep green, but the ester is recovered from the green solution unchanged. *4:4'-Dipyrylene-2:6:2':6'-tetracarboxylic acid* forms a brownish-red, infusible powder; the sodium salt,  $\text{C}_{14}\text{H}_4\text{O}_{10}\text{Na}_4 \cdot 3\text{H}_2\text{O}$ , is brownish-red. The formation of the above tetracarboxylate is preceded by that of an intermediate compound, *ethyl thiochelidonate*,  $\text{S}:\text{C} < \begin{array}{c} \text{CH}:\text{C}(\text{CO}_2\text{Et}) \\ \text{CH}:\text{C}(\text{CO}_2\text{Et}) \end{array} > \text{O}$ , bluish-green needles, m. p. 51°, which on heating decomposes into the ethyl dipyrylenetetracarboxylate and free sulphur. The thiochelidonate is conveniently isolated in the form of an additive compound with mercuric chloride, a deep yellow precipitate, m. p. 135—137°. E. H. R.

#### A Molecular Compound of Caffeine and Salicylic Acid.

A. REGENBOGEN and N. SCHOORL (*Pharm. Weekblad*, 1924, **61**, 34—36).—The melting-point curve for mixtures of the two substances shows the existence of an equimolecular compound with melting point about 135°. By fusing together equal molecular proportions of the components, and recrystallising from water, the compound is obtained as fine needles, m. p. 137°; it is unaltered by recrystallisation from chloroform, but decomposes in alcoholic solution. Its existence explains the solubility of caffeine in aqueous solutions of sodium salicylate. S. I. L.

**Strychnos Alkaloids. XXXXI. Various Observations on Derivatives of Brucine.** H. LEUCHS, W. GLADKORN, and E. HELLRIEGEL (*Ber.*, 1923, **56**, [B], 2472—2477).—Dihydrobrucinonic acid is decomposed by prolonged treatment with methyl-alcoholic ammonia at 100° into *isobrucinolone*, an amorphous substance, and aminodihydrobrucinolone.

The conversion of *isobrucinolone* by 5*N* nitric acid into the red quinone,  $\text{C}_{19}\text{H}_{16}\text{O}_5\text{N}_2$ , decomp. about 300°, is described in detail; the substance is reduced by sulphur dioxide to the corresponding *quinol*,  $\text{C}_{19}\text{H}_{18}\text{O}_5\text{N}_2$ , needles or prisms, m. p. 325—328° (decomp.) after darkening at 320°.

The oxidation of acetyl*isobrucinolone* dissolved in acetone by potassium permanganate does not take place smoothly and gives *dihydroxyacetyldihydroisobrucinolone*,  $\text{C}_{23}\text{H}_{26}\text{O}_8\text{N}_2$ , slender needles, m. p. 245°, as sole crystalline product in yield which does not exceed 12%. The acidic products of the oxidation are amorphous, but show the expected properties such as the red coloration with ferric chloride, the loss of carbon dioxide when heated, the decomposition by acidic hydrolysis into a hydrochloride (probably curbine hydrochloride in place of the expected *isocurbine* salt), and a nitrogen-free acid, apparently malonic acid. It therefore appears probable that *iso*-

brucinolone contains the same oxidisable group,  $\text{N}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{C}_2$ , as brucinolone-*b*, and yields a substance which is a semi-amide of malonic acid and a ketone. The study of the oxidation of *benzoyl-isobrucinolone*,  $\text{C}_{28}\text{H}_{26}\text{O}_6\text{N}_2$ , very slender needles, m. p.  $250^\circ$  after darkening at  $240^\circ$  when rapidly heated,  $[\alpha]_D^{25} +99^\circ$  in glacial acetic acid solution, did not lead to more favourable results.

Brucinolic acid is converted by methyl-alcoholic ammonia at  $100^\circ$  into brucinolone, glycollic acid, and aminodihydrobrucinolone.

Brucinolone-*b* is converted by benzoic anhydride and sodium benzoate at  $100^\circ$  into *benzoylbrucinolone-b*,  $\text{C}_{28}\text{H}_{26}\text{O}_6\text{N}_2$ , prismatic aggregates, m. p.  $235\text{--}236^\circ$ ,  $[\alpha]_D^{25} -148^\circ$  in glacial acetic acid solution, and by phosphorus pentachloride in the presence of chloroform at  $-20^\circ$  and treatment of the product with ethyl alcohol into *brucinolone diethyl phosphate*,  $\text{PO}(\text{OEt})_2\cdot\text{O}\cdot\text{C}_{21}\text{H}_{21}\text{O}_4\text{N}_2$ , large, colourless leaflets, m. p.  $232\text{--}235^\circ$ .

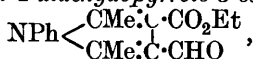
Brucinolone hydrate I and phenylcarbimide yield the compound  $\text{C}_{28}\text{H}_{29}\text{O}_7\text{N}_3\cdot\text{H}_2\text{O}$ , coarse, domatic prisms, m. p.  $191\text{--}192^\circ$  (decomp.).

Dihydroxydihydroacetylbrucinolone is converted by acetic anhydride and anhydrous sodium acetate at  $100^\circ$  into *diacetyldihydroxydihydrobrucinolone-b*,  $\text{C}_{25}\text{H}_{18}\text{O}_9\text{N}_2$ , colourless crystals, m. p. about  $280^\circ$  (decomp.) after darkening and softening at  $240^\circ$ ,  $[\alpha]_D^{20} -149\cdot2^\circ$  in glacial acetic acid solution.

The oximation of *ON*-diacetylcurbin by a boiling alcoholic solution of hydroxylamine causes the loss of the *O*-acetyl group and formation of *N*-acetylcurbinoxime,  $\text{C}_{20}\text{H}_{23}\text{O}_8\text{N}_2$ , lustrous, rectangular prisms, m. p.  $185\text{--}187^\circ$ . The attempted isomerisation of the oxime by acetyl chloride at  $100^\circ$  leads to the production of *triacetylcurbin-oxime*,  $\text{C}_{24}\text{H}_{27}\text{O}_8\text{N}_3$ , double pyramids, m. p.  $275^\circ$  (decomp.) after becoming yellow at  $250^\circ$ .  
H. W.

**The Behaviour of Eucupine and Uric Acid Gels during Dialysis. The Distribution of Ions.** P. RONA and W. B. MEYER (*Biochem. Z.*, 1923, **143**, 161—178).—In dialysing eucupine dihydrochloride ( $\text{C}_{24}\text{H}_{34}\text{O}_9\text{N}_2\cdot 2\text{HCl} + 2\text{H}_2\text{O}$ ) considerable membrane adsorption occurs. This is greater with collodion membranes than when Schleicher-Schüll shells are used, but diminishes with increasing acidity and disappears at  $p_{\text{H}}$  4. The adsorption may be overcome by previously saturating the membrane with eucupine. Eucupine dihydrochloride forms a true solution. Eucupine acetate gel and lithium urate gel are partly colloidal (60%) and partly true solutions. In dialysing the urate gel, lithium and uric acid pass into the external fluid in equimolecular concentrations. The transition between super-saturated uric acid solution in lithium hydroxide and lithium urate gel is sharp, the former behaving as a true solution. On dialysing urate against potassium chloride, the potassium diffuses inwards and the lithium outwards in proportional amounts, whilst the external uric acid concentration diminishes with increasing amounts of potassium chloride. The system illustrates the unequal distribution of electrolytes on the two sides of a membrane with a non-diffusible colloidal ion on one side.  
J. P.

**Some New N-Substituted Pyrrole-aldehydes ; and Oxindole-aldehyde.** HANS FISCHER and K. SMEYKAL (*Ber.*, 1923, 56, [B], 2368—2378).—The Gattermann aldehyde synthesis (cf. Fischer and Zerweck, A., 1922, i, 758) has been applied to the synthesis of a number of N-substituted pyrrole-aldehydes. *Ethyl 1-phenyl-2 : 5-dimethyl-4-aldehydopyrrole-3-carboxylate*,



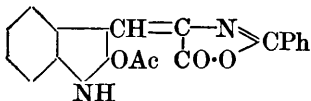
from ethyl 1-phenyl-2 : 5-dimethylpyrrole-3-carboxylate, forms colourless crystals, m. p. 82°; the free acid has m. p. 240°. The ethyl ester forms a *phenylhydrazone*, colourless crystals, m. p. 156—160°, and an *oxime*, m. p. 150°. *Ethyl 1-p-tolyl-2 : 5-dimethylpyrrole-3-carboxylate*, from *p*-toluidine, chloroacetone, and ethyl acetoacetate, forms colourless crystals, m. p. 55°; the free acid forms large crystals, m. p. 240°. By Gattermann's synthesis with hydrocyanic acid, the ester gives *ethyl 1-p-tolyl-2 : 5-dimethyl-4-aldehydopyrrole-3-carboxylate*, white, glistening crystals, m. p. 133°; the *phenylhydrazone* forms colourless, strongly refracting crystals, m. p. 92—96°; the *oxime* forms glistening leaflets, m. p. 138°, and the free acid forms colourless needles, m. p. 212°. The *semicarbazone* forms colourless needles, m. p. 240°. *Ethyl 1 : 2 : 5-trimethyl-4-aldehydopyrrole-3-carboxylate* forms long, white needles, m. p. 97°; the *phenylhydrazone* forms fine needles, m. p. 159—161°.

It has been suggested by Alessandri (A., 1915, i, 452) that a number of  $\alpha$ -pyrrole-aldehydes have a hydroxymethylene structure, since they do not react with dihydroxyammonia, whilst the corresponding N-substituted  $\alpha$ -pyrrole-aldehydes do so react. It is now found that neither ethyl 2 : 5-dimethyl-4-aldehydopyrrole-3-carboxylate, ethyl 2 : 4-dimethyl-3-aldehydopyrrole-5-carboxylate, nor the new N-substituted pyrrole-aldehydes reacts with benzenesulphohydroxamic acid. Probably all are true aldehydes, although not giving all the typical aldehyde reactions. There may be an equilibrium between the two forms.

The N-substituted pyrrole-aldehydes react with nitroacetic acid, with loss of carbon dioxide, forming nitrovinylpyrroles, and with ethyl cyanoacetate to give substituted vinylpyrroles. *Ethyl 1-phenyl-2 : 5-dimethyl-4-nitrovinylpyrrole-3-carboxylate* forms yellow crystals, m. p. 130—132°; the corresponding 1-p-tolyl compound forms glistening yellow leaflets, m. p. 125—133°. *Ethyl 2 : 5-dimethyl-4-[ $\omega$ -cyano- $\omega$ -carbethoxyvinyl]pyrrole-3-carboxylate* forms white needles, m. p. 139°. The 1-phenyl derivative forms colourless needles, m. p. 110°, and the 1-p-tolyl derivative, white needles, m. p. 121°.

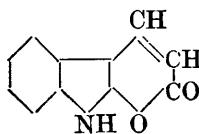
Oxindole-3-aldehyde condenses with hippuric acid to form an *azlactone* which forms an *acetyl* derivative, stout prisms, m. p. 185°.

It may have the annexed formula. Hydrolysis experiments failed to give an unsaturated acid, but merely removed the acetyl group, which may therefore be attached to the nitrogen.



The hydrolysed product had m. p. 260°. N-Methyloxindole-  
h\*

3-aldehyde also formed an *acetylazlactone*, glistening red needles, m. p. 205°, which when hydrolysed gave the *azlactone*, red needles, m. p. 287°. The acetyl group cannot, in this case, be attached to nitrogen, but it is still doubtful what positions are occupied in the molecule by the acetyl and benzoyl groups. Oxindole-3-aldehyde



gives by Perkin's reaction a compound,  $C_{11}H_7O_2N$ , yellow tablets, m. p. 247°, probably having the annexed coumarin formula. It forms a crystalline, molecular compound with 1 mol. of aniline, m. p. 160°. Oxindole-3-aldehyde forms an *acetyl* derivative, m. p. 185°, and a *benzoyl* derivative, m. p. 196°; *N*-methyloxindole-3-aldehyde gives an *acetyl* derivative, yellow needles, m. p. 135°, and a *benzoyl* derivative, greenish-yellow needles, m. p. 147°.

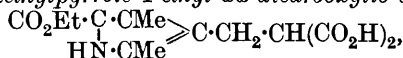
E. H. R.

**A New Synthesis of Hæmatic Acid.** W. KÜSTER and H. MAURER (*Ber.*, 1923, 56, [B], 2478—2481).—A new synthesis of hæmatic acid starting from ethyl 4-aldehydo-3:5-dimethylpyrrole-2-carboxylate (cf. Fischer, Weiss, and Schubert, A., 1923, i, 703) is recorded. The preliminary work is carried out with the more accessible ethyl 2-aldehydo-3:5-dimethylpyrrole-4-carboxylate.

Ethyl 2-aldehydo-3:5-dimethylpyrrole-4-carboxylate is condensed with ethyl malonate in the presence of acetic anhydride at a temperature not exceeding 150° to *ethyl 4-carbethoxy-3:5-dimethylpyrrole-2-vinyl- $\omega\omega$ -dicarboxylate*, small, yellow needles, m. p. 86°, which is reduced and partly hydrolysed by sodium amalgam to *4-carbethoxy-3:5-dimethylpyrrole-2-ethyl- $\omega\omega$ -dicarboxylic acid*,  $C_{13}H_{17}O_6N$ , a colourless powder, m. p. 218°. The acid loses carbon dioxide when heated and passes into *4-carbethoxy-3:5-dimethylpyrrole-2-propionic acid*, slender, colourless needles or rectangular prisms, m. p. 120°; the *iron* and *copper* salts are described.

Ethyl 4-aldehydo-3:5-dimethylpyrrole-2-carboxylate and ethyl malonate yield *ethyl 2-carbethoxy-3:5-dimethylpyrrole-4-vinyl- $\omega\omega$ -dicarboxylate*,  $CO_2Et \cdot \underset{HN \cdot CMe}{\underset{|}{C}} \cdot CMe \geq C \cdot CH \cdot C(CO_2Et)_2$ , colourless needles, m. p.

99—100°, which is transformed by sodium amalgam into *2-carbethoxy-3:5-dimethylpyrrole-4-ethyl- $\omega\omega$ -dicarboxylic acid*,



colourless leaflets or thick needles, m. p. 184—185° (decomp.); the *ferric* and *calcium* salts are described. The acid passes when heated above its melting point into *2-carbethoxy-3:5-dimethylpyrrole-4-propionic acid*,  $CO_2Et \cdot \underset{HN \cdot CMe}{\underset{|}{C}} \cdot CMe \geq C \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , colour-

less leaflets, m. p. 152°, the *silver* and *ferric* salts of which are described. Oxidation of 2-carbethoxy-3:5-dimethylpyrrole-4-propionic acid by chromic acid in glacial acetic acid solution gives the imide of hæmatic acid,  $\underset{NH-CO}{\underset{|}{C}} \cdot O \cdot CMe \geq C \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , which is

characterised by hydrolysis by means of barium hydroxide to the anhydride, m. p. 97°.

H. W.

**Pyrroles.** F. ANGELICO and F. MONFORTE (*Gazzetta*, 1923, 53, 795—800).—It has been shown (A., 1905, i, 938; 1909, i, 122; 1910, i, 444; 1911, i, 1032) that, when boiled with dilute sulphuric acid, diazotriphenylpyrrole yields azinetriphenylpyrrole. Further experiments show that diazotriphenylpyrrole is a highly stable compound and is not altered by iodine, sodium thiosulphate, alcohol, or organic acids. With mineral acids, it yields salts, and with nitric acid, also nitro-derivatives. Energetic oxidising agents cause profound decomposition of the molecule. Reducing agents such as zinc dust and acetic acid, zinc dust and ammonium chloride, ammonium sulphide, or hydroxylamine convert it into the amino-compound, whilst by the action of hydrogen in presence of palladium black it is converted into ammonia and triphenylpyrroline; the latter reduction resembles that of diphenyldiazomethane, which yields principally diphenylmethane and nitrogen (cf. Staudinger, Gaule, and Siegwart, A., 1921, i, 323), but it has not been found possible to convert diazotriphenylpyrrole by reduction into the corresponding hydrazine, although this is possible with certain of the aliphatic diazo-compounds. Like both the corresponding indole derivative and various aromatic diazo-compounds, diazotriphenylpyrrole is extremely sensitive to the action of light, this causing it to darken and to undergo transformation into a compound which has a lower melting point and a diminished proportion of nitrogen, but has not yet been identified.

2 : 5-Diphenylpyrrole-3-carboxylic acid readily yields the corresponding oximino-compound, but in the passage to the amine the carboxyl group is eliminated in the cold. Hence, to prepare the diazo-compound it is not necessary to convert the carboxylic acid into 2 : 3-diphenylpyrrole itself.

The compound,  $C_{22}H_{13}O_4N_5$ , obtained by the action of concentrated nitric acid in the cold on diazotriphenylpyrrole, forms crystals, m. p.  $185^\circ$ . If a mixture of nitric and sulphuric acids is employed, the product forms crystals, m. p.  $110^\circ$ , and contains rather more nitrogen than is represented by the above formula.

Oximino-2 : 5-diphenylpyrrole-3-carboxylic acid,  $C_{17}H_{13}O_3N_2$ , crystallises in golden-yellow scales, m. p.  $212^\circ$  (decomp.), and yields aminodiphenylpyrrole, m. p.  $186^\circ$ , when reduced in alcoholic solution by means of ammonium sulphide.

T. H. P.

**A Complex Silver Fluoride.** A. BURADA (*Ann. Sci. Univ. Jassy*, 1923, 12, 33—34; from *Chem. Zentr.*, 1923, iii, 1225).—By addition to a solution of silver fluoride of the theoretical quantity of pyridine and evaporation in a vacuum over sulphuric acid with exclusion of light, a compound is obtained of the composition  $AgF \cdot 2C_5H_5N \cdot 5H_2O$ ; it forms colourless, transparent crystals, unstable in air and light. When heated, it is decomposed completely leaving a residue of metallic silver.

G. W. R.

**Preparation of Amino-substitution Products of Pyridine and Quinoline Series.** A. E. TSCHITSCHIBABIN (D.R.-P. 374291; from *Chem. Zentr.*, 1923, iv, 725; cf., A., 1923, i, 1121).—Pyridine,

quinoline, their homologues or derivatives, or other bases containing the pyridine ring, or natural organic bases such as alkaloids, are treated in the absence or presence of indifferent solvents, with sodamide, or compounds of the general formula  $R \cdot NHNa$ , where  $R$ =aryl, alkyl, or a heterocyclic basic residue such as pyridyl or quinolyl, or mixtures of sodium with primary amines. After treatment of the products of reaction with water, the amino-compounds obtained are separated by distillation or other suitable method. The reactions are shown by the following equations: (i)  $C_5H_5N + NH_2Na = C_5H_4N \cdot NHNa + H_2$ , (ii)  $C_5H_4N \cdot NHNa + H_2O = C_5H_4N \cdot NH_2 + NaOH$ , (iii)  $C_5H_4N \cdot NHNa + C_5H_5N = (C_5H_4N)_2NNa + H_2$ , (iv)  $(C_5H_4N)_2NNa + H_2O = (C_5H_4N)_2NH + NaOH$ . The amino-group goes into the ortho-position relatively to the pyridine nitrogen. 2-Aminopyridine has m. p.  $56^\circ$ . Other compounds mentioned are: 6-amino-2-methylpyridine, a deliquescent substance, m. p.  $36.5^\circ$ , b. p.  $208-209^\circ$ ; 2-aminoquinoline, leaflets, m. p.  $129^\circ$ ; 2:6-diaminopyridine, obtained by heating pyridine and sodamide in the presence of vaseline oil at  $125^\circ$  and then at  $180^\circ$ , leaflets, m. p.  $121.5^\circ$ ; 2-anilinopyridine, from pyridine and sodium anilide, crystals, m. p.  $108^\circ$ ; 2:2-dipyridylamine, small needles, m. p.  $95^\circ$  (stable form), m. p.  $86-87^\circ$  (labile form); aminonicotine, crystals, m. p.  $125-126^\circ$ ; 6-amino-2-hydroxypyridine; 2:6-diaminopyridine couples with aromatic diazo-compounds with formation of colouring matters. Nitration of 2-aminopyridine yields 5-nitro-2-aminopyridine, yellow leaflets, m. p.  $188^\circ$ , and 3-nitro-2-aminopyridine, yellow needles, m. p.  $164^\circ$ . From 5-nitro-2-aminopyridine, 2:5-diaminopyridine is obtained by reduction. G. W. R.

**The Synthesis of Ricinine.** E. SPÄTH and G. KOLLER (*Ber.*, 1923, 56, [B], 2454-2460).—The constitution assigned previously to ricinine (Späth and Koller, A., 1923, i, 594) is confirmed by its synthesis from 4-chloroquinoline.

Ricinidine is converted by a molecular proportion of bromine in aqueous solution into a mixture of bromo-compounds which is transformed by boiling potassium carbonate solution into a product, m. p.  $287^\circ$ ; it is not identical with ricinic acid.

4-Hydroxy-1-methylpyrid-2-one reacts with a molecular proportion of bromine in aqueous solution to give a homogeneous bromo-derivative, m. p.  $219-219.5^\circ$ ; attempts to replace the halogen atom of this compound by the cyano-group were unsuccessful.

4-Chloroquinoline is oxidised by potassium permanganate in boiling aqueous solution in the presence of carbon dioxide to 4-chloropyridine-2:3-dicarboxylic acid, coarse, pale yellow crystals, m. p.  $173^\circ$  (decomp.) when rapidly heated. The acid is fairly smoothly converted by acetic anhydride into the corresponding anhydride, colourless needles, m. p.  $200-202^\circ$  (slight decomp.), in an evacuated tube, which is converted by ammonia in the presence of benzene into 4-chloro-2-carbamidopyridine-3-carboxylic acid, lustrous needles, m. p.  $148-150^\circ$  (decomp.) when rapidly heated. The latter acid is converted by bromine and potassium hydroxide into

*4-chloro-2-aminopyridine-3-carboxylic acid*, slender, colourless crystals, decomp.  $173^{\circ}$ , which is conveniently purified through the *ammonium* salt; it is transformed by nitrous acid in sulphuric acid solution into *4-chloro-2-hydroxypyridine-3-carboxylic acid*, colourless needles, m. p.  $220^{\circ}$  (decomp.). The constitution of the hydroxy-acid is established by its conversion by hydrogen in the presence of palladised barium sulphate into the previously described 2-hydroxypyridine-3-carboxylic acid, and thence into 2-hydroxypyridine. Attempts to effect the complete methylation of 4-chloro-2-hydroxypyridine-3-carboxylic acid with diazomethane or by the action of methyl iodide on the di-silver salt were not successful. The acid is therefore converted by the successive action of phosphoryl chloride and phosphorus pentachloride and of ammonia into 2 : 4-dichloropyridine-3-carboxylamide, colourless crystals, m. p.  $181-182^{\circ}$  (decomp.), which is transformed by phosphoryl chloride into 2 : 4-dichloro-3-cyanopyridine, m. p.  $112-113^{\circ}$ . When treated with boiling methyl-alcoholic sodium methoxide solution, both chlorine atoms are replaced by methoxy-groups with the production of 3-cyano-2 : 4-dimethoxypyridine, coarse, colourless crystals, m. p.  $145-146^{\circ}$ , and a substance, m. p.  $221-222^{\circ}$ , which has not been examined completely. The conversion of 3-cyano-2 : 4-dimethoxypyridine into ricinine, m. p.  $197^{\circ}$ , could not be effected by heating it at  $300^{\circ}$ , but occurs readily when it is treated with methyl iodide in an evacuated tube at  $120-130^{\circ}$ .  
H. W.

**Keto-anils. V. The Formation of Quinolines from Ketones and Aromatic Amines.** E. KNOEVENAGEL [with E. WAGNER and H. BÄHR] (*Ber.*, 1923, **56**, [B], 2414—2418).—The production of derivatives of quinoline from aniline and ketones or aldehydes has been ascribed to the intermediate formation of alkylidene ketones and aldols, respectively. Evidence is now brought forward, however, in favour of the view that in the formation of 2-methyl- or 2 : 4-dimethyl-quinolines an alkylidene- or a ketylidene-amine derivative is essential which passes into a dimeride and thence into a quinoline compound. It is quite possible that the formation of aldols from aldehydes, ketones, or mixtures occurs under the condensing influence of hydrogen chloride, but compounds of this type are decomposed by aromatic amines with formation of alkylidene- or ketylidene-amines and liberation of the equivalent quantity of aldehyde or ketone.

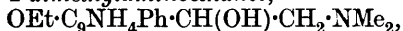
The preparation of methylisopropenylaniline (cf. Bähr, A., 1922, i, 750) from acetoneanil and methyl sulphate is described. It is converted by cyanoacetic or chloroacetic acid (but not by the dichloro- or trichloro-acid) into dimeric methylisopropenylaniline, m. p.  $148^{\circ}$ , which is identical with the by-product isolated by Bähr (*loc. cit.*) during the preparation of methylisopropenylaniline by means of methyl iodide. The dimeride is transformed by dry hydrogen chloride at  $180-200^{\circ}$  into 2 : 4-dimethylquinoline.

The action of mesityl oxide on aniline in the presence of a little iodine leads to the formation of acetoneanil and acetone. The condensation of mesityl oxide with aniline hydrochloride at  $180^{\circ}$

takes place with liberation of methane, and not of methyl chloride as stated by Beyer.

In the presence of iodine, phorone and mesityl oxide yield acetone, unchanged phorone, and acetoneanil. In the absence of iodine, condensation does not appear to occur. Under the influence of iodine and water, phorone does not appear to yield acetone. H. W.

**Amino-alcohols of the Quinoline Series.** SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 98482, 98712, and 98713; from *Chem. Zentr.*, 1923, iv, 829—830; cf. A., 1923, i, 148, 149).—6-Ethoxy-2-phenyl-4-quinolyl methyl ketone is halogenated in the methyl group and the resultant halogen derivative allowed to react with dimethylamine, diethylamine, or piperidine. The *N*-substituted 6-ethoxy-2-phenyl-4-quinolylamino-ethanone thereby obtained is then reduced to the corresponding aminoalcohol. 6-Ethoxy-2-phenyl-4-quinolyl methyl ketone forms yellow crystals, m. p. 107°; the hydrochloride, yellow crystals, has m. p. about 220° (decomp.). It is obtained by condensation of ethyl 6-ethoxy-2-phenylquinoline-4-carboxylate with ethyl acetate and elimination of carbon dioxide from the ethyl 6-ethoxy-2-phenylquinoline-4-acetate, m. p. 98—99°, thereby formed, or from 4-cyano-6-ethoxy-2-phenylquinoline by the Grignard reaction. By acting on the above-mentioned ketone with bromine in hydrobromic acid solution, 6-ethoxy-2-phenyl-4-quinolyl bromomethyl ketone hydrochloride, yellow crystals, m. p. 207° (decomp.), is obtained; the free ketone forms yellow crystals, m. p. 129°. By acting on the bromomethyl ketone with dimethylamine, 6-ethoxy-2-phenyl-4-quinolyl dimethylaminomethyl ketone,  $\text{OEt}\cdot\text{C}_9\text{H}_4\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NMe}_2$ , is obtained as the hydrobromide, yellow crystals, m. p. 230° (decomp.). The latter by reduction with hydrogen in the presence of a catalyst gives 6-ethoxy-2-phenylquinolyl-4-dimethylaminoethanol,



which forms colourless, rosette-like needles, m. p. 95°; the dihydrochloride forms light yellow crystals, m. p. about 210° (decomp.). 6-Ethoxy-2-phenyl-4-quinolyl diethylaminomethyl ketone monohydrobromide, yellow crystals, m. p. about 210° (decomp.), 6-ethoxy-2-phenyl-4-quinolyl piperidinomethyl ketone, a yellow powder, m. p. 82° (indef.), the hydrochloride, m. p. about 260° (decomp.), and the hydrobromide, m. p. 235—240° (decomp.), of the latter are similarly obtained. The corresponding amino-alcohols are obtained by reduction. 6-Ethoxy-2-phenyl-4-quinolyl diethylaminoethanol forms crystals, m. p. 89° after softening; the dihydrochloride, yellow crystals, has m. p. 205°. 6-Ethoxy-2-phenyl-4-quinolyl piperidinoethanol forms colourless crystals, m. p. 110°; the dihydrochloride, yellow crystals, has m. p. 218°.

G. W. R.

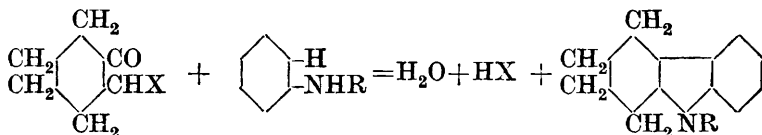
**Preparation of a 2-Phenylquinolinedicarboxylic Acid.** NEUMANN & Co. and J. ZELTNER (D.R.-P. 373285; from *Chem. Zentr.*, 1923, iv, 664—665).—Acetophenone-*o*-carboxylic acid, prepared, for example, from phthalic anhydride, acetic anhydride, and potassium acetate, is condensed with isatin by heating in the presence of potassium hydroxide solution at 100°. On acidifying,



*2-phenylquinoline-4 : 7-dicarboxylic acid* is obtained; it is a yellow, crystalline powder, m. p. 200°.

G. W. R.

**Preparation of Tetrahydrocarbazoles.** CHEMISCHE FABRIKEN VORM. WEILER-TER MEER (D.R.-P. 374098; from *Chem. Zentr.*, 1923, iv, 724).—2-Halogencyclohexanones are condensed with primary or secondary aromatic amines, unsubstituted in the ortho-position to the amino-group. The reaction takes place in the presence of such basic substances as potassium carbonate or anhydrous potassium acetate, and is represented by



The following compounds are mentioned: tetrahydrocarbazole, from aniline and chlorocyclohexanone; 3-methyltetrahydrocarbazole, m. p. 142°, from *o*-toluidine and chlorocyclohexanone; 1-methyltetrahydrocarbazole, m. p. 98°, from *p*-toluidine and chlorocyclohexanone; N-ethyltetrahydrocarbazole, a viscous oil, b. p. 220°/40 mm., from ethylaniline and 1 : 2-chlorocyclohexanone.

G. W. R.

**Preparation of Aromatic  $\alpha$ -Ketonic Acids.** R. SÖDERQUIST (*Svensk Kem. Tidskr.*, 1922, 34, 189—192; from *Chem. Zentr.*, 1923, iii, 1082—1083).—Aromatic  $\alpha$ -ketonic acids are prepared by condensation of aldehydes with 4-oxo-2-thio-3-phenyloxazolidine. After oxidation and fission of the substituted oxazolidine ring, aromatic  $\alpha$ -ketonic acids are obtained together with phenyl thio-carbimide. The condensation proceeds readily in acetic anhydride solution in the presence of anhydrous sodium acetate. Fission of the aryl-dihydroxyoxazolidines obtained by oxidation, takes place at the ordinary temperature on treatment with sodium ethoxide. The compounds may be separated by fractionation or by way of their hydrogen sulphite compounds. Anhydro-acids are also obtained from the elimination of a molecule of water from two ketonic acid molecules. 4-Oxo-2-thio-3-phenyl-5-benzylideneoxazolidine, from benzaldehyde and 4-oxo-2-thio-3-phenyloxazolidine, has m. p. 185—185.5°. On oxidation, it yields 2 : 4-dihydroxy-3-phenyl-5-benzylideneoxazolidine, m. p. 238—239°, whilst among the products of reaction with sodium ethoxide is phenylpyruvic acid. Other compounds mentioned are: 4-oxo-2-thio-3-phenyl-5-*o*-chlorobenzylideneoxazolidine, fine thread-like or prismatic crystals, m. p. 141.5°; 2 : 4-dihydroxy-3-phenyl-5-*o*-chlorobenzylideneoxazolidine, m. p. 152°; *o*-chlorophenylpyruvic acid, colourless leaflets, m. p. 145° (m. p. 152—152.5° when heated quickly); semicarbazone of the latter, m. p. 167.5°; phenylhydrazone, m. p. 141°; 4-oxo-2-thio-3-phenyl-5-*m*-chlorobenzylideneoxazolidine, light yellow prisms, m. p. 192°; *m*-chlorophenylpyruvic acid, prisms; semicarbazone of the latter, m. p. 176°; phenylhydrazone, m. p. 141°; 4-oxo-2-thio-3-phenyl-5-*p*-chlorobenzylideneoxazolidine, m. p. 237—237.5°; *p*-chlorophenylpyruvic acid, platelets; semicarbazone of the latter,

m. p. 184°; *phenylhydrazone*, m. p. 164°; 4-oxo-2-thio-3-phenyl-5-(3':4')methylenedioxybenzylideneoxazolidine, m. p. 240°; 2:4-methylenedioxyphenylpyruvic acid, colourless leaflets; *semi-carbazone* of the latter, m. p. 197°; *phenylhydrazone*, m. p. 144°; 4-oxo-2-thio-3-phenyl-5-m-nitrobenzylideneoxazolidine, m. p. 207°; 4-oxo-2-thio-3-phenyl-5-o-acetoxymethylideneoxazolidine, yellow prisms, m. p. 162.5—163°. G. W. R.

**Action of Hydroxylamine and of Hydrazine on the Aryl Monothioamides of Carbethoxyethylmalonate.** D. E. WORRALL (*J. Amer. Chem. Soc.*, 1923, **45**, 3092—3095; cf. A., 1922, i, 874).—*iso*Oxazoles and pyrazoles were obtained by the action of hydroxylamine and hydrazine, respectively, on carbethoxyethylmalonate monothioamides. Thus carbethoxyethylmalonate monothioanilide gave *ethyl 3-anilino-5-oxo-isooxazole-4-carboxylate*, small needles, m. p. 166°, and the corresponding *pyrazole* ester, fluffy, white needles, m. p. 194—195°. *Ethyl 3-o-toluidino-5-isooxazole-4-carboxylate*, flat needles, m. p. 165—167° (decomp.), and the corresponding *pyrazole* ester, white needles, m. p. 215° (decomp.); *ethyl 3-p-toluidino-5-oxoisooxazole-4-carboxylate*, needles and plates, m. p. 172—173° (decomp.), and the corresponding *pyrazole* ester, feathery needles, decomp. above 200°; *ethyl 3-p-bromoanilino-5-oxoisooxazole-4-carboxylate*, slender needles, m. p. 163—170° (decomp.), and the corresponding *pyrazole* ester, needles, m. p. 217°, were obtained. F. B.

**4'-Amino-1-phenyl-5-methylbenzthiazole and its Bromination in Glacial Acetic Acid. The Dibromo-product of Gatterman. The Fluorescence of some Benzthiazoles.** R. F. HUNTER (*Chem. News*, 1923, **127**, 385—386).—An alcoholic solution of dehydrothiotoluidine (4'-amino-1-phenyl-5-methylbenzthiazole) exhibits a green fluorescence in the light of a mercury lamp; its dibromide shows a blue fluorescence in glacial acetic acid solution, and the acetyl derivative is also strongly fluorescent. The dibromide is decomposed by nitrous acid and consequently cannot be diazotised. E. H. R.

**Absorption Colours of the Second Order.** J. PICCARD and F. DE MONTMOLLIN (*Helv. Chim. Acta*, 1923, **6**, 1011—1019).—It was shown previously that *meri*-quinonoid salts of tetraphenylbenzidine have a yellow colour of the second order (A., 1913, i, 895). It is now shown that Nietzki's rule also applies to such second order colours; the second absorption band can be moved further into the visible spectrum by increasing the molecular weight, changing the colour of the compound from yellow to red. This has been demonstrated by preparing a *meri*-quinonoid salt of diphenyldi-*p*-diphenylbenzidine,  $C_6H_4Ph \cdot NPh \cdot C_6H_4 \cdot C_6H_4 \cdot NPh \cdot C_6H_4Ph$ . *Diphenyl-p-diphenylamine*,  $C_6H_4Ph \cdot NPh_2$ , is formed by heating diphenylamine with *p*-iododiphenyl in nitrobenzene in presence of potassium carbonate and a little copper; it forms long, nearly colourless crystals, m. p. 114°. It forms a yellowish-green compound with chloranil, and gives a greenish-blue coloration with concentrated

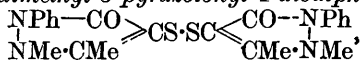
sulphuric acid. When oxidised in glacial acetic acid with sodium dichromate, it gives a red colour, changing to green; the green solution is reduced with zinc dust and from the diluted solution *diphenyldidiphenylbenzidine* can be extracted with chloroform, in 20% yield. It forms a brown powder, m. p. 135–140°. The same substance can be obtained in an impure form by condensing *s*-diphenylbenzidine with *p*-iododiphenyl. All solutions of the compound show a strong violet fluorescence which is excited by ultra-violet light at the limit of the visible spectrum. This benzidine derivative is oxidised by sodium dichromate in glacial acetic acid solution into a *meri*-quinonoid salt which can be precipitated by picric acid as *meri-diphenyldi-p-diphenyldiphenquinonedi-immonium picrate*, a red powder. Further oxidation gives the green *holo*-quinonoid salt.

E. H. R.

**Additive Reactions of Thiocyanogen.** H. P. KAUFMANN and J. LIEPE (*Ber.*, 1923, **56**, [B], 2514–2520).—Attempts have been made to estimate enols by titration with solutions of thiocyanogen in the hope of thereby avoiding secondary disturbances such as may be caused by the liberated hydrogen bromide in Meyer's bromine titration method. It is found, however, that the reagent can be applied only under definite conditions; in general applicability and rapidity of execution, the method is not equal to Meyer's process. Quantitative experiments with solutions of thiocyanogen are rendered very difficult on account of the ease with which it becomes polymerised, particularly on exposure to sunlight or to an elevated temperature.

Thiocyanogen reacts with antipyrine in the presence of chloroform to give a mixture of *antipyrine thiocyanate*, colourless, lustrous needles, m. p. 125° (which is also obtained from antipyrine sulphate and potassium thiocyanate) and 4-thiocyano-1-phenyl-2 : 3-dimethylpyrazol-5-one,  $\begin{array}{c} \text{C}(\text{SCN})\cdot\text{CO} \\ | \\ \text{CMe}\cdot\text{NMe} \end{array} > \text{NPh}$ , colourless crystals, m. p. 147–

148°; the constitution of the latter substance follows from its preparation from 4-bromoantipyrine and potassium thiocyanate in boiling aqueous solution. 4-Thiocyanoantipyrine thiocyanate has m. p. 84°. 4-Thiocyanoantipyrine is very readily hydrolysed by alkali hydroxide to potassium cyanide, potassium cyanate, and *bis*-1-phenyl-2 : 3-dimethyl-5-pyrazolonyl 4-disulphide,



very pale yellow, hexagonal plates, m. p. 256°; the compound can also be prepared by means of aqueous alcohol. 4-Thiocyanoantipyrine is reduced by zinc and hydrochloric acid in the presence of alcohol to the additive compound of zinc chloride and 4-thiolantipyrine,  $\text{C}_{11}\text{H}_{12}\text{ON}_2\text{S}\cdot\text{ZnCl}_2$ , a white precipitate from which the thiol could not be isolated.

[With M. THOMAS.]—Addition and substitution of free thiocyanogen occur much more slowly than in the case of bromine. Thus ethyl hydrocollidinedicarboxylate reacts with seven atomic proportions of chlorine and four of bromine, but not with iodine; with

thiocyanogen, it gives a *di-thiocyano-derivative*,  $C_{16}H_{19}O_4N_3S_2$ , m. p.  $115^\circ$  (decomp.). *Ethyl collidinedicarboxylate thiocyanate* crystallises in colourless, monoclinic plates, m. p.  $133^\circ$ .

[With M. THOMAS.]—Reactions with free cyanogen depend greatly on the solvent used, addition occurring particularly rapidly in the presence of nitromethane (as example of a solvent of high dissociating power). The action of sunlight and of certain catalysts, notably iron, is advantageous. Thus, whereas salicylic acid is indifferent towards thiocyanogen under the usual conditions, it is converted in nitromethane solution in the presence of iron powder into *2-hydroxy-5-thiocyanobenzoic acid*, monoclinic leaflets, m. p.  $167-168^\circ$ .

H. W.

**New Methods of Splitting Pyrimidines. II. Decomposition of Pyrimidines by means of Ferrous Salts.** M. H. PFALTZ and O. BAUDISCH (*J. Amer. Chem. Soc.*, 1923, **45**, 2972—2980; cf. A., 1921, ii, 337).—The splitting of pyrimidines under conditions closely resembling those in the metabolism of plants and animals was accomplished by the action of the system ferrous sulphate-sodium hydrogen carbonate-air and the system sodium pentacyanoaquoferroate-oxygen or air (A., 1900, i, 591) on uracil and thymine. In each case the pyrimidine ring was partly hydrolysed, with the formation of highly coloured intermediate substances which were completely hydrolysed by warm sodium hydrogen carbonate with the production of carbamide. The action was retarded by hydrogenation of the pyrimidine ring as in hydro-uracil and by the presence of a methyl group in the 5-position as in thymine, and by the addition of any substance possessing a strong affinity for iron, e.g., ammonia, potassium cyanide. F. B.

**5-Benzoylbarbituric Acids.** H. BILTZ and T. KÖHLER (*Ber.*, 1923, **56**, [B], 2482—2489).—In continuation of the work on 5-acylbarbituric acid (cf. Biltz and Wittek, A., 1921, i, 454), 5-benzoylbarbituric acid has been examined in detail. The position of the benzoyl group is placed beyond doubt by the observed ketonic properties of the compound, by the existence of similar derivatives of 1 : 3-dimethyl- and 1 : 3-diethyl-barbituric acids, and by the inability of alkalis to effect hydrolysis.

*5-Benzoylbarbituric acid*,  $CO < \begin{smallmatrix} NH \cdot CO \\ NH \cdot CO \end{smallmatrix} > CHBz$ , pale yellow aggregates of prisms, m. p.  $275^\circ$  (decomp.), is prepared by heating barbituric acid with benzoic anhydride at  $175^\circ$  during five hours; it cannot be prepared from barbituric acid, benzoyl chloride, and sodium hydroxide or from barbituric and benzoic acids. The *potassium* salt, rhombic leaflets, decomp. about  $315^\circ$ , is described. It is stable towards sodium hydroxide solution or concentrated hydrochloric acid. It is decomposed by hot fuming nitric acid into alloxan and benzoic or nitrobenzoic acids, and by bromine in aqueous solution at the atmospheric temperature into benzoic and 5 : 5-dibromobarbituric acids. It gives a *hydrazone*,  $C_{11}H_{10}O_3N_4$ , slender, pale yellow needles, decomp.  $260^\circ$ , and a *phenylhydrazone*,  $C_{17}H_{14}O_3N_4$ , small, pale yellow needles decomp.  $218^\circ$ ; a semi-

carbazone could not be obtained. It is decomposed by thiosemi-carbazide in boiling aqueous-alcoholic solution into barbituric acid and 2-amino-5-phenylthiodiazole (cf. Young and Eyre, T., 1901, 79, 57); 5-acetylbarbituric acid yields, in a similar manner, barbituric acid and 5-amino-2-methylthiodiazole. The action of hydroxylamine on 5-benzoylbarbituric acid in boiling alcoholic solution gives a *substance*, colourless, lustrous, hexagonal platelets, m. p. 261°, which is regarded as the oxime of 5-amino-5-benzoylbarbituric acid,

$\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{C}(\text{NH}_2) \cdot \text{CPh} \cdot \text{N} \cdot \text{OH}$ ; it is converted by hot, concentrated nitric acid into alloxan, by highly concentrated hydriodic acid into benzoylbarbituric acid, and by bromine water into alloxan and benzaldehyde. 5-Benzoylbarbituric acid is converted by sodium hydroxide and methyl sulphate into the *methyl ether* of the enolic form of 5-benzoylbarbituric acid,  $\text{CO} \begin{smallmatrix} \text{NH} \text{---} \text{CO} \\ \text{NH} \cdot \text{C}(\text{OMe}) \end{smallmatrix} \text{CBz}$ ,

colourless, lustrous prisms, decomp. 105°; the corresponding *phenylhydrazone*,  $\text{C}_{18}\text{H}_{16}\text{O}_3\text{N}_4$ , decomp. 225°, is described. The ethylation of 5-benzoylbarbituric acid could not be effected by ethyl sulphate or ethyl bromide, magnesium oxide, and carbon tetrachloride at 140°.

1-Methylbarbituric acid and benzoic anhydride react at 130—140° to give 5-benzoyl-1-methylbarbituric acid, small, pale brown prisms, decomp. 225° (*phenylhydrazone*, slender, yellow needles, decomp. 205°). 5-Benzoyl-1-ethylbarbituric acid, flattened prisms, m. p. 205° (decomp.), and its *phenylhydrazone*, slender needles, decomp. 190° after darkening at 175°, are described. 1:3-Dimethylbarbituric acid reacts with benzoic anhydride at 130°, but the expected 5-benzoyl-1:3-dimethylbarbituric acid could not be isolated from the product of the reaction in the homogeneous condition; it is characterised as the *phenylhydrazone*,  $\text{C}_{19}\text{H}_{18}\text{O}_3\text{N}_4$ , colourless, quadratic leaflets, decomp. 218°. 5-Benzoyl-1:3-diethylbarbituric acid could not be caused to crystallise; the *phenylhydrazone*,  $\text{C}_{21}\text{H}_{22}\text{O}_3\text{N}_4$ , forms long, yellow leaflets, decomp. 164°.

Attempts to cause interaction between barbituric acid and oxalic acid, oxalyl chloride, oxalyl bromide, or phthalic anhydride were not successful. Thiobarbituric acid does not react smoothly with acetic or benzoic anhydrides. The acetyl group of 5-acetylbarbituric acids does not appear to be capable of condensing with aldehydes.

H. W.

**Alkylisopropylbarbituric Acids.** F. HOFFMANN LA ROCHE & Co. (Austr. Pat. 92386; from *Chem. Zentr.*, 1923, iv, 665).—In modification of an earlier patent (A., 1922, i, 872) other alkyl halides are used in place of allyl bromide. 5-Methyl-5-isopropylbarbituric acid, from isopropylbarbituric acid and methyl iodide, forms crystals, m. p. 186—187°. 5:5-Diisopropylbarbituric acid forms crystals, m. p. above 230° (decomp.).

G. W. R.

**Preparation of New Barbituric Acid Compounds.** CHEMISCHE FABRIK AUF AKTIEN, VORM. E. SCHERING (Brit. Pat. 198379; addn. to 158558; cf. A., 1922, i, 582).—New compounds,

similar in properties to that previously described (*loc. cit.*) are obtained by replacing the diethylbarbituric acid in the original process by dipropyl-, diallyl-, or phenylethyl-barbituric acid. The products of these three fusions melt respectively at 82—86°, 85—88°, and 106—120°.

W. T. K. B.

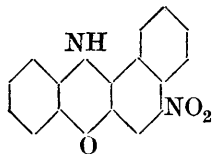
**Diketopiperazine Derivatives.** P. KARRER, C. GRÄNACHER, and A. SCHLOSSER (*Helv. Chim. Acta*, 1923, 6, 1108—1112).—Benzyl chloride reacts with the silver salt of glycine anhydride to give 2 : 5-dihydroxydihydropyrazine dibenzyl ether, crystallising in white leaflets, m. p. 164°. The reaction therefore follows a different course from that of methyl iodide on the anhydride (A., 1922, i, 235). The new compound is readily hydrolysed by boiling dilute acids to benzyl alcohol and glycine, and in this respect differs markedly from its isomerides, *N* : *N'*-dibenzylglycine anhydride and diketo-2 : 5-dibenzylpiperazine.

E. H. R.

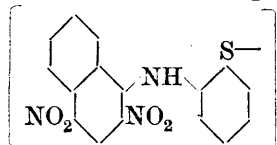
**New Syntheses in the Quinoneimide Dye Group. I. Syntheses with 1-Chloro-2 : 4-dinitronaphthalene.** F. KEHRMANN (with A. VAN BAERLE) (*Ber.*, 1923, 56, [B], 2385—2390).—A number of known and some new quinoneimide dyes have been prepared by condensing 1-chloro-2 : 4-dinitronaphthalene with different bases. In many cases the toluene-*p*-sulphonic ester of Martius's yellow (2 : 4-dinitro- $\alpha$ -naphthol) can also be used.

*o*-2 : 4-Dinitronaphthylaminodiphenylamine is obtained by condensing the dinitrochloronaphthalene with *o*-aminodiphenylamine in alcohol; it forms large, brownish-red prisms containing benzene from that solvent, which lose benzene and turn black at 70°, m. p. 140°. With 5-chloro-2-aminodiphenylamine, the corresponding 5-chloro-2-(2 : 4-dinitronaphthylamino)diphenylamine is obtained, dark brown leaves, m. p. 110°. Both these compounds are reduced smoothly by stannous chloride to rosinduline and chlororosinduline respectively. The rosindones are obtained by fusing the dinitro-compound with benzoic acid.

By condensing 2 : 4-dinitro-1-naphthyltoluenesulphonate with *o*-aminophenol, *o*-2 : 4-dinitronaphthylaminophenol is obtained which, by careful treatment with aqueous sodium hydroxide is converted into 5-nitro-7 : 12-naphthaphenoxazine (annexed formula), a violet precipitate which decomposes when heated. An acetyl derivative could not be obtained, but instead the known phenonaphthoxazone was formed. With *oo'*-diaminodiphenyl disulphide



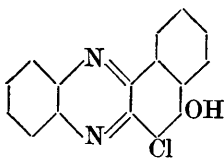
the above toluenesulphonate condenses to give *o*-bis-2 : 4-dinitronaphthylaminophenyl disulphide (annexed formula), orange-yellow leaflets, m. p. 169°. With *o*-aminothiophenol it gives *o*-2 : 4-dinitronaphthylaminophenyl mercaptan, a lemon-yellow, crystalline powder, m. p. 198°, which by careful treatment with alkali gives 5-nitro-7 : 12-naphthaphenthiazine, nearly black needles with a brassy reflex, m. p. 156° (decomp). It is much



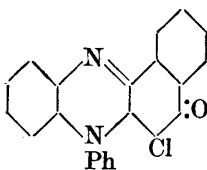
more stable than the corresponding oxazine. A by-product of the last condensation, yellow, glistening crystals, m. p. 150°, appeared to be 2:4-dinitronaphthyl-o-aminophenyl sulphide.

E. H. R.

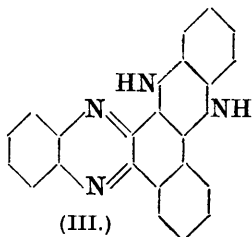
**New Syntheses in the Quinoneimide Dye Group. II. Steric Influence in the Condensation of Hydroxyquinones with o-Diamines.** F. KEHRMANN [with C. BUFFAT] (*Ber.*, 1923, 56, [B], 2390—2394).—It has long been known that substituted quinones such as chloranilic acid and 3-chloro-4-hydroxy-1:2-naphthaquinone react with difficulty or not at all with o-diamines, but it is now found that these reactions proceed under suitable conditions. Thus when chloranilic acid is heated with o-phenylenediamine hydrochloride and a large quantity of benzoic acid at the boiling point, 1:4-dichloro-2:3-dihydroxyphenazine is formed, dark brownish-red, metallic crystals, blackening at 310°. It gives a dichroic sulphuric acid solution, brown in thick, greenish-yellow in thin layers. With o-aminodiphenylamine, chloranilic acid gives 1:4-dichloro-2-hydroxyaposafranone, dark, reddish-brown crystals with a weak, brassy lustre, decomposing at 285°. 3-Chloro-4-hydroxy-1:2-naphthaquinone with o-phenylenediamine gives 6-chloro-5-hydroxy- $\alpha\beta$ -naphthaphenazine (formula I), dark red, brassy crystals decomposing at about 280°. It gives a dirty yellowish-green colour with concentrated sulphuric acid, ponceau-red with hot alkali. With o-aminodiphenylamine, 3-chloro-2-hydroxy-1:4-naphthaquinone gives 6-chlororosindone (formula II), red needles with golden lustre, m. p. 255°, giving a dark yellowish-green colour in sulphuric acid. With 2-amino-5-chlorodiphenylamine, 6:9-dichlororosindone is formed, red needles with strong gold reflex, m. p. 242—243°, giving a dirty violet-red colour in sulphuric acid.



(I.)



(II.)



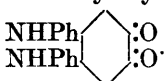
(III.)

When the above 5-hydroxy-6-chloronaphthaphenazine is fused with o-phenylenediamine, a new dihydronaphthadiphenazine (formula III) is formed, golden-yellow leaflets with brassy reflex, m. p. 263°. Its hydrochloride forms dark red, metallic needles, and it gives a pure green colour in concentrated sulphuric acid.

E. H. R.

**New Syntheses in the Quinoneimide Dye Group. III. Syntheses of Induline-3B and -6B.** F. KEHRMANN [with W. KLOPFENSTEIN] (*Ber.*, 1923, 56, [B], 2394—2397).—The con-

stitutional formulæ assigned to Induline-3*B* and -6*B* have now been confirmed by synthesis of these dyes from dianilino-

*o*-quinone, . When this is condensed with 2-amino-

5-chlorodiphenylamine hydrochloride in alcohol, 3-chloro-8-anilino-phenylaposafranine (annexed formula) is formed, crystallising in needles with a green reflex. The free base forms brownish-red needles, m. p. 258°. The colour in concentrated sulphuric acid is violet-blue, becoming violet and then Bordeaux-red on dilution.

When this is boiled with aniline and aniline hydrochloride, the ring chlorine is replaced by the anilino-group, forming 8-anilino-3:7-diphenylphenosafranine, identical with Induline-3*B*. The free

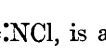
base forms nearly black leaflets with a weak green reflex, m. p. 242°. Induline-3*B* is converted into Induline-6*B*, 2:8-dianilino-3:7-diphenylphenosafranine (annexed formula), by boiling with aniline and aniline hydrochloride in presence of 1 mol. of mercuric oxide. The free base forms greenish-black metallic crystals, m. p. 286—288°; the *hydrochloride* and *hydrobromide* both form crystals with a coppery lustre, insoluble in water.

E. H. R.

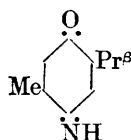
### New Syntheses in the Quinoneimide Dye Group. IV. The Colour of the Simple Quinoneimines. F. KEHRMANN

[with B. CORDONE] (*Ber.*, 1923, 56, [B], 2398—2405).—In a previous paper (*A.*, 1922, ii, 333), the rule was established that the effect of salt formation on the colour of basic nitrogen compounds is to intensify the colour if the unsaturated condition persists. This rule has now been found to apply to compounds of the quinoneimine series, of which several new members have been prepared.

*Thymoquinonemonoimine* (annexed formula) was prepared by oxidising *p*-aminothymol with silver oxide in ethereal solution; it crystallises in bright yellow, silky leaflets, m. p. 74—75°. It is stable for some time in the dark at low temperatures and is much less sensitive to light than *p*-benzoquinonemonoimine. Its salts are deeper yellow in colour than the compound itself; the *hydrochloride* is obtained as a voluminous, yellow precipitate from ether; the *picrate*, which is stable for some time in water, forms bright yellow, sparingly soluble crystals. The monoimines of benzo- and tolu-quinone were prepared afresh to confirm their yellow colour.

Benzoquinonechloroimine, , is also yellow, but benzoquinonedi-imine is colourless, whilst its dihydrochloride is yellow.

Benzoquinonedichlorodi-imine, , is colourless; it

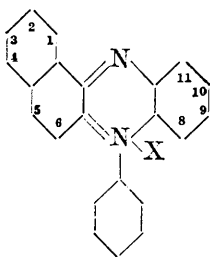




gives a salt only with concentrated sulphuric acid, and this is yellow. *Duroquinonedi-imine* (annexed formula) was obtained by oxidising diaminodurene with silver oxide in ether; it forms colourless crystals, not very sensitive to light, m. p. 134—135°. It dissolves in dilute mineral acids, giving bright yellow solutions which soon decompose with deposition of duroquinone. The salts, which can be obtained in crystalline form from ether, are bright yellow. The results show that the carbonyl group is a stronger chromophore than the iminocarbonyl group  $\cdot\text{C}=\text{NH}$ . This is also shown by the fact that whilst tetramethyldiaminobenzophenone is yellow, auramine base is colourless.

E. H. R.

**Determination of the Constitutional Formulæ of Colouring Matters from their Absorption Spectra. V.** F. KEHRMANN and M<sup>r</sup> SANDOZ (*Helv. Chim. Acta*, 1923, 6, 982—994).—The

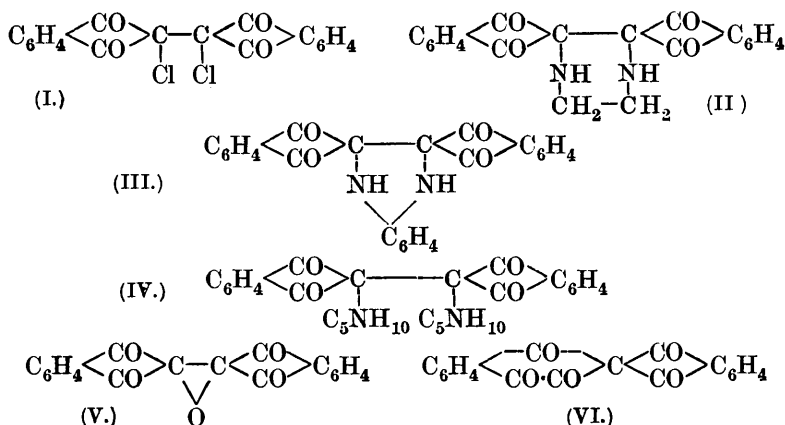


absorption spectra of the mono-acid and di-acid salts of phenyl- $\alpha\beta$ -benzophenazonium (annexed formula) and of the mono-, di-, and tri-acid salts of nine of its monoamino-derivatives have been measured. The mono-salt of the parent substance is yellow with orange fluorescence, the di-salt violet; both have an ortho-quinonoid structure. The amino derivatives, 1-, 2-, 3-, and 4- form a group. Their mono-salts are bluish-green, except that of the 3-amino-derivative, which is brown; their di-salts are yellow, similar to the mono-salt of the parent substance, and their tri-salts deep red, comparable with the di-salt of the parent. The 1-amino-compound does not form a tri-salt, probably on account of steric hindrance. All these salts are given an ortho-quinonoid structure. The mono-salt of the 10-amino-derivative (violet) is probably also ortho-quinonoid. The 9- and 5-amino-compounds form another group; they behave similarly to *aposafranine* (A., 1920, ii, 142). The mono-acid salt (scarlet) and the di-acid salt (green) are para-quinonoid, whilst the tri-acid salt (violet) has the ortho-quinonoid structure. The fact that the di-acid salts can be diazotised indicates that the solutions contain a small amount of the yellow, ortho-quinonoid di-acid salt in equilibrium with the para-quinonoid form. Two amino-derivatives, the meta- and para-, were prepared having the amino-group in the external benzene ring. Here the auxochromic effect of the amino-group is reduced to a minimum, and there is little difference between the colours of the mono-acid salt and of the di-acid salt, both being yellow in solution; the tri-acid salt is violet, and all three are ortho-quinonoid. Curves are given showing the absorption spectra of all the salts examined.

E. H. R.

**Spirans. XII. Heterocyclic Dispirans and the Nature of the Basic Properties of the Imino-group.** D. RADULESCU (*Bul. Soc. Științe Cluj*, 1922, 1, 356—360; from *Chem. Zentr.*, 1923, iii, 1081; cf. this vol., i, 58).—Heterocyclic dispirans have

been prepared by the author by the action of *o*-diamines on dichlorobisdiketohydrindene (I). *Piperazinebis-3-1 : 3-diketohydrindene-2 : 2 : 3 : 2-dispiran*,  $C_{20}H_{14}O_4N_2$ , (II) forms yellow prisms, m. p.  $249^\circ$  (corr.). The *spiran* (III),  $C_{24}H_{14}O_4N_2$ , forms microcrystalline brown prisms, m. p.  $272^\circ$  (corr.). Spiran III is scarcely basic, whilst the dispiran II is moderately basic. This is explained by Thiele's theory of partial valencies, which is also applicable to the slight basicity of pyrrole and indole. Spirans with tertiary nitrogen



are more basic. *N : N'-Dipiperidylbis-1 : 3-diketohydrindene* (IV) forms orange prisms, m. p.  $174^\circ$ . The *diethylamino*-derivative of the latter forms yellow prisms, m. p.  $129^\circ$ , and the *dibenzylamino*-derivative yellow needles, m. p.  $178^\circ$ . The author concludes that the hydroxy-derivatives corresponding with the amines must be strongly acid. The compound described by Gabriel and Leupold (A., 1898, i, 481) as bisdiketohydrindene oxide (V) is really a spiran pinacone (VI). It is hydrolysed by weak acids and alkalis to diketohydrindene, and its decomposition products, and phthalonic acid. G. W. R.

### Reactions of certain Substituted Guanidines with Sulphur.

G. BRUNI and T. G. LEVI (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 313—316).—When heated together in a sealed tube at  $260$ — $270^\circ$ , *s*-diphenylguanidine and sulphur give a good yield of mercaptobenzthiazole. In aniline solution, subjected to prolonged boiling in a reflux apparatus, the reaction gives rise to little or no mercaptobenzthiazole, but to anilinobenzthiazole (cf. Hofmann, A., 1880, 388; Jacobson and Frankenbacher, A., 1891, 1048; Huguershoff, A., 1903, i, 865; and Rassow and Döhle, A., 1916, i, 747):  $\text{NHPh} \cdot \text{C}(\text{NH}) \cdot \text{NHPh} + \text{S} = \text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{C} \cdot \text{NHPh} + \text{NH}_3$ ; the acetyl derivative of anilinobenzthiazole has m. p.  $162$ — $163^\circ$ .

Mercaptobenzthiazole is formed in good yield when phenylguanidine, and in poor yield when *s*-triphenylguanidine, is heated



by the system ferrous sulphate-oxygen. The action was similar to that which occurred with pyrimidines. F. B.

**Action of Alkali on Substituted Uric Acids. I. 9-Phenyl-1:3-dimethyluric Acid.** E. S. GATEWOOD (*J. Amer. Chem. Soc.*, 1923, **45**, 3056—3064; cf. A., 1923, i, 253).—This substituted uric acid was decomposed instantaneously at 100° with 4*N* sodium hydroxide with the elimination of methylamine. On acidifying the solution, carbon dioxide was evolved, and crystals, m. p. 249—250°; of 3-phenylisohydantoin-5-carboxyl-o-methylamide separated. This was further decomposed by alkali into phenylcarbamide, methylamine, oxalic acid, and formic acid, whilst oxidation with hydrogen peroxide in alkaline solution yielded 5-hydroxy-3-phenylhydantoin 5-carboxyl-o-methylamide, large, thin, rectangular plates, m. p. 195—196°. This was further decomposed by alkali into methylamine, phenylcarbamide, and meso-oxalic acid. 9-Phenyl-1:7-dimethyluric acid was synthesised. It did not melt below 280° and was not affected by boiling with 4*N* sodium hydroxide for ten minutes. F. B.

**The Activation of Halogen and Methyl in Aromatic Compounds by the Azo-group, ·N:NR.** W. BORSCHÉ and I. EXSS (*Ber.*, 1923, **56**, [B], 2353—2357).—Experiments with 4-chloro-3-nitroazobenzene and 6-chloro-3-nitro-4'-methoxyazobenzene, show that the azo-group in ortho- or para-position to the halogen imparts to it increased activity. These compounds react more readily with hydrazine, ammonia, aniline, or sodium ethoxide than *o*- or *p*-chloro-nitrobenzene, although not so readily as chloro-2:4-dinitrobenzene. On the other hand, benzeneazo-2-nitro-*p*-toluene does not react with benzaldehyde to form a stilbene derivative as does 2:4-dinitro-toluene.

4-Chloro-3-nitroazobenzene, from 4-chloro-3-nitroaniline and nitrosobenzene, forms brown needles, m. p. 84°. 6-Chloro-3-nitro-4'-hydroxyazobenzene, from diazotised 6-chloro-3-nitroaniline and phenol, forms red needles, m. p. 218°; it is methylated by methyl sulphate to 6-chloro-3-nitro-4'-methoxyazobenzene, deep yellow leaflets, m. p. 103°. Benzeneazo-2-nitro-*p*-toluene, from 2-nitro-*p*-toluidine and nitrosobenzene, forms brown needles, m. p. 106°.

3-Nitro-4-hydrazinoazobenzene,  $\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{NH} \cdot \text{NH}_2$ , forms red needles, m. p. 206° (decomp.); with acetophenone it forms the corresponding hydrazone,  $\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{NH} \cdot \text{N} \cdot \text{CMePh}$ , red needles, m. p. 195°. 2-Nitro-4-benzeneazo-4'-hydroxyazobenzene,  $\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , obtained from the above hydrazine and *p*-benzoquinone, forms brown needles, m. p. 203° (decomp.); with quinoneoxime, the hydrazine forms an oximehydrazone,  $\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{NH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{OH}$ , a red, crystalline powder, m. p. 235° (decomp.).

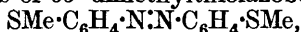
3-Nitro-4-aminoazobenzene forms red needles, m. p. 173·5°. 3-Nitro-4-piperidinoazobenzene, by condensing 4-chloro-3-nitroazobenzene with piperidine, forms orange-red tablets, m. p. 64°. 3-Nitro-4-anilinoazobenzene,  $\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{NHPh}$ , forms brown needles,

m. p. 124°. 3-Nitro-4-methoxyazobenzene crystallises in orange-red needles, m. p. 107°.

3-Nitro-4'-methoxy-6-hydrazinoazobenzene forms red needles, m. p. 173°; with *p*-anisaldehyde it gives the corresponding *hydrazone*, red needles, m. p. 208°. 5-Nitro-2-amino-4'-methoxyazobenzene forms brownish-yellow needles, m. p. 136°. 3-Nitro-6 : 4'-dimethoxyazobenzene forms orange-yellow needles, m. p. 123°. E. H. R.

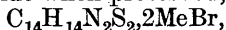
**Thiophenols. V. Salts and Additive Compounds of *oo'*-Azophenyl Methyl Sulphide and *oo'*-Azoxyphenyl Methyl Sulphide.** K. BRAND and P. GROBEL (*Ber.*, 1923, 56, [B], 2563—2567).—An extension of the work of Brand and Wirsing (*A.*, 1912, i, 666; 1913, i, 406) on the para-compounds to the ortho-series.

The following salts of *oo'*-dimethylthiolazobenzene,



are described: the *perchlorate*,  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_2 \cdot \text{HClO}_4$ , bluish-violet needles which are very sensitive to moisture, m. p. 154°; the *sulphate*,  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_2 \cdot 2\text{H}_2\text{SO}_4$ , dark violet needles; the very unstable *hydrochloride*, blue needles, and its additive compounds with stannic chloride,  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_2 \cdot \text{HCl} \cdot \text{SnCl}_4$ , blackish-violet needles, with ferric chloride,  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_2 \cdot \text{HCl} \cdot \text{FeCl}_3$ , dark violet, almost black needles, and mercuric chloride, an unstable, blue compound.

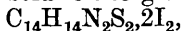
*oo'*-Dimethylthiolazobenzene is transformed by methyl sulphate into the *methosulphate*,  $\text{N}_2(\text{C}_6\text{H}_4 \cdot \text{SMe}_2 \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OMe})_2$ , coarse crystals, m. p. 189° (decomp.), which is converted into the corresponding *iodide*,  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_2 \cdot 2\text{MeI}$ , long, red needles, m. p. 154°, which readily loses methyl iodide when preserved, the *bromide*,



m. p. 154°, and the unstable *thiocyanate*, decomp. 102—105°.

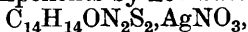
*o*-Nitrophenyl methyl sulphide is reduced by sodium and methyl alcohol to *oo'*-dimethylthiolazoxybenzene, crystals, m. p. 72°, from which the corresponding *methosulphate*,  $\text{C}_{14}\text{H}_{14}\text{ON}_2\text{S}_2 \cdot 2\text{Me}_2\text{SO}_4$ , yellow leaflets, m. p. (indefinite) 167—169° (decomp.) after becoming red at 160—162°, and the *methiodide*,  $\text{C}_{14}\text{H}_{14}\text{ON}_2\text{S}_2 \cdot 2\text{MeI}$ , m. p. 103° (decomp.), are obtained.

*oo'*-Dimethylthiolazobenzene and the azoxy-compound combine with iodine in chloroform solution to give the *compounds*,

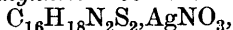


m. p. 155° after evolving iodine at 140°, and  $\text{C}_{14}\text{H}_{14}\text{ON}_2\text{S}_2 \cdot 2\text{I}_2$ , dark green needles, m. p. 113—114°; the corresponding *sulphonium methosulphates* when treated in aqueous solution with iodine and potassium iodide yield the *compounds*  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_2 \cdot 2\text{MeI} \cdot 2\text{I}_2$ , m. p. 113—115° (decomp.), and  $\text{C}_{14}\text{H}_{14}\text{ON}_2\text{S}_2 \cdot 2\text{MeI} \cdot 2\text{I}_2$ , m. p. 103° (decomp.) after darkening at 100°.

The following additive compounds are described: the *substance*,  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_2 \cdot \text{AgNO}_3$ , from the components in boiling aqueous-alcoholic solution, orange-coloured needles, which is completely decomposed into its components by hot water; the *salt*,



yellow needles; *oo'*-diethylthiolazobenzene *silver nitrate*,



orange-coloured leaflets; *o*-nitrophenyl methyl sulphide silver nitrate,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SMe}, \text{AgNO}_3$ , yellow leaflets, m. p.  $122^\circ$ . H. W.

**The Influence of Sulphonic Groups on the Colour of Azo-dyes.** W. MEULY (*Helv. Chim. Acta*, 1923, 6, 931—935).—To determine the influence of the number and position of sulphonic groups on the colour of azo-dyes, spectroscopic comparison was made of a large number of secondary bisazo-dyes, in which the first component was an aniline mono- or di-sulphonic or a naphthylamine mono-, di-, or tri-sulphonic acid, the middle component was cresidine (3-amino-*p*-cresol ether) and the end component an  $\alpha$ - or  $\beta$ -naphthol mono-, di-, or tri-sulphonic acid. In every case, an additional sulphonic group, in either the first or the end component, deepens the colour, but the effect diminishes as the number of sulphonic groups increases. In the naphtholsulphonic acids, the effect of changing the position of the sulphonic group is smaller than the effect of an additional group. Similar results were obtained with a number of monoazo- and trisazo-dyes. As an example of the effect of additional sulphonic groups, the dye from sulphanilic acid, 3-amino-*p*-cresol ether and 1:4-naphtholsulphonic acid is red, whilst the corresponding dye using 1:3:6:8-naphtholtrisulphonic acid is violet. An absorption band may be shifted 10 to 20  $\mu\mu$  by a single sulphonic group, the influence being generally greater in the end component than in the first component. These results apply both to aqueous and to alcoholic solutions; in sulphuric acid and formic acid solutions the absorption bands are shifted in the opposite direction by sulphonic groups. [Cf. *B.*, 86.]

E. H. R.

**Certain Double Salts of Diazo-compounds with Lead Tetrachloride.** E. SAKELLARIOS (*Ber.*, 1923, 56, [B], 2536—2541).—A series of double salts of the general formula  $(\text{ArN}_2\text{Cl})_2\text{PbCl}_4$  has been prepared. They are generally yellow in colour and insoluble in water. They are decomposed when heated with water with production of phenols. Thermal decomposition in the presence of inert solvents, such as carbon tetrachloride or benzene, gives *p*-chloronitrobenzene from the *p*-nitrodiazonium compound and mixtures of chlorinated benzenes from the benzenediazonium salt. The *p*-tolyl-, *m*-nitrophenyl-, and *p*-chlorophenyl-diazonium compounds are remarkably stable towards heat. The double salts dissolve in concentrated sulphuric acid with separation of lead tetrachloride and production of the diazonium sulphate. They couple immediately with an alkaline solution of  $\beta$ -naphthol and retain this power after being preserved during many months in a desiccator; an exception is, however, provided by the benzenediazonium salt which undergoes rapid decomposition. Direct sunlight and increased temperature facilitate the decomposition in a remarkable degree.

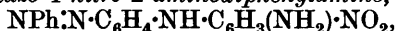
The lead tetrachloride solution is prepared by dissolving lead carbonate in concentrated hydrochloric acid and passing chlorine into the mixture at  $10^\circ$  until the suspended lead chloride is dissolved; excess of chlorine is removed in a current of air. The solution thus

prepared is added to the requisite diazonium solution at  $-5^{\circ}$  when the double salts separate. The following individual substances are described: the salt  $(\text{PhN}_2\text{Cl})_2\text{PbCl}_4$ , straw-yellow leaflets, and the similarly constituted compounds from *p*-toluidine (a yellow, crystalline powder), *p*-chloroaniline (yellow leaflets), *p*-nitroaniline (yellow leaflets), and *m*-nitroaniline.

Ethylamine hydrochloride and lead tetrachloride give the compound  $(\text{EtNH}_2\cdot\text{HCl})_2\text{PbCl}_4$ , yellow leaflets, which is decomposed by water with formation of ethyldichloroamine, b. p.  $89^{\circ}$ . H. W.

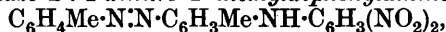
**Characterisation of Aminoazo-derivatives.** G. CHARRIER and A. BERETTA (*Gazzetta*, 1923, 53, 729—760).—The authors find that the reaction suggested by Nietzki and Ernst (A., 1890, 1114) for characterising the primary aromatic amino-group (cf. Reitzenstein, A., 1903, i, 815; Meigen, A., 1908, i, 580; Küchel, *Diss. Giessen*, 1909) and based on the action of 1-chloro-2:4-dinitrobenzene in alcoholic solution and in presence of sodium acetate, followed by reduction of the resulting 2:4-dinitrodiarylaminoderivative to nitroaminodiarylaminocompound by means of sodium sulphide, is general for all aminoazo-derivatives irrespective of the position of the amino-group to the azo-group. The yield of the condensation product is moderately good from the *p*- and *m*-aminoazo-compounds, but less from the ortho-compounds, especially those of the naphthalene series. However, no resin is formed and the product is usually almost insoluble in alcohol, so that purification is easy.

[With A. NANI, L. ALBANI, A. DE LEONIBUS, G. DRISALDI, P. PAVESI, and O. TAVAZZANI.]—2'-Benzeneazo-2:4-dinitrodiphenylamine,  $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ , obtained by the action of 1-chloro-2:4-dinitrobenzene on *o*-aminoazobenzene, forms slender, orange-yellow needles, m. p.  $206^{\circ}$ , dissolves in concentrated sulphuric acid with a green coloration, and resists boiling acetic anhydride. When suspended in alcohol and treated with sodium sulphide, it yields 2'-benzeneazo-4-nitro-2-aminodiphenylamine,

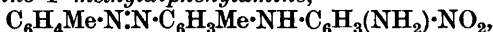


which crystallises in slender, deep red needles, m. p.  $151^{\circ}$ , and gives a benzoyl derivative,  $\text{C}_{25}\text{H}_{19}\text{O}_3\text{N}_5$ , crystallising in slender, yellow needles, m. p.  $199^{\circ}$ .

2'-*p*-Tolueneazo-2:4-dinitro-4'-methylidiphenylamine,



prepared from *o*-tolueneazo-*p*-toluidine, forms lustrous, red needles, m. p.  $232^{\circ}$ , gives a green solution in concentrated sulphuric acid, and on reduction with sodium sulphide yields 2'-*p*-tolueneazo-4-nitro-2-amino-4'-methylidiphenylamine,



which crystallises in reddish-brown needles, m. p.  $166^{\circ}$ , and gives a benzoyl compound,  $\text{C}_{27}\text{H}_{23}\text{O}_3\text{N}_5$ , separating in yellow needles, m. p.  $206^{\circ}$ .

*m*-Aminoazobenzene may be obtained in satisfactory yield by benzoylating *m*-nitroaniline, reducing the *m*-nitrobenzanilide to *m*-aminobenzanilide, and converting the latter, by means of nitroso-

benzene, into the benzoyl derivative of *m*-aminoazobenzene. The melting point of *m*-aminoazobenzene, given by Mills (T., 1895, 67, 917) as 56—57°, is found to be 62°.

3'-Benzeneazo-2:4-dinitrodiphenylamine,



prepared from *m*-aminoazobenzene, crystallises in orange-yellow leaflets, m. p. 162°, and dissolves in concentrated sulphuric acid, giving a red coloration.

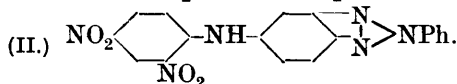
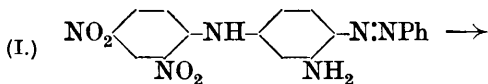
4'-Benzeneazo-2:4-dinitrodiphenylamine, prepared from *p*-aminoazobenzene, has m. p. 176° (cf. Walther and Lehmann, A., 1904, i, 352). 4'-Benzeneazo-4-nitro-2-aminodiphenylamine,  $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}_5$ , obtained by reducing the preceding compound, forms minute, deep red crystals, m. p. 164°; its *acetyl* compound crystallises in slender, yellow needles, m. p. 153°, and its *benzoyl* derivative in yellow needles, m. p. 226°.

4'-o-Tolueneazo-2:4-dinitro-2'-methyldiphenylamine,

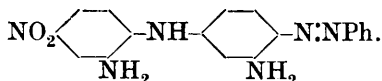


prepared from *o*-tolueneazo-*o*-toluidine, forms deep red needles, m. p. 186°, dissolves in concentrated sulphuric acid to a reddish-violet solution, and, on reduction with sodium sulphide and alcohol, yields 4'-*o*-tolueneazo-4-nitro-2-amino-2'-methyldiphenylamine, which separates in reddish-brown needles, m. p. 159°. 4'-*p*-Tolueneazo-2:4-dinitro-2'-methyldiphenylamine, prepared from *p*-tolueneazo-*o*-toluidine, crystallises in slender, lustrous, red needles, m. p. 151°, and dissolves in concentrated sulphuric acid, giving a violet-red coloration.

The action of 1-chloro-2:4-dinitrobenzene on *m*-diaminoazobenzenes results in the replacement by 2:4-dinitrophenyl of a hydrogen atom of the amino-group situate in the para-position to the azo-group. The amino-group in the ortho-position to the azo-group does not enter into the reaction, even when the chloro-dinitrobenzene is taken in large excess; this appears to be due to the fact that the mono-condensation product is insoluble in alcohol and is hence removed from the sphere of reaction. The resulting diphenylamine derivatives have constitutions analogous to (I) and on oxidation yield the corresponding triazole compounds (II):

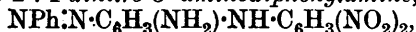


They readily yield monoacetyl and monobenzoyl derivatives, the substituent groups entering the amino-group in the ortho-position to the azo-group. By sodium sulphide in alcoholic solution they are reduced to benzeneazonitrodiaminodiphenylamines of the general formula,



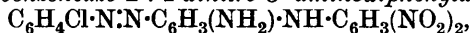


*4'-Benzeneazo-2 : 4-dinitro-3'-aminodiphenylamine,*



obtained by the action of 1-chloro-2 : 4-dinitrobenzene on 4-benzene-azo-1 : 3-diaminobenzene (chrysoidine), crystallises in bright red needles, m. p.  $187^\circ$ , and gives a violet solution in concentrated sulphuric acid; its *acetyl* compound forms slender, orange-red needles, m. p.  $218^\circ$ , and its *benzoyl* compound, silky, red needles, m. p.  $241^\circ$ . *N*-Phenyl-2' : 4'-dinitrophenylamino(3)benztriazole (formula II, above), crystallises in slender, yellow needles, m. p.  $188^\circ$ , and dissolves in concentrated sulphuric acid giving a reddish-yellow coloration.

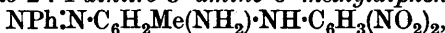
*4'-p-Chlorobenzeneazo-2 : 4-dinitro-3'-aminodiphenylamine,*



prepared from 4-*p*-chlorobenzeneazo-1 : 3-diaminobenzene, forms lustrous, reddish-brown leaflets, m. p.  $220^\circ$ , and gives a blue solution in concentrated sulphuric acid.

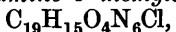
4-*p*-Chlorobenzeneazo-1 : 3-diaminobenzene (*p*-chlorochrysoidine),  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{NH}_2)_2$ , prepared by the interaction of *p*-chlorophenyldiazonium chloride on *m*-phenylenediamine hydrochloride, crystallises in lustrous, yellow needles, m. p.  $140^\circ$ , and its *hydrochloride* in slender, red needles, m. p.  $225^\circ$ . 4-*p*-Bromobenzeneazo-1 : 3-diaminobenzene (*p*-bromochrysoidine),  $\text{C}_{12}\text{H}_{11}\text{N}_4\text{Br}$ , similarly prepared, forms lustrous, golden-yellow needles, m. p.  $155^\circ$ , and its *hydrochloride* red needles, m. p.  $213^\circ$ . 4'-*p*-Bromobenzeneazo-2 : 4-dinitro-3'-aminodiphenylamine,  $\text{C}_{18}\text{H}_{13}\text{O}_4\text{N}_6\text{Br}$ , prepared from the preceding compound, forms lustrous, brick-red needles, m. p.  $218^\circ$ , and dissolves in concentrated sulphuric acid, giving a blue coloration.

*4'-Benzeneazo-2 : 4-dinitro-3'-amino-6'-methyldiphenylamine,*



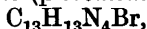
forms deep red needles, m. p.  $273\text{--}274^\circ$ , and dissolves to an emerald-green solution in concentrated sulphuric acid; its *acetyl* derivative forms orange-yellow needles, m. p.  $196^\circ$ , and its *benzoyl* derivative, orange-red needles, m. p.  $252^\circ$ . 4'-Benzeneazo-4-nitro-2 : 3'-diamino-6'-methyldiphenylamine,  $\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_6$ , formed on reduction of the preceding compound by means of sodium sulphide and alcohol, crystallises in lustrous, garnet-red prisms with metallic reflection, m. p.  $244^\circ$ .

4-*p*-Chlorobenzeneazo-1 : 3-diamino-6-methylbenzene (*p*-chloromethylchrysoidine),  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_2\text{Me}(\text{NH}_2)_2$ , prepared from *p*-chlorophenyldiazonium chloride and *m*-tolylenediamine hydrochloride, forms lustrous, golden-yellow leaflets, m. p.  $169^\circ$ , and its *hydrochloride*, lustrous, red needles, m. p.  $235^\circ$ . 4'-*p*-Chlorobenzeneazo-2 : 4-dinitro-3'-amino-6'-methyldiphenylamine,

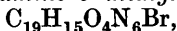


prepared from the preceding compound, crystallises in reddish-brown, lustrous needles, m. p.  $286^\circ$ , and dissolves in concentrated sulphuric acid, giving a green coloration; its *acetyl* compound forms slender, orange-yellow needles, m. p.  $248^\circ$ , and its *benzoyl* compound, orange needles, m. p.  $285^\circ$ . On reduction with sodium sulphide in alcoholic solution, it gives 4'-*p*-chlorobenzeneazo-4-nitro-

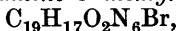
2 : 3'-diamino-6'-methyldiphenylamine,  $C_{19}H_{17}O_2N_6Cl$ , which forms slender, reddish-brown crystals, m. p.  $262^\circ$ . 4-p-Bromobenzeneazo-1 : 3-diamino-6-methylbenzene (p-bromomethylchrysoidine),



crystallises in lustrous, golden-yellow leaflets, m. p.  $177^\circ$ , and its hydrochloride in lustrous, red needles, m. p.  $236^\circ$ . 4'-p-Bromobenzeneazo-2 : 4-dinitro-3'-amino-6'-methyldiphenylamine,

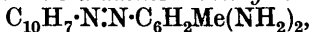


prepared from the preceding compound, crystallises in brownish-red leaflets, m. p.  $290^\circ$ , and yields a green solution in sulphuric acid; its acetyl derivative forms orange needles, m. p.  $242^\circ$ , and its benzoyl derivative, orange-yellow needles, m. p.  $275^\circ$ . 4'-p-Bromobenzeneazo-4-nitro-2 : 3'-diamino-6'-methyldiphenylamine,



forms reddish-brown leaflets, m. p.  $265^\circ$ .

4- $\alpha$ -Naphthaleneazo-1 : 3-diamino-6-methylbenzene,

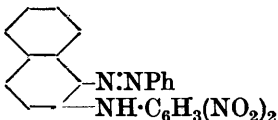


prepared from  $\alpha$ -naphthyl diazonium chloride on *m*-tolylenediamine hydrochloride, crystallises in brown needles with green, metallic reflection, m. p.  $148^\circ$ . 4'- $\alpha$ -Naphthaleneazo-2 : 4-dinitro-3'-amino-6'-methyldiphenylamine,  $C_{10}H_7 \cdot N \cdot N \cdot C_6H_2Me(NH_2) \cdot NH \cdot C_6H_3(NO_2)_2$ ,

obtained from the preceding compound, forms reddish-brown needles with violet metallic reflection, m. p.  $286^\circ$ ; its acetyl compound forms red needles, m. p.  $268^\circ$ , and its benzoyl compound, yellow needles, m. p.  $246^\circ$ . 4'- $\alpha$ -Naphthaleneazo-4-nitro-2 : 3'-diamino-6'-methyldiphenylamine,  $C_{23}H_{20}O_2N_6$ , forms reddish-brown needles, m. p.  $214^\circ$ . 4- $\beta$ -Naphthaleneazo-1 : 3-diamino-6-methylbenzene ( $\beta$ -naphthylmethylchrysoidine),  $C_{17}H_{16}N_4$ ,

crystallises in yellow needles, m. p.  $242^\circ$ . 4- $\beta$ -Naphthaleneazo-2 : 4-dinitro-3'-amino-6'-methyldiphenylamine forms a reddish-brown, crystalline powder, chars, without melting, above  $300^\circ$ , and gives a green solution in concentrated sulphuric acid; its acetyl compound separates in slender, yellow needles, m. p.  $272^\circ$ , and its benzoyl compound in orange needles, m. p.  $267^\circ$ . 4- $\beta$ -Naphthaleneazo-4-nitro-2 : 3'-diamino-6'-methyldiphenylamine,  $C_{23}H_{20}O_2N_6$ , forms minute, reddish-brown crystals, m. p.  $261^\circ$ .

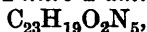
$\alpha$ -Benzeneazo- $\beta$ -naphthyl-2 : 4-dinitrophenylamine (annexed formula), prepared by the action of 1-chloro-2 : 4-dinitrobenzene on  $\alpha$ -benzeneazo- $\beta$ -naphthylamine, crystallises in slender, red needles, m. p.  $285^\circ$ , and gives a greenish-blue solution in concentrated sulphuric acid.



$\alpha$ -Benzeneazo- $\beta$ -naphthyl-4-nitro-2-aminophenylamine,  $NPh \cdot N \cdot C_{10}H_6 \cdot NH \cdot C_6H_3(NH_2) \cdot NO_2$ , forms reddish-brown needles, m. p.  $147^\circ$ .

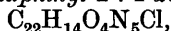
$\alpha$ -o-Tolueneazo- $\beta$ -naphthyl-2 : 4-dinitrophenylamine,  $C_{23}H_{17}O_4N_5$ , obtained from  $\alpha$ -o-tolueneazo- $\beta$ -naphthylamine, crystallises in slender, red needles, m. p.  $223^\circ$ , and dissolves in concentrated sulphuric acid to a greenish-blue solution.  $\alpha$ -m-Tolueneazo- $\beta$ -naphthylamine has m. p.  $103-104^\circ$ .  $\alpha$ -m-Tolueneazo- $\beta$ -naphthyl-2 : 4-dinitrophenylamine forms slender, red needles, m. p.  $245^\circ$ ,

and gives a greenish-blue solution in concentrated sulphuric acid. *α-m-Tolueneazo-β-naphthyl-4-nitro-2-aminophenylamine*,



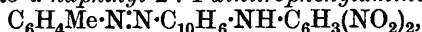
is obtained as a dark red, microcrystalline powder, m. p. 116°. *α-p-Tolueneazo-β-naphthyl-2:4-dinitrodiphenylamine* crystallises in slender, red needles, m. p. 280°, and dissolves in concentrated sulphuric acid to a green solution. *α-p-Tolueneazo-β-naphthyl-4-nitro-2-aminophenylamine* forms microscopic, reddish-brown crystals, m. p. 155°.

*α-p-Chlorobenzeneazo-β-naphthyl-2:4-dinitrophenylamine*,



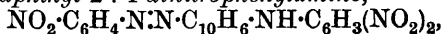
crystallises in slender, bright red needles, m. p. 278°, and dissolves in concentrated sulphuric acid to a deep blue solution. *α-p-Bromobenzeneazo-β-naphthylamine*,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ , forms red crystals, m. p. 135—136°. *α-p-Bromobenzeneazo-β-naphthyl-2:4-dinitrophenylamine* crystallises in slender, red needles, m. p. 263°, and gives a deep blue solution in concentrated sulphuric acid. *4-Benzeneazo-α-naphthyl-2:4-dinitrophenylamine*, obtained from *4-benzeneazo-α-naphthylamine*, forms long, bright-red, silky needles, m. p. 200°, and colours concentrated sulphuric acid bright blue. *4-Benzeneazo-α-naphthyl-4-nitro-2-aminophenylamine* separates in minute, reddish-brown crystals, m. p. 181°, and its *acetyl* compound slender, red needles, m. p. 216°.

*4-o-Tolueneazo-α-naphthyl-2:4-dinitrophenylamine*,



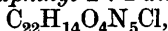
forms lustrous, reddish-brown crystals, m. p. 224°, and dissolves in concentrated sulphuric acid to a deep blue solution. *4-p-Tolueneazo-α-naphthyl-2:4-dinitrophenylamine* crystallises in lustrous, bright red needles, m. p. 207°, and gives a blue solution in concentrated sulphuric acid. *4-p-Tolueneazo-α-naphthyl-4-nitro-2-aminophenylamine* separates in reddish-brown crystals, m. p. 200°.

*4-o-Nitrobenzeneazo-α-naphthylamine*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$ , crystallises in slender, metallic green needles, m. p. 165°. *4-o-Nitrobenzeneazo-α-naphthyl-2:4-dinitrophenylamine*,



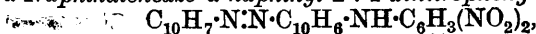
forms a reddish-brown, microcrystalline powder, m. p. 212°, and yields a blue solution in concentrated sulphuric acid. *4-p-Nitrobenzeneazo-α-naphthylamine* crystallises in deep red needles with metallic reflection, m. p. 252°. *4-p-Nitrobenzeneazo-α-naphthyl-2:4-dinitrophenylamine* separates in slender, brownish-red needles, m. p. 263°, and dissolves in concentrated sulphuric acid giving a violet coloration.

*4-p-Chlorobenzeneazo-α-naphthyl-2:4-dinitrophenylamine*,



forms slender, orange needles, m. p. 258°, and gives a green solution in concentrated sulphuric acid. *4-p-Chlorobenzeneazo-α-naphthyl-4-nitro-2-aminophenylamine* separates in slender, deep red crystals, m. p. 228°.

*4-α-Naphthaleneazo-α-naphthyl-2:4-dinitrophenylamine*,



crystallises in slender, brownish-red needles, m. p. 203°, and dis-

solves to a blue solution in concentrated sulphuric acid. 4- $\beta$ -Naphthaleneazo- $\alpha$ -naphthyl-2:4-dinitrophenylamine forms reddish-brown needles, m. p. 241°, and dissolves in concentrated sulphuric acid giving a blue solution. T. H. P.

**Reduction of Semicarbazones.** E. J. POTH and J. R. BAILEY (*J. Amer. Chem. Soc.*, 1923, 45, 3001—3008; cf. A., 1922, i, 880).—Semicarbazones were reduced to the corresponding semicarbazides under a pressure of  $1\frac{3}{4}$ — $2\frac{1}{2}$  atm. of hydrogen in the presence of colloidal platinum. The minimum proportion of platinum necessary for efficient reaction varied considerably and when the reduction produced a basic substance the yield was increased by the addition of acid; the amount of acid required varied greatly. The following semicarbazides were prepared. *Fenchylsemicarbazide*, short needles, m. p. 181°. *Benzoylfenchylsemicarbazide*, a crystalline powder, decomp. 226°.  $\alpha$ -*Phenylcarbamylfenchylsemicarbazide*, thin plates, m. p. 192°. *Carvomenthylsemicarbazide*, thin plates, m. p. 126° (decomp.), and its *hydrochloride*, short needles, decomp. 186°. *Benzoylcarvomenthylsemicarbazide*, m. p. 235°.  $\alpha$ -*Phenylcarbamylcarvomenthylsemicarbazide*, clusters of radiating needles, m. p. 205°. *cycloHexylsemicarbazide*, needles, decomp. 185°, and its *hydrochloride*, m. p. 176—178°. *Benzoylcyclohexylsemicarbazide*, fine needles, m. p. 267° (decomp.).  $\alpha$ -*Phenylcarbamylcyclohexylsemicarbazide*, microscopic short needles, decomp. 236°. *Benzylsemicarbazide*. *Benzylmenthylsemicarbazide*, a crystalline powder, m. p. 216° (decomp.).  $\alpha$ -*Phenylcarbamylmenthylsemicarbazide*, radiating needles, decomp. 184°. In the preparation of isopropyl, bornyl, and menthyl semicarbazides the proportion of colloidal platinum may be considerably reduced with advantage. The following triazoles were obtained by boiling the corresponding acyl semicarbazide with caustic alkali. 3-*Hydroxy-5-phenyl-1-fenchyltriazole*, thick, triangular plates, m. p. 234°. 3-*Hydroxy-5-phenyl-1-carvomenthyltriazole*, thin plates, m. p. 187°. 3-*Hydroxy-1-cyclohexyl-5-phenyltriazole*, slender prisms, m. p. 232—234°. F. B.

### Behaviour of Semicarbazides at Elevated Temperatures.

E. J. POTH and J. R. BAILEY (*J. Amer. Chem. Soc.*, 1923, 45, 3008—3012; cf. preceding abstract).—*cycloHexylsemicarbazide*, when heated at 200° during twelve minutes yielded *dicyclohexylcarbazine* (I),  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_{11})_2$ , plates, m. p. 187°, and unchanged semicarbazide. When the semicarbazide was heated for one and a half hours at 180—185° the products were *cyclohexylurazole* (II)  $\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{CO}\cdot\text{NH} \end{smallmatrix} > \text{N}\cdot\text{C}_6\text{H}_{11}$ , thin, prismatic plates, m. p. 271°, and *dicyclohexylurazine* (III),  $\text{C}_6\text{H}_{11}\cdot\text{N} < \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{CO}\cdot\text{NH} \end{smallmatrix} > \text{N}\cdot\text{C}_6\text{H}_{11}$ , needles or prisms, m. p. 197°; (I) was obtained in good yield when the semicarbazide was mixed with half its weight of urethane and heated at 160°, (II) was prepared by heating the semicarbazide and carbamide in molecular proportions, and (III) by decomposing the hydrochloride of the corresponding semicarbazide. F. B.

**Arylazides. I. Conversion of *p*-Methylarylazides into Homologues of Quinol in Presence and Absence of Phenol.**

E. BAMBERGER and J. BRUN (*Helv. Chim. Acta*, 1923, 6, 935—941).—Some further experiments on the conversion of arylazides into homologues of quinol (cf. A., 1921, i, 716) are described. *p*-Tolylazide (5 g.) boiled with dilute sulphuric acid (1 : 3 by volume) gives about 1 g. of toluquinol, with some *p*-toluidine, a strong odour of cresol, but no aminocresol. From 25 g. of *m*-4-xylylazide, boiled for nine hours with dilute sulphuric acid, there were obtained 1.8 g. 1 : 3-dimethylquinol, 0.2 g. *as*-*m*-xylenol, 4.2 g. *as*-*m*-xylidine, and a considerable quantity of amorphous acids, bases, and resin. When *p*-tolylazide was boiled as before in dilute acid in presence of excess of phenol, from 6 g. of azide, 4.27 g. of *p*-hydroxyphenyl-*p*-tolylamine was obtained, and about 0.32 g. of toluquinol. The theory of the reactions involved has been previously discussed (*loc. cit.*).

E. H. R.

**Arylazides. II. The Conversion of *p*-Methylarylazides into Imino- $\psi$ -quinols and  $\psi$ -Quinols.** E. BAMBERGER and J. BRUN (*Helv. Chim. Acta*, 1923, 6, 942—951).—Practical details are given of experiments previously reported (A., 1921, i, 716).

E. H. R.

**Partial Decomposition of Proteins.** E. ABDERHALDEN (*Z. physiol. Chem.*, 1923, 131, 284—295).—A general description is given of the method of isolating the products of the partial hydrolysis of proteins. The protein is treated with 70% sulphuric acid at a low temperature, *e.g.*, at the ordinary temperature, or at blood heat, and the course of hydrolysis is followed by estimating the amino-nitrogen and comparing it with the total nitrogen, of which an estimation is made on the original protein. The sulphuric acid is removed as barium sulphate, and the filtrate is concentrated in a vacuum. If the product is a solid, it is extracted directly with ether in a Soxhlet apparatus; if it is a syrup, it is mixed with sand to a thick consistency and then extracted. It is afterwards extracted in turn with ethyl acetate, acetone, or methyl alcohol, and if necessary with other solvents such as chloroform or butyl alcohol. It is usually possible after evaporation of the solvent to obtain the fractions in a crystalline form, and they are purified according to their particular composition. In particular cases, variations at any stage may be advisable.

In an attempt to obtain the maximum yield of *d*-alanylglycine anhydride from silk clippings, the residue after hydrolysis, removal of sulphuric acid, and concentration, was treated with alcohol and hydrogen chloride, evaporated to dryness, and the residue dissolved in alcohol. The ammonium chloride separating at once on saturation with ammonia was filtered off. On keeping at 37°, a series of crystalline fractions was obtained, which were extracted in a Soxhlet apparatus with ethyl acetate. Eighty-five g. of pure glycylalanine anhydride was obtained from 1 kg. of silk clippings. Small quantities of glycyl-*l*-tyrosine anhydride and of *d*-alanyl anhydride (dimethylpiperazine) were also obtained.

One kg. of casein was hydrolysed with 10% sulphuric acid at 80°, and the product extracted with ethyl acetate, when 2.5 g. of crystals were obtained, decomp. 280°, and this compound proved to be *L*-leucyl-*D*-valine anhydride. On extracting the residue from the ethyl acetate extraction with acetone, crystals were obtained which on hydrolysis yielded leucine, valine, and glutamic acid, but there was no guarantee that the compound was pure. On further extraction with methyl alcohol, *D*-alanyl-*L*-leucine was obtained along with a crystalline compound,  $C_{14}H_{23}O_3N_3$ , m. p. 192°,  $[\alpha] -183^\circ$ , which yielded proline, *L*-leucine, and *D*-alanine on hydrolysis. It is apparently an anhydride formed from these acids by the elimination of 3 mols. of water. W. O. K.

**The Formation of Carbon Dioxide during the Breakdown of Proteins in the Autoclave.** V. S. SADIKOV (*Biochem. Z.*, 1923, **143**, 492—495).—The method used for the catalytic hydrolysis of proteins by dilute hydrochloric acid under pressure (A., 1923, i, 867) leads in the case of gelatin to a slight formation of carbon dioxide amounting to 2% of the protein. It is suggested that this arises by decarboxylation of the amino-acids under the conditions used. Increasing pressure favours carbon dioxide formation. Nitrogen is also present in the residual gas in the autoclave and oxygen is largely absorbed during the process. J. P.

**Hydrolysis in an Autoclave containing Nitrogen.** V. S. SADIKOV (*Biochem. Z.*, 1923, **143**, 496—503).—Arising from the author's work on the catalytic hydrolysis of proteins under pressure (cf. preceding abstract), it is found that a retention of nitrogen results when this is carried out in an atmosphere of the gas. Dextrose gives negative results, but a fixation is observed in the case of aspartic acid and to a less extent in the case of glycine. Similar treatment of fumaric and succinic acids in the autoclave leads to a notable retention of nitrogen, which is ascribed to the unsaturated compounds arising from these acids. J. P.

**Separation of Proteins of White of Egg by the Acetone Method.** M. PIETTRE (*Compt. rend.*, 1924, **178**, 91—93).—Details are given for the separation of the proteins of white of egg into a globulin, ovalbumin (coagulating at 52.5—53°, and having  $\alpha_D -41.25^\circ$ ), and a glucoprotein. The latter ( $\alpha_D -62.47^\circ$ ) reduces boiling Fehling's solution, and, at a moderate temperature, mercury and bismuth salts (in presence of alkali) and ammoniacal silver nitrate. E. E. T.

**A Further Method of Determining the Isoelectric Point of Proteins and its Application to the Serum-albumins of Various Animals.** L. MICHAELIS and T. NAKASHIMA (*Biochem. Z.*, 1923, **143**, 484—491).—The optimum precipitation point of a mixture of mastic and gelatin in the presence of an acetate buffer approaches the isoelectric point of the latter as its relative amount is increased. This observation is made the basis of a method of determining the isoelectric points of various serum-albumins. To a series of tubes containing mastic sol and an acetate buffer at

varying known  $p_H$ , increasing amounts of the albumin are added, and the  $p_H$  of the zone of optimum precipitation is observed to rise to a constant value beyond which addition of the albumin produces no further shift. This maximum  $p_H$  corresponds with the isoelectric point. The following values for the albumins examined were found: ox and guinea-pig, 4.65; dog, 4.66; puppy, 4.67; turtle and man, 4.68. J. P.

**Nature of the Reaction between Carbophosphide and Blood-serum.** G. CUNEO (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 294—298; cf. this vol., i, 100).—The interaction of carbophosphide and blood-serum yields a phospho-albumin which contains phosphorus in organic combination and either in the most highly oxidised state or as metaphosphoric acid. Since, further, nuclein bases occur among its products of hydrolysis, this phospho-albumin probably owes its existence to a hydrolytic process coupled with atmospheric oxidation, as a result of which the phosphorus of the carbophosphide enters the protein molecule as phosphoric oxide or as a hydrate of the latter. T. H. P.

**Nature of the Reaction between Carbophosphide and Blood-serum.** G. CUNEO (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 353—357; cf. this vol., i, 100, and preceding abstract).—The author has now investigated the behaviour of blood-serum towards a number of different compounds, some free from, and others containing phosphorus. Certain of these compounds do not denature the serum albumin molecule, which remains phosphorus-free, normally digestible by gastric juice, and without hindering effect on putrefactive processes. On the other hand, phosphorus diiodide, ethylphosphine, and sodium hypochlorite effect denaturation of the protein molecule, the reaction, like that produced by carbophosphide, being probably of the nature of an auto-oxidation. The reaction of the serum-albumin with hypochlorite is complex, but the principal product is devoid of iron and phosphorus and exhibits the chemical and biological properties of the nucleic acids. T. H. P.

**Formation of Methæmoglobin.** II. W. HEUBNER and H. RHODE. III. R. MEIER. IV. W. HEUBNER and R. MEIER. V. W. HEUBNER, R. MEIER, and H. RHODE (*Arch. expt. Path. Pharm.*, 1923, 100, 117—127, 128—136, 137—148, 149—161).—I. A comparison of various substances which convert oxyhæmoglobin into methæmoglobin shows that the actions of potassium ferricyanide and of *p*-benzoquinone are almost identical in this respect.

Although the compound of hæmoglobin with nitric oxide is resistant to the action of reducing agents, it may be decomposed by means of indifferent gases and also by dialysis.

II. Optical and gasometric observations show that by the use of ferricyanide or of *p*-benzoquinone in varying proportions it is possible to produce a mixture of oxyhæmoglobin and methæmoglobin with the two constituents in any desired proportions. The

last traces of oxyhæmoglobin are converted into methæmoglobin more easily by ferricyanide than by *p*-benzoquinone.

III. In the presence of hæmoglobin, quinol, *p*-aminophenol and hydrazobenzene are rapidly oxidised by atmospheric oxygen. Whereas the oxidation products of the first two of these substances are active in forming methæmoglobin, that of hydrazobenzene is not; the formation of methæmoglobin by hydrazobenzene therefore, must be due to an activation of the atmospheric oxygen in the process of oxidation of this substance.

Nitrosobenzene converts oxyhæmoglobin in part into methæmoglobin and in part into reduced hæmoglobin.

IV. Phenylhydroxylamine converts oxyhæmoglobin into methæmoglobin and is itself simultaneously converted into azoxybenzene; excess of phenylhydroxylamine in this reaction reduces the methæmoglobin first formed to hæmoglobin. Reduced hæmoglobin is unaltered optically by phenylhydroxylamine.

*m*-Nitrophenylhydroxylamine reacts similarly to phenylhydroxylamine but not so strongly. C. R. H.

**The Natural Porphyrins. IV. Ooporphyrin.** HANS FISCHER and F. KÖGL (*Z. physiol. Chem.*, 1923, **131**, 241—261).—Three hundred g. of gull's egg-shells were extracted with methyl alcohol containing hydrogen chloride, the extract was concentrated, made alkaline with sodium carbonate, and the precipitate washed and dried at 100°. The material was extracted with chloroform, which was then distilled off, and the residue dissolved in a little chloroform, precipitated by the addition of light petroleum, collected on a filter, and dried. It was then again dissolved in a little chloroform, and boiling methyl alcohol was added. *Ooporphyrin dimethyl ester*,  $C_{34}H_{36}O_2N_4(OMe)_2$ , was obtained as leaflets grouped in rosettes, m. p. 225—230°. The absorption bands of this compound are described at length. They resemble those of Kammerer's porphyrin. When ooporphyrin methyl ester from the shell of the gull or of the plover egg is treated with powdered iron in boiling acetic acid, crystals are obtained which although similar, are not identical, crystallographically and spectroscopically. The absorption bands of solutions of ooporphyrin from the egg-shells of various species of birds are described. W. O. K.

**The Precipitation of the Lactoproteins by Copper Salts.** A. J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1923, **32**, 376—386).—The lactoproteins have been precipitated by the addition of various salts of copper (sulphate, chloride, nitrate, and acetate) and the effect of washing the precipitates by water has been examined. With the sulphate, chloride, and nitrate, the results obtained are practically identical. Apart from the case of the acetate precipitate, washing by water appears to have no influence on the composition of the precipitate and its copper content. A second series of experiments was carried out to determine the composition of the solid and liquid phases forming the primitive complex. The results obtained show that the quantity of copper in the precipitates increases as the initial concentration of the copper increases,



whilst the ratio of the quantity of copper precipitated to the total quantity of copper employed diminishes, generally in proportion as the initial concentration of the copper increases. The anion present is shown to have a visibly marked effect on the precipitation of the metallic kation. Galeotti's conclusions (A., 1904, i, 355) as to the equilibrium between the proteins and sulphate of copper are not upheld. F. G. P.

**Triphosphonucleic Acid and Thymic Acid.** S. J. THANNHAUSER (*Z. physiol. Chem.*, 1923, **131**, 296—303; cf. Feulgen and Rosenbeck, A., 1923, i, 618, and Feulgen, *ibid.*, i, 964; also Thannhauser and Sachs, A., 1920, i, 201).—The author has found that after hydrolysing triphosphonucleic acid by alkali, the adenosine may be precipitated as picrate and has obtained almost the theoretical yield of this picrate. He does not admit the validity of the criticism of Feulgen (*loc. cit.*), who doubts the existence of the acid, but he considers that triphosphonucleic acid is with great probability a pure substance. The author also criticises the results of Feulgen (cf. *loc. cit.*) regarding thymic acid. W. O. K.

**Influence of Time on the Physico-chemical Properties of Gelatin Solutions.** R. DE IZAGUIRRE (*Kolloid Z.*, 1923, **33**, 337—347).—The effect of time on the viscosity, multi-rotation, and the action of electrolytes on gelatin solutions has been examined. It is shown that in the presence of hydrochloric acid the influence of time on the viscosity of gelatin solutions passes through a minimum with increasing concentration of hydrochloric acid. This minimum corresponds with the initial viscosity of the solution. The same regularity is found with the time change of the osmotic pressure, whereby the change with time is smaller the larger the osmotic pressure. Since the maximum of the viscosity and the osmotic pressure is closely connected with the swelling, it follows that the time change takes place in the opposite sense to the swelling, that is, the greater the degree of swelling the smaller the time change. Since the viscosity serves as a measure of the gelatinisation this must be regarded as an "unmixing" process and not as the formation of a hypothetical new modification of the gelatin. The optical rotation of gelatin solutions increases with time in such a way that a curve plotted between the logarithm of the angle of rotation and the logarithm of the time is a straight line. The multirotation is expressed by the formula  $[\alpha]_D = K.t^n$ , in which for a 1% solution of gelatin  $K=209$  and  $n=0.082$ . J. F. S.

**The Isoelectric Point of Gelatin from Hide and Bone.** O. GERNGROSS and S. BACH (*Biochem. Z.*, 1923, **143**, 542—552).—The isoelectric points of various preparations of gelatin have been found to range from  $p_H$  4.45 to 5.55 according to their source. [Cf. also B. Feb.] J. P.

**The Displacement of the Isoelectric Point of Gelatin by Formaldehyde.** O. GERNGROSS and S. BACH (*Biochem. Z.*, 1923, **143**, 533—542).—The isoelectric points of two preparations of

gelatin were lowered from  $p_H$  5.05 to 4.6 and from  $p_H$  4.75 to 4.3, respectively, by the presence of formaldehyde. J. P.

**Points of Minimum Swelling of Ash-free Gelatin.** J. A. WILSON and E. J. KERN (*J. Amer. Chem. Soc.*, 1923, **45**, 3139—3140; cf. A., 1923, i, 68).—The two points of minimum in the curve showing the degree of swelling of gelatin as a function of the  $p_H$  value, namely at 4.7 and 7.7, were confirmed when using ash free gelatin. The points coincide with those at which minimum values for the wave-length of maximum absorption in the ultra-violet are observed. F. B.

**Diffusion of Arsenic [Trioxide] in Gelatin.** R. SCHAEFER (*Kolloid Z.*, 1923, **33**, 286—289).—A clear, transparent gel containing arsenious oxide and suitable for dental purposes, may be prepared by adding a few c.c. of hot 30% gelatin solution to a hot solution of arsenious oxide with vigorous stirring. The solution is evaporated slowly on a water-bath and every fifteen minutes a quarter of the evaporated water is replaced by gelatin solution. This process is continued until the concentration desired is reached and the whole allowed to cool to a clear gel. In this way, a gel containing 12—15% of arsenious oxide and 20—30% of gelatin is obtained. The diffusion of arsenious oxide in gelatin has been investigated by laying small portions of the above described gel, and a paste of the powdered oxide and water on a large piece of gelatin and, after sufficient time has elapsed, examining the gelatin by exposing it to hydrogen sulphide. In the case of the arsenic gel, it is found that the amount of arsenic diffused falls off quite regularly as the distance travelled increases, but with the paste there is no apparent diffusion beyond the surface of the gelatin, although this has undoubtedly taken place. The author is of the opinion that in the paste simple molecules are present, but in the gel more complicated molecules are present and these move more slowly, but the total amount of arsenic diffused is greater in the latter case than in the former. J. F. S.

**Reaction of Alkaloids with Gelatin [Solutions] containing Iodine.** H. HANDOVSKY and E. DU BOIS-REYMOND (*Kolloid Z.*, 1923, **33**, 347—348).—Liesegang rings are produced when a solution of 1 : 1000 pilocarpine hydrochloride is placed on a gel containing 3% of gelatin, 0.6% of potassium iodide, and 0.4% of iodine. The rings are alternately reddish-yellow and dark brown, and are about 1—2 mm. apart. Similar, but differently coloured, rings are produced with strychnine nitrate 1 : 1000 and papaverine hydrochloride 1 : 100. J. F. S.

**The Composition of Spinning Silk.** E. ABDERHALDEN (*Z. physiol. Chem.*, 1923, **131**, 281—283).—From the product of the hydrolysis of spinning silk by 70% sulphuric acid at 37° there has been isolated glycyl-L-tyrosine anhydride, m. p. 282°, and glycyl-D-alanine anhydride, m. p. 245°. W. O. K.

**The Influence of Temperature on the Action of Amylase. The Action on the Saccharifying Power of Amylase.** T. CHRZĄSZCZ (*Biochem. Z.*, 1923, **142**, 417—439).—The influence of temperature on the activity of the amylases of various cereals at the optimum  $p_H$  of 4.9 is not uniform. The optimum ranges found are : for barley amylase 49—54°, for rye and wheat amylases 49—55°, for oats amylase 51—53°, and for buckwheat amylase 50—55°. In the cases of maize (56—57°) millet (58—59°), and African millet (62—64°) the optima quoted in brackets lie above the temperatures at which destruction of the enzyme begins. In aqueous solutions, barley amylase is inactivated at 61—62°, rye and wheat amylases at 63—64°, and the other varieties at 65—66°. In general, plant amylases are completely destroyed in one hour when exposed to a temperature of 75°. Amylases from the same genera but of different varieties show the same susceptibility to alteration of temperature at the optimum  $p_H$ . Aqueous malt extracts prepared by shaking for at least one hour give a precipitate when heated at 50°, but if the shaking be of shorter duration (thirty minutes), precipitation does not commence below 55—60°. The precipitate does not affect the activity of the enzyme. Rye-malt extract is exceptional in giving at most a slight opalescence even at 80°.

J. P.

**Potato Amylase.** H. HAEHN and H. SCHWEIGART (*Biochem. Z.*, 1923, **143**, 516—526).—Potato amylase is activated by sodium chloride and fluoride, and by potassium, calcium, barium, and magnesium chlorides. It is inhibited by the salts of the heavy metals. Amino-acids have an activating effect (cf. Doby, *Biochem. Z.*, 1914, **67**, 166). Potato amylase after being freed from most of its salts by dialysis or ultra-filtration loses much, but not all, of its activity, but is reactivated by the addition of the salts of the alkali or alkaline-earth metals. A method of combined dialysis and ultra-filtration yields inactive, salt-free preparations of the amylase, which are reactivated by salts. It is concluded that potato amylase consists of an inactive organic constituent together with an indispensable activating mineral salt.

J. P.

**The Hexose Monophosphatase of Takadiastase.** J. NOGUCHI (*Biochem. Z.*, 1923, **143**, 190—194).—A phosphatase is present in takadiastase which hydrolyses barium and sodium hexose monophosphates at 37°. In the former case, barium phosphate separates as a gel, and in the latter the extent of the hydrolysis, which may be practically quantitative, is dependent on the concentration of the enzyme.

J. P.

**The Cellase of Takadiastase.** C. NEUBERG and O. ROSENTHAL (*Biochem. Z.*, 1923, **143**, 399—401).—Takadiastase contains a cellase which at 37° completely hydrolyses cellobiose to dextrose in five days.

J. P.

**Hemicellulose. IV. Cellobiase and Lichenase.** H. PRINGSHEIM and J. LEIBOWITZ (*Z. physiol. Chem.*, 1923, **131**, 262—268).—Lichenin, which is hydrolysed to dextrose by malt extract, has

been acetylated and then hydrolysed to octoacetylcellobiose (Karrer and Joos, A., 1923, i, 541). It ought therefore to be possible to show that malt extract hydrolyses it first to cellobiose by means of a lichenase, and then to glucose by cellobiase, *i.e.*, to show that both lichenase and cellobiase are present in malt extract. This is verified as cellobiose is hydrolysed to dextrose by malt extract at 37°, and  $p_H$  5, and on the other hand, malt extract, after being kept for three months, hydrolyses lichenin only to cellobiose, as the cellobiase apparently disappears on keeping. The presence of cellobiose was determined by the determination of the reducing power and of the rotation of the solution, and also by the formation of the osazone.

W. O. K.

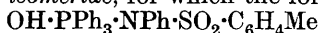
**Synthetic Action of  $\alpha$ -*d*-Mannosidase in Presence of some Monohydric Alcohols.** H. HÉRISSEY and J. CHEYMOL (*Compt. rend.*, 1924, 178, 123—125).— $\alpha$ -*d*-Mannosidase effects a partial conversion of mannose, in presence of ethyl, propyl, isopropyl, and *n*-butyl alcohols, into the corresponding *d*-mannosides (cf. A., 1923, i, 497).

E. E. T.

**The Separation of the Anti-neuritic Vitamin by Means of its Picrate.** G. BERTRAND and A. SEIDELL (*Bull. Soc. Chim. biol.*, 1923, 5, 794—796).—The crude extract containing the active material is separated from inorganic substances as far as possible, dissolved in 60% alcohol and treated with a solution of picric acid in methyl alcohol. The crude picrate thus obtained is active in amounts of 2 mg. per diem when added to a diet of polished rice and administered to pigeons. On recrystallisation of the picrate from water two separate substances are obtained; one crystallises in needles, m. p. 202°, and is inactive; the other forms a crystalline powder, m. p. 160°, and is active.

C. R. H.

**Additive Products of the Phosphineimines.** M. MASRIERA (*Anal. Fís. Quím.*, 1923, 21, 418—435; cf. Staudinger and Hauser, A., 1922, i, 68).—The constitution of the additive products formed from phosphineimines and alkyl or acyl chlorides is discussed. Triphenylphosphinephenylimine reacts with acetyl chloride in ethereal solution, giving a white compound to which the formula  $PPh_3 \cdot NPh \cdot AcCl$  is assigned. It is unstable and gives on decomposition acetanilide and triphenylphosphine oxide. The additive compound of triphenylphosphinephenylimine with methyl iodide is a white substance having m. p. 235°. Attempts to obtain addition of a second molecule of methyl iodide were unsuccessful. The additive compound of toluene-*p*-sulphonyl chloride with triphenylphosphineimine is a white, crystalline substance which decomposes when heated, forming resins. On keeping a mixture of triphenylphosphinephenylimine and toluene-*p*-sulphonyl chloride in ethyl-alcoholic solution for three months, two substances are obtained, namely, triphenylphosphine-*p*-toluenesulphonylphenylammonium hydroxide,  $PPh_3 \cdot NPh(SO_2 \cdot C_6H_4Me) \cdot OH$ , a white crystalline substance, m. p. 191°, and its isomeride, for which the formula



is suggested; it is crystalline and has m. p. 115°.

G. W. R.

**The Syntheses of Arsenic Acids by Means of Diazonium Salts.** Z. FÖLDI (*Ber.*, 1923, 56, [B], 2489—2498).—Evidence is adduced in favour of the view that the diazonium arsenite is the primary product of Bart's arsenic acid synthesis (cf. Schmidt, A., 1920, i, 897). The transformation of the arsenious ion into the arsenic group is simply explained in accordance with Werner's

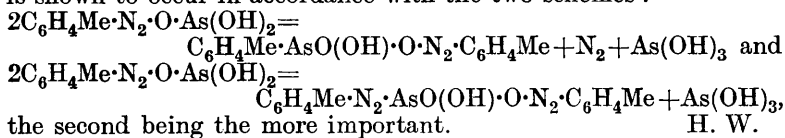
theory if the constitution  $\text{H} \begin{bmatrix} \text{OH} \\ \text{HO} \cdot \text{AsOH} \\ \text{OH} \end{bmatrix}$  or  $\text{H} \begin{bmatrix} \text{OH} \\ \text{OAs} \\ \text{OH} \end{bmatrix}$  is assigned

to arsenious acid, and it is regarded as functioning as a monobasic acid, as is generally the case towards alkali kations including the diazonium-ion. In arsenious acid, the arsenic group exists therefore preformed. The production of the arsinic acid can therefore be explained by assuming that the diazonium kation present in the second sphere of the central arsenic atom enters the first sphere thereby transforming the tervalent into quinquivalent arsenic atom and that the diazoarsenic acid decomposes with evolution of nitrogen.

*p*-Toluidine is diazotised in hydrochloric acid solution by means of sodium nitrite; the cooled solution is saturated with hydrogen chloride, filtered to remove the precipitated sodium chloride, and treated with arsenic chloride, whereby a paste of colourless, granular crystals is produced without evolution of nitrogen. The product can be coupled with phenols or amines, thus showing the diazonium group to be intact. The addition of alkali hydroxide to the aqueous solution causes immediate evolution of nitrogen and the development of the colours and odours characteristic of Bart's reaction. In the presence of sodium hydrogen carbonate, the arsenious acid can be titrated with iodine, the end-point being shown by the formation of a dark coloured diazonium periodide. According to experimental conditions, the compounds  $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2\text{Cl} \cdot \text{AsCl}_3$ ,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2\text{Cl} \cdot 2\text{AsCl}_3$ ,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2\text{Cl} \cdot \text{AsCl}_2 \cdot \text{OH}$ , and  $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2\text{Cl} \cdot \text{AsCl}_3 \cdot \text{AsCl}_2 \cdot \text{OH}$  can be obtained. The first two of these are extremely labile and particularly sensitive to moisture; they can only be obtained from solutions which are completely saturated with hydrogen chloride. The fourth substance has m. p. 94—98° (decomp.); it readily loses hydrogen chloride and passes into the *pentachloro*-salt,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2(\text{As}_2\text{Cl}_5\text{O})$ , pale pink octahedra, m. p. 111—112° (decomp.), whereas when its solution in absolute alcohol is treated with anhydrous ether it gives the compound  $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2\text{Cl} \cdot \text{AsCl}_2 \cdot \text{OH}$ , colourless crystals, m. p. about 90° (decomp.). The salt,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2(\text{AsBr}_3 \cdot \text{OH})$ , m. p. 105°, is described. The hydroxy-chloro-salts can also be prepared from solid *p*-toluenediazonium chloride and arsenic trichloride in concentrated, absolute alcoholic solution.

The diazonium chloroarsenites decompose vigorously in aqueous or alcoholic solution, or in suspension in organic media with evolution of nitrogen in the presence of Gattermann's copper powder or cuprous chloride. In alcoholic solution, the reaction is very complex, giving di-*p*-tolyl, *p*-tolyl ethyl ether, arsenic acid, *p*-tolylarsinic acid, ethyl *p*-tolylarsinate, and *p*-tolylchloroarsine.

A study of the action of *p*-toluenediazonium sulphate on barium arsenite in the presence of water shows that diazonium arsenites are capable of existence in aqueous solution in the presence of an excess of arsenious acid, but attempts to obtain them in the solid state were not successful. Attempts to prepare solutions of diazonium arsenites in the absence of excess of arsenious acid are rendered difficult by the impossibility of preparing undecomposed diazonium hydroxide solutions. When, however, solutions of *p*-toluenediazonium sulphate, barium hydroxide, and arsenious acid in the molecular proportion 1 : 1 : 1 are mixed a pale yellow, turbid alkaline solution is obtained which is alkaline towards litmus but gradually becomes acidic; decomposition of the diazonium arsenite is shown to occur in accordance with the two schemes :



### Physiological Chemistry.

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#### **The Influence of Various Carbohydrates and Amino-acids on the Blood and Urinary Sugar of the Healthy Organism.**

A. SCHÄTTI (*Biochem. Z.*, 1923, **143**, 201—220).—In general, the ingestion by normal individuals of 20 g. of the following carbohydrates produces a hyperglycæmia the intensity of which diminishes in the order given: dextrose, lævulose, sucrose, lactose, galactose. The same amounts of starch, glycine, and alanine produce no hyperglycæmia, but after the ingestion of 100 g. of starch the rise in blood-sugar is as great as, but more delayed than, that produced by 100 g. of dextrose. Peptone and coffee give no hyperglycæmia. Lævulose is excreted more quickly and in greater amount than dextrose, and the sugar excreted after ingestion of sucrose consists chiefly of lævulose. Galactose seems to be excreted largely unchanged by the kidneys. Glycosuria following ingestion of dextrose increases with increasing hyperglycæmia, but the former shows a more delayed maximum than the latter. Glycosuria is not dependent on diuresis, but is regarded as a secretory process. J. P.

#### **Blood-clotting as an Agglutination Process.**

E. HEKMA (*Biochem. Z.*, 1923, **143**, 105—110).—A theoretical paper in which the view is advanced, as a result of the author's previous work, that fibrin formation is a crystallisation process involving the dehydration and agglutination of fibrinogen amicrons. Thrombin is regarded, not as a fibrin ferment, but as an agglutinin, and fibrin consists of fibrinogen plus agglutinin. J. P.

**The Influence of Chemicals on Erythrocyte Membranes by Changes in Corpuscular Volume.** B. S. NEUHAUSEN and J. E. BRESLIN (*Bull. Johns Hopkins Hosp.*, 1923, **34**, 199—201).—A study of the effects of the salts of the blood and of dextrose on the erythrocyte membranes as shown by a comparison of cell volumes in iso-osmotic solutions. Ions cause swelling in the order,  $\text{Ca} < \text{Na} < \text{K}$ . The contracting action of calcium, as opposed to the swelling action of potassium, is specially pointed out. In the case of blood-corpuscles, the membranes are very complex colloidal mixtures, the swelling or precipitation of any component of which will loosen the whole structure.

## CHEMICAL ABSTRACTS.

**The Rôle of Pancreatic Juice in the Digestion of Proteins. Relative Importance of Trypsin and Erepsin.** E. F. TERROINE and ST. J. PRZYLECKI (*Arch. internat. physiol.*, 1923, **20**, 377—396; *Ber. ges. Physiol.*, 1923, **20**, 64; from *Chem. Zentr.*, 1923, iii, 1290).—Pancreatic juice not activated by kinase attacks the normal products of gastric digestion. With activation by kinase, the action is increased. The relative importance of erepsin and trypsin depends on the degree of previous gastric digestion; where this is small, trypsin plays the more important part, but is less important where gastric digestion is more complete. As pancreatic digestion proceeds, the effect of trypsin recedes relative to that of erepsin.  
G. W. R.

**Effect of Magnesium Sulphate and Metallic Magnesium on Metabolic Exchanges.** R. REDING and A. SLOSSE (*Compt. rend. Soc. biol.*, 1923, **88**, 644—646; from *Chem. Zentr.*, 1923, iii, 1108).—Intramuscular injection of 70 c.c. of 10% magnesium sulphate solution decreases the output of total nitrogen, uric acid, and sodium chloride, whilst the output of magnesium is increased. In a rectal carcinoma, injection of 20 c.c. of 10% magnesium sulphate solution was followed by decreased output of total nitrogen, amino-nitrogen, and sodium chloride, and increased output of uric acid and creatine. Similar effects were observed in a rabbit after introduction under the skin of a piece of metallic magnesium.  
G. W. R.

**The Internal Secretion of the Genital Organs. I. The Genital Organs and Carbohydrate Metabolism.** S. TSUBURA (*Biochem. Z.*, 1923, **143**, 248—290).—Castration has no effect on the blood-sugar of fasting dogs, but in the sexually mature animal the operation produces a lowered sugar tolerance. The same effect is produced by ligature of one spermatic cord and extirpation of the opposite testicle, by ligature of both cords, or by exposing the genital glands to X-rays. These operations produce a degeneration of the sperm-cells, but do not affect the interstitial cells. The lowered sugar tolerance may be temporarily raised by transplantation of the sexual organs of another animal, but not by feeding the organs or by injection of extracts. Glycogen formation, glycogenolysis, and glycolysis of the blood-sugar in vitro are somewhat delayed after castration, but the blood amylase is unchanged.



After castration, the reactions of the blood-sugar to adrenaline, diuretin, and pituitrin are increased, but thyroid feeding has no effect, although it raises the low sugar tolerance of the castrated animals. The kidneys of the latter are more permeable to sugar, but the excretion of phenolsulphonephthalein is delayed as compared with the normal condition. In general, parallel experiments on male and female dogs gave similar results. The other endocrine organs show alterations after castration, and the observed results may not be wholly due to disturbances of the internal secretory functions of the genital organs. J. P.

**The Internal Secretion of the Genital Organs. II. The Genital Organs and Respiratory Gaseous Metabolism.** S. TSUBURA (*Biochem. Z.*, 1923, **143**, 291—322).—Castration produces a lowered gaseous metabolism which becomes apparent about one month after the operation. A similar effect is produced by ligature of one spermatic cord and removal of the opposite testicle. Transplantation of the testes of another animal raises the gaseous exchange whilst feeding experiments are ineffective. Dogs in heat show no increased gaseous metabolism. Thyroid feeding raises the low gaseous exchange of castrated animals. The combined results of thyroid feeding on the sugar tolerance (cf. preceding abstract) and gaseous metabolism of castrated dogs are explained as being due to a moderate stimulation of the sluggish carbohydrate metabolism by the thyroid hormone. J. P.

**The Ferments in the Placenta.** K. MAEDA (*Biochem. Z.*, 1923, **143**, 347—364).—Extracts of the placenta contain diastase in considerable amount, in part derived from the parental blood. Carboxylase and small quantities of lactase and invertase are present, but glycolytic enzymes are not found. Of proteolytic enzymes, erepsin, a weak trypsin, and traces of pepsin, but no rennin, are found. An asparagine deaminase is present. Mono- and tributyrases are found, and the latter, being stable to both quinine and atoxyl, is thus differentiated from serum lipase. Histozyyme, a feeble salicylase, and an oxydase acting on pyrocatechol, adrenaline, and dihydroxyphenylalanine, but not on tyrosine, are present. J. P.

**The Site of Origin of Bilirubin.** A. R. RICH (*Bull. Johns Hopkins Hosp.*, 1923, **34**, 321—329).—Hæmoglobin introduced into the blood-stream of a dog without a liver, and circulating actively for as long as five and a half hours is not transformed into bilirubin. Since, however, the production of bilirubin from circulating hæmoglobin takes place rapidly and readily in a dog with a liver through which the blood-stream passes, it is concluded that the liver is necessary for the transformation of circulating hæmoglobin into bilirubin. The conclusions are applicable only to hæmoglobin circulating in the blood-stream, not to hæmoglobin liberated into the tissues from extravasated blood; the conversion of hæmorrhage hæmoglobin into bilirubin (hæmatoidin) is a purely local phenomenon, the exact mechanism of which is unknown.

CHEMICAL ABSTRACTS.

**[Fish] Liver Oils.** M. TSUJIMOTO (*J. Chem. Ind. Japan*, 1923, 26, 482—486).—The oil from the Jewfish (*Stereolepis ischinagi* (Hilg.)), contains a large amount of peculiar unsaponifiable matter (up to 50%), which is a viscous substance of reddish-orange colour, having a resinous odour, and showing much resemblance to colophony when dried at 100° for several hours. The name "liver-resin" is proposed for it. Liver oil from *Erilepis zonifer* (Lock.) also contains a similar substance (about 4%). These oils and the unsaponifiable matter (especially in carbon disulphide solution) give a deep violet coloration with sulphuric acid. With a sample of *S. ischinagi* liver oil, the coloration was observed to be about one hundred times as strong as that of a cod-liver oil. K. K.

**The Highly Unsaturated Acids in Cod-liver Oil.** M. TSUJIMOTO and K. KIMURA (*J. Chem. Ind. Japan*, 1923, 26, 1162).—By the potassium salt-ether method, and the lithium salt-acetone method, a mixture of highly unsaturated acids was obtained. By converting it into the methyl ester, a fraction (about 4% of the oil) boiling at 220—226°/5 mm. was isolated. The analysis of the ester and the fatty acid from the ester gave  $C_{22}H_{33}O_2Me$  and  $C_{22}H_{34}O_2$  respectively, and behenic acid was produced from the latter by hydrogenation. Cod-liver oil therefore contains a large amount of clupanodonic acid,  $C_{22}H_{34}O_2$ . The part of the methyl ester boiling below 220°/5 mm. is supposed to contain a large amount of a highly unsaturated acid containing eighteen or twenty carbon atoms. K. K.

**Further Studies on Autoxidations and Oxido-reduction Processes.** V. E. ABDERHALDEN and E. WERTHEIMER (*Pflüger's Archiv*, 1923, 200, 176—193; from *Chem. Zentr.*, 1923, iii, 1290).—The reducing power of muscle in which thermal rigor has been induced is three or four times that of normal muscle. In chemical rigor and rigor mortis, there is a similar increase in reducing power. An increase also occurs during normal or tetanic contraction. It is supposed that such increases are associated with the presence of a thiol group in the muscle fibres. Cysteine serves as a hydrogen carrier and acceptor. A scheme for a stable oxido-reduction system is given. G. W. R.

**A Methylation Function of the Thyroids and the Biological Significance of Iodine.** B. STUBER, A. RUSSMAN, and E. A. PROEBSTING (*Biochem. Z.*, 1923, 143, 221—234).—If guanidineacetic acid be administered intravenously to young dogs, an increase of blood creatine-creatinine follows. No such increase occurs in thyroidectomised animals, but if these be given dried thyroid or potassium iodide per os, before the injection of guanidineacetic acid, they react like the normal animals. The blood of normal dogs, but not of thyroidectomised dogs, is also effective in this respect. It is concluded that the capacity of the organism to methylate guanidineacetic acid, and so form creatine and creatinine, is dependent on the integrity of the thyroids, and that iodine compounds are necessary for this methylation process. J. P.

**The Oxytocic-Pressor-Diuretic Principle of the Infundibular Portion of the Pituitary Gland.** J. J. ABEL, C. A. ROUILLER, and E. M. K. GEILING (*J. Pharm. exp. Ther.*, 1923, **22**, 289—316).—After a purification of the gland material by precipitation with mercuric chloride, phosphotungstic acid, and tannic acid in succession, the residue is dissolved in an alcoholic solution of tartaric acid and re-precipitated with ether. The resulting precipitate is called the tartrate of the active principle. Its action on the isolated uterus of the guinea-pig may be as much as 1,250 times as great as that of histamine phosphate, whilst it also retains the diuretic and pressor action characteristic of the pituitary extract. C. R. H.

**Anaërobic Processes Involved in Muscular Activity.** W. HARTREE and A. V. HILL (*J. Physiol.*, 1923, **58**, 127—137).—In muscle, 0.1% of lactic acid can be produced so rapidly by exercise or by stimulation that no appreciable escape of carbon dioxide or of acid is possible. Hence if the hydrogen-ion concentration inside a muscle is not to rise to an excessive degree during exercise, there must be some buffer in it, much more effective than a bicarbonate solution. Meyerhof (*Pflüger's Archiv*, 1922, **195**, 22) has emphasised that in a frog's muscle the absolute amount of bicarbonate present, as determined from the carbon dioxide driven out from the muscle by excess of acid, is quite inadequate to neutralise the lactic acid liberated in severe stimulation. Even if all the carbon dioxide were driven out, only one-seventh to one-tenth of the lactic acid could be neutralised.

The authors further calculate that the 0.3% inorganic phosphate in muscle (a mixture of  $\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{HPO}_4$ ) is also quite inadequate to keep the  $P_{\text{H}}$  within the extreme limits observed, viz., a change from 7.5 to 6.9). Bicarbonate and phosphate together are insufficient to neutralise half the lactic acid formed. There must be, as Meyerhof assumes, some other powerful buffer, doubtless an alkali-protein salt. The addition of lactic acid to shed blood also produces only a fraction of the change in the hydrogen-ion, which would result in a bicarbonate solution of the same concentration; here also alkali protein must play a considerable part.

The authors confirm the existence of a secondary maximum in the production of heat in a muscle in the absence of oxygen; this maximum occurs after about two and a half minutes (see the following abstract for its interpretation). A "balance sheet" is given of the heat evolved in the different phases of muscular contraction; it shows that during the recovery process something between 1/4.7 and 1/6 of the lactic acid removed is oxidised, the rest being reconverted into glycogen. G. B.

**Heat of Combustion of Glycogen in Relation to Muscular Contraction.** W. K. SLATER (*J. Physiol.*, 1923, **53**, 163—167).—Glycogen (from *Mytilus edulis*, a convenient source) only becomes anhydrous at 100° in a vacuum over phosphoric oxide (cf. Harden and Young, *T.*, 1902, **81**, 1224). Dried by the method of Atkins and Wilson (*T.*, 1915, **107**, 916), it has the composition  $(\text{C}_6\text{H}_{10}\text{O}_5, \text{H}_2\text{O})_n$ .

The heat of combustion seems previously to have been determined with slightly hydrated material. The author finds the heat of combustion of hydrated glycogen to be 3,883 cal. per gram, which is about 100 cal. higher than that calculated from Stohmann and Schmidt's value, 4,190 (A., 1895, ii, 102), for (presumably imperfectly) dehydrated glycogen, for this would give for the hydrated form  $162/180 \times 4,190 = 3,771$  cal. The heat of wetting is found to be about 9 cal., hence the heat of combustion of hydrated glycogen in solution is 3,874 cal. The heat of combustion of lactic acid is, according to Meyerhof, 3,601 cal., leaving 273 cal. for the conversion of 1 g. of glycogen into 1 g. of lactic acid. The heat of neutralisation of lactic acid by acid salts is, according to Meyerhof (*loc. cit.*), 19 cal. per g., which leads to the value  $273 + 19 = 292$  cal. for the heat liberated during contraction and relaxation of a muscle, per g. of lactic acid formed. The total initial heat, given by Hartree and Hill in their balance-sheet (as the result of physical measurement, see preceding abstract) is 296 cal., in close agreement with that calculated above. The salt buffering of the lactic acid is, however, probably only of a temporary character and is replaced by the more efficient buffering by alkali-protein. Meyerhof has shown that the neutralisation of 1 g. of lactic acid by alkali-protein produces 138 cal., or 119 more than that by salts. The whole of these 119 cal. are, however, not produced; according to Hartree and Hill the delayed anaërobic heat production is 74 cal. per g. of lactic acid, so that only about 60% of the lactic acid formed is neutralised by alkali protein (the rest remains neutralised by salts). The delayed heat production, presumably due to a transfer of alkali from protein to acid phosphate and carbonic acid, is the cause of the secondary maximum in the heat production occurring after two and a half minutes (preceding abstract). The velocity of this reaction is independent of the temperature, and thus probably depends on a physical process (rate of diffusion of acid phosphate- and carbonic acid-ions) through the muscle-tissue. This theory demands some special distribution of phosphate and carbonate molecules in the muscle substance, and may be represented by the following scheme :

*Contraction* (a) Glycogen  $\rightarrow$  lactic acid; (b) lactic acid and contractile mechanism produce mechanical response.

*Relaxation* (a) Lactic acid +  $K_2HPO_4$  and  $KHCO_3 \rightarrow K$  lactate +  $KH_2PO_4$  and  $H_2CO_3$ .

*Anaërobic recovery* (a)  $KH_2PO_4$  and  $H_2CO_3 + K$  protein  $\rightarrow K_2HPO_4 + KHCO_3 + H$  protein. G. B.

**Products of the Catalytic Hydrolysis of Horse Hair.** V. S. SADIKOV (*Biochem. Z.*, 1923, 143, 504—511).—Fractionation of the product obtained by the catalytic hydrolysis of horse hair under pressure yielded the following substances : (1) A peptide anhydride (m. p.  $258^\circ$ ) of alanine and leucine to which the formula  $C_{21}H_{36}O_4N_4$  or  $C_{21}H_{38}O_4N_4$  is ascribed. (2) A peptide anhydride of alanine and leucine (m. p.  $260^\circ$ ) of the formula  $C_9H_{16}O_2N_2$ . (3) A peptide anhydride of leucine and valine (m. p.  $246^\circ$ ) of the formula

$C_{11}H_{20}O_2N_2$ . (4) Butylalanyl-leucine anhydride,  $C_{10}H_{18}O_2N_2$ , or its unsaturated derivative,  $C_{10}H_{16}O_2N_2$  (m. p.  $224^\circ$ ). (5) Diketomethylpiperidine,  $C_8H_{12}O_2N$  (m. p.  $196^\circ$ ). (6) A cyclic nitrogen substance,  $C_{15}H_{30}N$ , of an alkaloidal nature. (7) A substance of the formula  $C_{13}H_{20}O_3N_2$  (m. p.  $170^\circ$ ). Various other less well characterised derivatives of the nature of diketopiperazines and keto- and diketo-piperidines were obtained. J. P.

**Calcium Fixation by Animal Tissues. IX.** E. FREUDENBERG and P. GYÖRGY (*Biochem. Z.*, 1923, **142**, 407—416).—A study has been made of the extent to which calcium phosphate and carbonate are formed, when solutions of casein and egg-albumin are treated with sodium phosphate or carbonate at different  $p_H$ , and dialysed against calcium chloride. After dialysis the distribution of calcium, phosphate, and fixed carbon dioxide was determined both externally and internally, and the bearing of the results on the process of calcification occurring in animal tissues is discussed. The conclusion is drawn that a reversible fixation of calcium by the tissue proteins takes place. With diminishing metabolic activity, the fixed calcium reacts with phosphate and carbonate to give rise to complex protein-calcium-phosphate-carbonate compounds from which the carbonate is gradually eliminated by the acid nature of the proteins under tissue conditions. The excess of calcium phosphate is then split off, leaving the original active group of the protein free to combine with more calcium (cf. also György, this vol., i, 120). J. P.

**The Basis of the Oxidation Theory of Wieland.** O. WARBURG (*Biochem. Z.*, 1923, **142**, 518—523).—A criticism of Wieland's views on the mechanism of oxidation. In place of the theory that organic oxidations proceed in two phases, first hydration followed by abstraction of hydrogen by interaction with molecular oxygen, the theory advanced by the author supposes that molecular oxygen is first activated by combination with a catalyst (iron, platinum, or organic catalyst) and then reacts directly with the oxidisable substance. It is argued that Methylene-blue, quinone, etc., do not react like molecular oxygen when substituted for the latter (Wieland, A., 1913, i, 1304), but as activated oxygen, i.e., molecular oxygen + catalyst. The action of hydrocyanic acid in inhibiting oxidations is regarded as opposing Wieland's theory, whilst it receives a ready interpretation on the author's views, since it combines with the catalyst (e.g., iron) and prevents the activation of the oxygen. J. P.

**Carnisapidine in Animal Tissues.** F. BATTELLI and L. STERN (*Compt. rend. Soc. Biol.*, 1923, **88**, 575—577; from *Chem. Zentr.*, 1923, iii, 1037).—The constituent of animal tissues to which the taste is due is named by the author *carnisapidin*. The amount present in different tissues was determined approximately by dilution of extracts until the taste was just perceptible. The highest content was found in muscles, liver, spleen, and kidneys, lower amounts were found in the thymus, brain, and lungs. G. W. R.

**Sarcochromogen in Animal Tissues.** F. BATTELLI and L. STERN (*Compt. rend. Soc. Biol.*, 1923, **88**, 679—681; from *Chem. Zentr.*, 1923, iii, 1037; cf. preceding abstract).—Aqueous extracts of animal tissues contain a sarcochromogen which differs from sarcochrome in not being precipitated by metaphosphoric acid. Sarcochromogen is not changed into sarcochrome on evaporation to dryness if the temperature remains below 80°. G. W. R.

**The Rôle of Carnisapidin and Sarcochromogen in Animal Tissues.** L. STERN and F. BATTELLI (*Compt. rend. Soc. Biol.*, 1923, **88**, 681—683; from *Chem. Zentr.*, 1923, iii, 1037; cf. preceding abstracts).—The occurrence of carnisapidin and sarcochromogen in animal tissues appears to have no direct correlation with metabolic exchange. Certain proteins such as casein give, on treatment with pepsin, substances analogous to sarcochromogen. Carnisapidin and sarcochromogen are easily dialysable, and are not attacked by digestive ferments. Carnisapidin, administered intravenously, is eliminated in the urine, but when administered orally or subcutaneously it is retained or decomposed, probably in the liver. G. W. R.

**The Extractives of *Actinia equina*.** D. ACKERMANN, F. HOLTZ, and H. REINWEIN (*Z. Biol.*, 1924, **80**, 131—136; cf. A., 1923, i, 1155).—The extractives of *Actinia equina* were subjected to fractionation by Kossel and Kutscher's method. The histidine and arginine fractions have not yet been worked up. In the purine fraction there was obtained adenine, isolated in the form of its picrate. From the lysine fraction there was obtained (1) tetramethylammonium hydroxide (as picrate); (2) a base, identified as pyridylmethylammonium hydroxide (*chloroaurate*, m. p. 252—253°, and *chloroplatinate*); (3) a base of unknown constitution, *actinine*,  $C_{13}H_{24}O_5N_2$ ; from it there were prepared a *chloroaurate*, m. p. 169°, a *chloroplatinate*, dark red, crystalline nodules, decomp. 209°, and a *hydrochloride*, m. p. 207—208°. C. R. H.

**The Chemical Differential Diagnosis of Transudates and Exudates.** K. HIRUMA (*Biochem. Z.*, 1923, **142**, 506—517).—Exudates contain an albumin precipitable by an acetate mixture at  $C_H 0.36 \times 10^{-4}$ , by a phosphate mixture at  $C_H 0.214 \times 10^{-2}$ , and by a citrate mixture at  $C_H 1.13 \times 10^{-4}$ . Inflammatory cerebrospinal fluids contain the same type of albumin as the exudates formed in pleurisy and in peritonitis. The average sugar content of transudates is 0.115% and of exudates 0.07%, the former being in general above the plasma sugar value of the patient, and the latter somewhat lower. The residual nitrogen of transudates, and the amino-nitrogen and ammonia of both transudates and exudates, are approximately the same as those of the blood, whilst the residual nitrogen of exudates is higher than that of transudates. In nephritis, the residual nitrogen is greater the more marked is the cedematous condition. J. P.

**The Distribution of Nitrogen in the Urine of Young Dogs and its Dependence on Diet.** F. SERIO (*Biochem. Z.*, 1923, **142**, 440—453).—The distribution of nitrogen in the urine of young dogs

kept on a diet rich in fat but poor in, or free from, nitrogen is similar to that of starved animals. The urea is diminished and the ammonia increased due to starvation acidosis. The excretion of amino-acids is not influenced by a low nitrogen diet, but it is lowered on a milk diet. The "urease" method for estimating urea gives lower results than the Mörner-Sjöquist method, a difference which is more marked the smaller the ratio of urea nitrogen to total nitrogen becomes. During the period of pre-mortal increase in the nitrogen excretion, the difference disappears, and it is less apparent on a milk diet. The suggestion is made that the difference is due to allantoin and creatinine being estimated along with urea in the Mörner-Sjöquist method, and that the excretion of these urinary constituents varies under the conditions studied, ceasing during the pre-mortal period.

J. P.

**Sulphatase. III. The Enzymatic Fission of the Ethereal Sulphates in the Urine of the Horse, Camel, and Dog.** J. NOGUCHI (*Biochem. Z.*, 1923, **143**, 186—189).—By treating horse and camel urine with preparations of sulphatase at 37°, hydrolysis of the ethereal sulphates varying from 60 to 90% was obtained. Similar extensive hydrolysis of the organic sulphates occurred in the urine of a dog to which phenol had been administered.

J. P.

**Acetonuria and Acidosis.** D. ADLERSBERG (*Biochem. Z.*, 1923, **143**, 527—532).—From a study of the effect of orally administered ammonium dihydrogen phosphate on normal subjects kept on a diet free from carbohydrate, and on diabetic subjects, it is concluded that acidosis diminishes the urinary excretion of ketone substances in these conditions.

J. P.

**Thymolglycuronic Acid.** K. TAKAO (*Z. physiol. Chem.*, 1923, **131**, 304—306).—According to Blum (A., 1892, 1116), thymol is not excreted by the dog as thymolglycuronic acid, although it is so in man. It is now shown, however, that a very small fraction of it is so excreted by the dog. By treatment with sodium hypochlorite and fuming hydrochloric acid, thymolglycuronic acid in the urine was converted into *dichlorothymolglycuronic acid*,  $C_{16}H_{22}O_8Cl_2$ , colourless needles, m. p. 118—119°,  $[\alpha]_D^{20} - 66.46^\circ$  ( $c = 3.9497\%$ ) (barium salt,  $[C_{16}H_{21}O_8Cl_2]_2Ba$ ).

W. O. K.

**Phosphorus Metabolism in Avitaminosis.** K. MORINAKA (*Biochem. Z.*, 1923, **142**, 381—384).—The phosphorus content of the livers of avitaminosed rats to which sodium phosphate, lecithin, or phosphoprotein has been administered does not differ appreciably from that of the livers of similarly fed normal rats. The conclusion is drawn that in avitaminosis the soft tissues do not lose their power of phosphorus retention.

J. P.

**The Kephalin and Lecithin Content of the Brain in Avitaminosis.** H. NARTO (*Biochem. Z.*, 1923, **142**, 385—392).—The percentage content of kephalin and lecithin in the brains of avitaminosed rats and guinea-pigs does not depart appreciably from normal, although there is a diminution in the total mass of brain-tissue.

J. P.

**The Lecithin Content of the Brain and Liver of Normal and Avitaminosed Pigeons after Forced Lecithin Feeding.** H. NAITO (*Biochem. Z.*, 1923, **142**, 393—397).—Lecithin feeding slightly increases the amount of the lipid found in the livers of normal, but not in the livers of avitaminosed pigeons. The lecithin of the brain is not affected in either case. It is concluded that in the avitaminosed liver, phosphorus compounds other than lecithin increase at the expense of the latter (cf. Morinaka, above). J. P.

**Fat Metabolism in Avitaminosis. IV. The Gaseous Metabolism of Starved Avitaminosed Rats during Digestion and after Adrenaline Injection.** K. ASADA (*Biochem. Z.*, 1923, **143**, 387—398).—The oxygen consumption of partly and completely avitaminosed rats is sub-normal, both during a period of starvation and while a vitamin-free meal is being digested. The extent of the increase observed under the latter conditions compared with the requirements of the starved animals varies inversely with the severity of the avitaminosis. Adrenaline injections produce a greater increase in oxygen consumption in avitaminosed than in normal rats. A discussion is appended of the earlier results obtained in the study of carbohydrate and fat metabolism in avitaminosis.

J. P.

**Uric Acid and Allantoin Metabolism in Avitaminosis.** A. ADACHI (*Biochem. Z.*, 1923, **143**, 408—422).—In avitaminosis, the excretion of allantoin in dogs shows no notable variations, whilst that of uric acid is variable and may show transitory increases. In long-continued avitaminosis, the uric acid excretion is markedly increased and may reach values three times those obtained in normal animals. It is concluded that an increased consumption of nucleins occurs in the later stages of avitaminosis.

J. P.

**The Pharmacology of the Rare Earths. I. Cerium.** S. HARA (*Arch. exp. Path. Pharm.*, 1923, **100**, 217—253).—In general, cerium bears a close resemblance to aluminium and to the heavy metals in its pharmacological action. Proteins are precipitated by moderate but not by strong concentrations of its salts.

C. R. H.

**The Pharmacology and Toxicology of Carbon Tetrachloride.** P. D. LAMSON, G. H. GARDNER, R. K. GUSTAFSON, E. D. MAIRE, A. J. MCLEAN, and H. S. WELLS (*J. Pharm. exp. Ther.*, 1923, **22**, 215—288).—A comprehensive study of the pathological effects following administration to dogs of carefully purified carbon tetrachloride. Oral administration produced only slight and transitory symptoms unless accompanied or preceded by administration of fats or alcohol. When given intravenously, it is lethal in doses of 0.154 c.c. per kg. body-weight.

The pathology of carbon tetrachloride poisoning consists essentially (apart from local irritant effects such as bronchitis following inhalation) in damage done to the liver, one of the first indications of which is the appearance of abnormal amounts of bilirubin in the blood.

C. R. H.



**The Rôle of certain Carbohydrates in the Organism.** E. O. FOLKMAR (*Bibliotek læger*, 1923, **115**, 120—125; from *Chem. Zentr.*, 1923, iii, 1291).—With continued intravenous injection of pentoses in small amounts at a rate comparable to intestinal absorption, approximately one-half is excreted in the urine. Galactose can be assimilated at the daily rate of 1—2 g. per kg. of live weight without glycosuria or appreciable increase in blood-sugar. Maltose is well utilised, after becoming hydrolysed by maltase. There is an appreciable retention of sucrose in certain circumstances; invertase is, however, not present in blood. Raffinose is completely excreted. The small amounts of ethyl alcohol normally present in blood are attributed to casual decomposition of carbohydrates and not to the action of an alcoholase. G. W. R.

**The Influence of Oral Administration of Dextrose on the Blood-sugar and on Glycosuria in Healthy Individuals.** G. CONSTAM (*Biochem. Z.*, 1923, **143**, 75—104).—The elimination of sugar in the urine is best followed by estimating the amount excreted in unit time. Observations based purely on changes in concentration do not give dependable results. In normal individuals a mixed meal is followed by a definite glycosuria. Tap water produces a dilution glycosuria which reaches a maximum in about one hour. The assimilation limit for sugar in the same individual is variable and is higher after five hours' than after fourteen hours' abstention from food, whilst the assimilation capacity varies in the opposite sense. In the cases quoted, the tolerance lay between 100 and 150 g. of dextrose in 500 c.c. of water after five hours, and between 20 and 30 g. in the same volume after fourteen hours' starvation; less concentrated solutions caused dilution glycosuria which diminished with increasing concentration of dextrose until the assimilation limit was reached, when a true glycosuria supervened. The blood-sugar reaches its maximum about half an hour before the urinary sugar. The suggestion is made that the power of the organism to raise the sugar tolerance is a protective mechanism which prevents loss of sugar during periods of diminished rate of assimilation. J. P.

**A New Method of Preparing *s*-Diphenylguanidine. Its Pharmacological Effects.** O. RIESSER (*Z. physiol. Chem.*, 1923, **131**, 204—213).—Diphenylguanidine is formed together with a small amount of triphenylmelamine when dicyanodiamine is heated with aniline hydrochloride at 190—200°. It crystallises from alcohol in white needles, m. p. 145—148°, and forms a chloroaurate. The pharmacological action of this substance has been investigated. It increases the reflex irritability and also causes central paralysis. In warm-blooded animals, it causes death by arrest of the respiration. It produces progressive paralysis when applied to isolated frog's muscle. W. O. K.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Biology of *Bacillus coli communis*. Attempts at "Dysmutation."** O. FERNÁNDEZ and T. GARMENDIA (*Anal. Fis. Quím.*, 1923, **21**, 481—492).—A study of the effect of various reagents on the fermentation of dextrose by *B. coli communis*. Dysmutation consists in the formation of alcohol, acetic acid, and glycerol from sugars through the acetaldehyde formed as an intermediate stage undergoing the Cannizzaro reaction yielding ethyl alcohol and acetic acid. The dysmutation effect, as judged by the amount of acetic acid produced from dextrose was considerable in the case of cultures to which sodium hydrogen carbonate was added. Less appreciable effects were produced where amino-acids were added.  
G. W. R.

**The Decomposition of *d*-Glucosamine by Micro-organisms.** K. TAKAO (*Z. physiol. Chem.*, 1923, **131**, 307—318).—*Bacillus subtilis*, grown on a synthetic medium, with or without the addition of peptone, in presence of *d*-glucosamine forms from the latter succinic acid and a small quantity of lactic acid. If a modified medium is used in which no carbonate is present, lactic acid, but no succinic acid is formed. *B. coli* also forms lactic acid and succinic acid, whilst *B. prodigiosus* forms only lactic acid when grown on a synthetic medium containing *d*-glucosamine.  
W. O. K.

**The Sulphur Cycle in Soil. (The Biology of Thiosulphate Bacteria.)** G. KLEIN and A. LIMBERGER (*Biochem. Z.*, 1923, **143**, 473—483).—The thiosulphate bacteria present in soil can be cultured aërobically in inorganic or organic media, and are capable of oxidising the various inorganic compounds of sulphur which occur in soils to sulphuric or polythionic acids. They also oxidise the sulphur of cystine, and to a less extent that of albumin and nuclein to sulphuric acid. Sulphur is an intermediate product in all cases and may separate in a crystalline condition. In the presence of potassium nitrate, the oxidation is accompanied by the formation of nitrite and ammonia, whilst the presence of ammonium chloride gives rise to the former. The spores of the bacteria are found in water and air as well as in the soil. Considerable importance is attached to the part played by these bacteria in the sulphur cycle occurring between the plants and animals.  
J. P.

**The Influence of Oxygen on the Assimilatory and Dissimilatory Activity of Yeast. III. The Behaviour of Added Alcohol in a Yeast Suspension.** H. LUNDIN (*Biochem. Z.*, 1923, **142**, 454—462).—Arising from the author's previous work (A., 1923, i, 1268), a study has been made of the capacity of aqueous yeast suspensions, containing no carbohydrate or source of nitrogen, to assimilate added ethyl alcohol both under normal conditions and in the presence of excess of oxygen. In contrast to the results

obtained with "nascent" alcohol formed from carbohydrate which is assimilated both with and without excess of oxygen, added alcohol is only assimilated when a stream of oxygen is passed through the solution. Carbohydrate alone is formed and the yeast-cells increase in mass, but not in numbers. On the assumption that no direct oxidation of part of the added alcohol occurs (*loc. cit.*), it is shown that a utilisation of a portion of the assimilated carbohydrate takes place which runs parallel with its formation. A summary is given of the present results, together with the author's earlier observations.

J. P.

**The Influence of Oxygen on the Assimilatory and Dissimilatory Activity of Yeast. IV. The Behaviour of certain Organic Acids.** H. LUNDIN (*Biochem. Z.*, 1923, **142**, 463—492).—The methods already described (cf. preceding abstract) have been extended to a study of the capacity of a yeast suspension to assimilate various organic acids. The sodium and ammonium salts of citric, malic, tartaric, and succinic acids are not assimilated even in the presence of an excess of oxygen, and the added salts are without influence on the course of self-fermentation of the yeast. Potassium acetoacetate is assimilated more especially in concentrations of about 1%. Potassium carbonate is formed at the same time, and unless the  $p_H$  is adjusted the process is arrested. It is supposed that acetone and carbon dioxide are formed, and the former, in the nascent state, is assimilated to form carbohydrate when an excess of oxygen is provided. The newly-formed carbohydrate may then undergo oxidation. As in the previous experiments, carbohydrate alone is formed, and no alteration in the protein constituents of the yeast is noted.

J. P.

**Carboligase. VI. A New Type of Change of Acetaldehyde by Fermenting Yeast.** C. NEUBERG and E. REINFURTH (*Biochem. Z.*, 1923, **143**, 553—565).—The addition of acetaldehyde to dextrose, lævulose, or sucrose undergoing fermentation by top- or bottom-yeasts, leads to the formation of optically active acetyl-methylcarbinol,  $CH_3 \cdot CH(OH) \cdot CO \cdot CH_3$ . This "acyloin" synthesis also occurs in cell-free fermentations. Part of the acetaldehyde undergoing condensation arises from the sugar (cf. A., 1923, i, 973).

J. P.

**The Fermentation Co-enzyme (Co-zymase) of Yeast. I.** H. v. EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1923, **131**, 179—203).—Yeast was obtained free from co-enzyme by grinding up the dry yeast with water, centrifuging, again grinding up with water, and centrifuging. The product was then diluted to a given volume with water. A solution of co-enzyme was obtained by boiling yeast with water for a few minutes and if necessary filtering. The co-enzyme is completely precipitated by 50—80% alcohol.

The effect of variation of the  $p_H$  on the rate of fermentation of dextrose by various yeasts has been investigated (cf. Euler and Heintze, A., 1920, i, 513). Fermentation is most rapid at  $p_H$  6.2—6.8. Fresh yeast preserves its maximum fermentation over a

greater range of  $p_H$  than dried yeast. For autofermentation, the optimum  $p_H$  is 5—6. The observation of Harden that the activity is very dependent on the amount of phosphate-ion present is confirmed. The activity is a maximum at a certain optimum phosphate content. If there is a constant amount of washed yeast present, then the activity is at first approximately proportional to the amount of the co-enzyme present, and gradually, with increasing co-enzyme, becomes less than required by this relation, and ultimately is approximately constant. Similarly, if the co-enzyme is constant, the activity is at first approximately proportional to the amount of washed yeast, but with large amounts of washed yeast ultimately constant. In presence of constant quantities of washed yeast and of activator, the fermentation increases with increase in the amount of dextrose present to a maximum, and it then decreases. In the absence of phosphate, arsenate does not cause marked fermentation. The co-enzyme is apparently stable in aqueous solution for at least twenty-three hours, and is dialysable through a collodion membrane. It is precipitable by lead acetate and it is not identical with vitamine-*D* as it is not contained in orange juice or malt extract.

W. O. K.

**Is Lactic Acid Produced in Alcoholic Fermentation?** A. FERNBACH and M. SCHOEN (*Compt. rend. Soc. Biol.*, 1923, 89, 475—477; from *Chem. Zentr.*, 1923, iii, 1035).—From the products of the alcoholic fermentation of sucrose in the presence of calcium carbonate, *d*- and *l*-lactic acid were isolated as the zinc salts. The *d*-lactate was in excess.

G. W. R.

**Formation of Organic Acids by *Sterigmatocystis nigra* [*Aspergillus niger*] in Unbalanced Media.** M. MOLLIARD (*Compt. rend.*, 1924, 178, 41—45).—Previous work (A., 1922, i, 611) is continued from a more quantitative point of view. Known weights of the fungus were allowed to grow in presence of media of different composition (varying the proportions of sucrose and inorganic salts), and the amounts of citric and gluconic acid produced determined from time to time. It is shown that reduction of the proportion of nitrogen present favours the production of gluconic acid, reduction of the other inorganic constituents of the culture medium (phosphorus, potassium, magnesium, iron, and zinc) causing the formation of oxalic and citric acids.

E. E. T.

**Antiseptic Action of the Zinc Chloride Salt of Aniline.** J. W. HOWARD and F. D. STIMPert (*J. Amer. Chem. Soc.*, 1923, 45, 3106—3108; cf. A., 1899, i, 40; 1911, i, 191; 1912, i, 363).—The salt  $(NH_2Ph)_2ZnCl_2$  was formed by intimately mixing aniline and fused zinc chloride; it melts at 255°, and is soluble to the extent of 0.64 g. in 100 c.c. of water at 20°, 0.87 g. in 100 c.c. of 0.4% hydrochloric acid at 20°, and 0.066 g. in 100 c.c. of 95% alcohol at 20°. It is readily decomposed by *N* sodium hydroxide or boiling water. Tests with a culture of *Staphylococcus aureus* indicate that the salt has greater bactericidal action than either aniline or zinc chloride, the respective relative efficiency being approximately 10:7½:2.

F. B.

**The Evolution of Phosphorus during Germination.** M. H. VAN LAER and R. DUVINAGE (*Bull. Soc. chim. Belg.*, 1923, **32**, 355—357).—Determinations of the amount of phosphorus and its distribution in the various parts of the grain have been carried out in the case of barley, the grains themselves, the straw, endosperm, seeds, and roots being examined. The grains were first soaked and then allowed to germinate at 15°. The following facts were established: (1) soaking involves an elimination of about 10% of phosphorus; this takes effect both on the straw and on the endosperm; (2) during germination, a migration of phosphorus from the endosperm to the embryo occurs; (3) kilning of the grain has little effect. In the raw barley, the embryo is rich in phosphorus whilst the straw is poor; during germination the phosphorus content of the endosperm diminishes. It is shown that in the embryo, although the amount of phosphorus is greatly increased, the percentage amount remains practically constant, owing to the development of the embryo itself. During germination, a portion of the phosphorus is rendered soluble, and it is this soluble phosphorus which migrates to the embryo.  
F. G. P.

**Theory of Carbonic Acid Assimilation.** WO. OSTWALD (*Kolloid Z.*, 1923, **33**, 356—368).—A theoretical paper in which the experimental work on this subject is briefly summarised and the points are noted which must be covered by any theory of assimilation. The following new hypothesis is developed. The primary process of assimilation is a photo-autoxidation, which consists in the formation of a lipid peroxide sparingly soluble in water. The second process is the formation of an additive compound of albumin and carbon dioxide; this is followed by the interaction of the lipid peroxide and the albumin-carbon dioxide complex with water in which oxygen is given up, whereby, either, according to Wislicenus's reaction, carbonate is reduced by hydrogen peroxide, or through the formation of an albumin-carbon peroxide compound the reduction through formic acid to formaldehyde takes place. The fourth process consists in the recombination of an oxygen atom with the lipid oxide to re-form the lipid peroxide. This combination takes place in the presence of light in chlorophyll-bearing cells and brings the system back to its initial condition. The lipid peroxide appears to be the "photochemical motor" of the assimilation process. The photochemical reaction in assimilation is not a photo-reduction, but a photo-autoxidation. The whole of the reactions take place in the interface albumin-lipoid, and all work in such a way that the interface is maintained. Chlorophyll appears not to take part in the assimilation process; stoichiometrically its action probably consists in a physico-chemical promotion of the photo-autoxidation of the lipid.  
J. F. S.

**Composition of Vegetable Juices obtained by Pressure.** G. ANDRÉ (*Compt. rend.*, 1924, **178**, 114—116).—Previously (*ibid.*, 1922, **175**, 286) it was shown that when certain fruit juices are filtered through porous porcelain impregnated with collodion, inorganic, but not organic, phosphorus passed through, whilst the

fraction of the total nitrogen passing through was of the same order as the fraction not coagulable by heating at 100°. The relative proportions of filtrable, coagulable, and total nitrogen remain almost constant during growth in the case of potatoes; with increase of filtration pressure, the ratio inorganic phosphorus : total phosphorus increases, that of total phosphorus to total nitrogen remaining constant.

E. E. T

**Wood Sap. I. Presence of Enzymes in Wood Sap. II. Variations in the Amount of Oxydases in Wood Sap during the Bleeding Period.** E. PH. VOTCHAL (*Pamphlet*, Moscow, 1916).—The sap in the outer annual rings in healthy trees is completely sterile. Oxydases and diastases are shown to be present. The maximum oxydase content is reached when trees break into leaf.

G. W. R.

**The Anthocyanins in Norton and Concord Grapes. The Chemistry of Grape Pigments.** R. J. ANDERSON (*J. Biol. Chem.*, 1923, **57**, 795—813).—The pigments present in two varieties of American grapes, namely, Norton (*Vitis æstivalis*, *V. labrusca*) and Concord (*V. labrusca*), have been examined by the methods of Willstätter and Zollinger (A., 1915, i, 285; 1917, i, 47). The same anthocyanin chloride,  $C_{23}H_{25}O_{12}Cl \cdot 3H_2O$ , has been isolated from both varieties. On hydrolysis, it yields dextrose and an anthocyanidin chloride,  $C_{17}H_{15}O_7Cl \cdot 1\frac{1}{2}H_2O$ . The substances are identical in composition with the oenin and oenidin chlorides obtained by Willstätter and Zollinger from European grapes (*V. vinifera*), but they differ from these substances in that the anthocyanidin contains only one methoxyl group, whereas oenidin contains two. The colour reactions are, moreover, different. The anthocyanin gives with ferric chloride in aqueous solution a purple colour which quickly fades to light brown, and in alcoholic solution an intense blue which changes to purple and finally to wine-red; the anthocyanidin gives with the same reagent both in aqueous and alcoholic solution a momentary purple colour fading to an almost colourless or faintly yellow solution. Evidence of the presence of a diglucoside has also been obtained.

E. S.

**Constituents of *Milletia taiwaniana*, Hayata.** T. KARIYONE, K. ATSUMI, and M. SHIMADA (*J. Pharm. Soc. Japan*, 1923, No. **500**, 739—746).—Nagai (*J. Tokyo Chem. Soc.*, 1902, **23**, 744) isolated rotenone as one of the poisonous constituents of *Milletia taiwaniana*, Hayata, produced in Formosa. Later, Ishikawa (A., 1918, i, 94) isolated anhydroderride from the mother-liquor of rotenone and pointed out that rotenone was not identical with tubotoxin, a poisonous constituent of *Derris elliptica* (*J. Pharm. Soc. Japan*, 1923, No. **491**, 10). The authors have established the identity of rotenone and tubotoxin from the coincidence of the following properties: Crystalline forms (rhombic plates from hot alcohol or needles from benzene); m. p. 163°; (mixed sample gave the same m. p.), empirical formula,  $C_{18}H_{18}O_5$ ,  $[\alpha]_D^{20}$  —236.5° to —244°, oxime,

m. p. 245°, and phenylhydrazone, m. p. 255°. The authors have retained the name rotenone, as it was the first proposed. From crude rotenone, a white, wax-like, amorphous substance was isolated; it has m. p. 80°, acid value 15.85, saponification value 33.92 (118.70 after acetylation), and iodine number 17.02. K. K.

**The Acids and Red Colouring Matter of the Horned Poppy (*Glaucium luteum*).** H. SCHMALFUSS (*Z. physiol. Chem.*, 1923, **131**, 166—167).—The following acids have been obtained from the juice expressed from the horned poppy: citric acid, 25.82%, lactic acid, 18.24%, acetic acid, 11.88%, succinic acid, 1.99%, fumaric acid, 21.59%, malic acid, 13.50%, anhydromalic acid, 5.92%,  $\beta\gamma$ -dihydroxy- $\Delta^2$ -butene- $\alpha\delta$ -dicarboxylic acid, 1.07%, the steric configuration of which has not been determined, and traces of formic acid. The hydrochloric acid extract of the pulp left contained fumaric acid 34.33%, malic acid 12.53%, and oxalic acid 53.14%. No trace of maleic acid could be detected in the plant. The red colouring matter appears to be a lipochrome. W. O. K.

**Lipase in Sunflower (*Helianthus annuus*) Seeds.** F. TRAETTA-MOSCA and F. MILLETTI (*Ann. Chim. Applicata*, 1923, **13**, 270—288).—The authors give a summary of the literature dealing with the lipolytic enzymes of seeds and describe experiments which show that sunflower seeds exhibit lipolytic activity, this being only slight in the quiescent seeds, but becoming more intense in germinating and also in de-fatted seeds. Experiments with oleic acid and glycerol yield results showing that the lipase of sunflower seeds exerts also a synthetic action. Acid is liberated in gradually increasing proportions from linseed, cotton-seed, and castor oils by the agency of sunflower seeds. T. H. P.

**Phosphate Behaviour in Soils.** J. S. BURD and J. C. MARTIN (*Science*, 1923, **58**, 227—228).—By use of the authors' method (*J. Agr. Sci.*, 1923, **13**, 265) for the extraction of what is probably the true soil solution, it has been shown that after a volume of solution equal to the amount of water initially contained in the compacted soil has been removed, the solutions obtained from a second displacement of the same mass of soil with an equal amount of water have decreasing total concentrations of electrolytes, but the phosphate concentrations increase. Thus, at the approach of the end of the growing season, the diminished total concentration in the soil solution is probably accompanied by a tendency towards enhancement of the concentration of phosphate. An apparent result of this effect has been observed, although it may easily become masked by experimental error in soils of low total concentration or by increased absorption of phosphate by the plant in the later stages of growth. A. A. E.

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## Organic Chemistry.

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**The Combustion of Methane to Formaldehyde.** H. TROPSCH and O. ROELEN (*Brennstoff-Chem.*, 1924, 5, 37—42).—A gas mixture containing methane and oxygen was passed through a quartz tube (without a catalyst), heated in an oven, and the formaldehyde produced absorbed in water and determined titrimetrically. The effect of varying the methane : oxygen ratio in the gas, the diameter of the tube, the reaction temperature, and the gas velocity through the tube, was studied. The yield of formaldehyde first increases with increasing gas velocity (the other factors being kept constant), reaches a maximum, and then decreases, a characteristic curve being obtained by plotting the results graphically. In the experiment in which the highest yield of formaldehyde was obtained the gas velocity was as high as 20 m. per sec. The tubes employed had cross-sectional areas of 63.5, 13.5, and 1.4 sq. mm., respectively, and the highest yields were obtained with the second of the three. If the oxygen content of the gas used is maintained constant (about 16—19%) and the methane content is varied, the highest concentration of formaldehyde in the resulting gas is obtained with a methane : oxygen ratio of 1 : 1, as required by theory. When working at high temperatures, the maximum is only obtained by starting with a high gas velocity and gradually diminishing it, much lower results being obtained by working conversely. With increasing reaction temperature, the absolute quantity of formaldehyde produced increases, but the yield per unit of methane decomposed diminishes. The highest yield of formaldehyde, viz., 5.96% of the methane treated, was obtained with a gas containing 1.2% of methane and 19.4% of oxygen, whilst a maximum yield of 70% of the methane decomposed was obtained at a reaction temperature of 700°, showing that formaldehyde is formed as the principal product in the action of oxygen on methane. Discrepancies between the present results and those of previous workers are discussed.

W. T. K. B.

**The Influence of some Non-inflammable Vapours of Organic Liquids on the Limits of Inflammability of Mixtures of Methane and Air.** W. P. JORISSEN and J. VELÍŠEK (*Rec. trav. chim.*, 1924, 43, 80—86).—The limits of inflammability of mixtures of methane and air are found to be 5.4% and 14.1% of methane. These limits are considerably modified by the presence of vapours of non-inflammable liquids. In presence of 0.7 to 0.8% of perchloroethylene, the limits are 7.35 and 10.15%; with 0.7 to 0.8% of tetrachloroethane, 7.15 and 9.15%; with 1% of pentachloroethane, 5.95 and 10.3%. In presence of 20% of dichloroethylene, 5% of trichloroethylene, or of 12.2% of carbon tetrachloride explosion is entirely inhibited, whilst with 8.5% of carbon tetrachloride the limits are 9.0 and 9.9% of methane.

E. H. R.



**The Cracking Process of Burton.** H. I. WATERMAN and H. J. W. REUS (*Rec. trav. chim.*, 1924, **43**, 87—92).—It has been claimed that condensation under pressure in the oil-cracking process leads to the production of distillates free from unsaturated hydrocarbons. The authors are unable to verify this claim. [Cf. *B.*, 1924, 207.] E. H. R.

**The Generation of Ethylene from Alcohol.** T. HISAMURA and Y. IMAOKA (*Kwaken Hôkoku*, 1923, No. 7, 1—21).—Ethylene is prepared by passing alcohol vapour over "adsol" electrically heated at 390—400°, the yield being about 83%. (Adsol is a product used for drying air and is prepared from Japanese acid clay by pressing and burning; cf. Japan. Pat. 42368.) The rate of passing alcohol is 60—80 c.c. (in liquid) per hour, the thickness of the layer of the catalyst is 7 cm., and the resulting gas contains 98% of ethylene. After ten hours' passage of the vapour the yield decreases to 71%; the catalyst may, however, be re-activated by heating it for about thirty minutes at 650—700° in a current of air. K. K.

**The Additive Power of Iodine with regard to Ethylenic Compounds.** E. ANDRÉ (*Bull. Soc. chim.*, 1923, **33**, [iv], 1641—1647).—The author has studied the action of iodine in various solvents on olive, sesamé, poppy, and cod-liver oils, also on *iso*-heptene and phenylbutylene. The results obtained are compared with the iodine values furnished by Hanus' method, and show that the element itself is fairly active. Least activity is shown by the violet solutions in carbon tetrachloride and carbon disulphide; the brown solution in acetic acid and the violet-red chloroform solution exhibit much greater activity, the latter in some cases fixing 97% of the amount used in an iodine value determination. A second series of experiments, in which the iodine concentration was in each case *N*/10, gave similar results from the comparative point of view, although the ratio of iodine fixed to iodine value decreases considerably on dilution. The additive action in respect of ethylenic compounds seems to be capricious, as the same reactants under apparently similar conditions yielded discordant results in many cases. H. J. E.

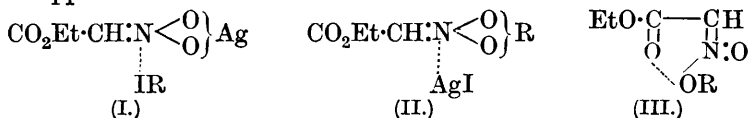
**Aliphatic Nitro-compounds. XIV. The Preparation of Nitroacetic Esters and the Alkylation of their Silver Salts.** W. STEINKOFF [and, in part, E. A. HAUGEN, A. SCHKADE, T. HÖPNER, and B. NOWY] (*Annalen*, 1923, **434**, 21—34).—Ethyl nitroacetate, b. p. 97°/13 mm., is prepared by passing dry hydrogen chloride into a solution of the acid, or a suspension of its potassium salt, in absolute alcohol at 0°, or by the gradual addition of concentrated sulphuric acid to a solution of the acid in alcohol at -15°. Its ammonium salt, long needles, has m. p. 124° (cf. Bouveault and Wahl, A., 1901, i, 4). The silver salt, if prepared from the pure ammonium salt, may be kept for a week before it becomes discoloured; it darkens at 40°, and decomposes at 117—119°. The following esters are similarly prepared: methyl, b. p. 106—110°/31 mm.; *propyl*, b. p. 105°/18 mm.; *isopropyl*, b. p. 92.2—

93.2°/12 mm. (*ammonium* salt, m. p. 107—109°); *isobutyl*, b. p. 111.5—112.5°/15 mm. (*ammonium* salt, m. p. 110—112°); *isoamyl*, b. p. 122—123°/16 mm. (*ammonium* salt, m. p. 112—115°).

The silver salt of ethyl nitroacetate (1 mol.) is gradually added to methyl iodide (2 mols.) at or below 0°. The product contains ethyl  $\alpha$ -nitropropionate (cf. Steinkopf and Supan, A., 1911, i, 4) and *ethyl nitroacetate acimethyl ether*,  $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{NO}_2\text{Me}$ , a colourless liquid, b. p. 84°/2.5 mm., which gives a red coloration with ferric chloride, and is decomposed by means of concentrated hydrochloric acid at 70° into formaldehyde and *isonitrosoacetic acid*. Similarly, the use of ethyl iodide leads to the formation of ethyl  $\alpha$ -nitrobutyrate (cf. Schmidt and Widmann, A., 1909, i, 453) and *ethyl nitroacetate aciethyl ether*, a colourless liquid, b. p. 81°/3 mm. These *acinitroethers*, in which, in addition to the nitro group, there is only one other negative radical, are quite stable, and do not show any tendency to undergo isomerisation to the *C*-alkyl derivative. The view of Hantzsch and Voigt (A., 1912, i, 151), that two such radicals are necessary to stabilise an *acinitroether*, is therefore incorrect.

It is probable that the compound, m. p. 114°, obtained by Ratz (A., 1906, i, 238) from silver nitroacetamide and ethyl iodide is an *acinitroether* of the formula  $\text{CH}_2\text{ON}\cdot\text{CH}\cdot\text{NO}_2\text{Et}$ .

During the action of methyl iodide on silver ethyl nitroacetate (above), the following phenomena are observed. If the salt is added at about -20°, it dissolves immediately to give a deep brown solution, the colour of which rapidly gives place to a white opalescence; silver iodide is then precipitated. If the addition is made at -60°, there is no reaction; as the mixture is allowed to become warm the solid is gradually dissolved, to give a colourless solution. This is stable over quite a wide range of temperature. Suddenly, however, the solution becomes dark. The brown colour then disappears as before, and silver iodide makes its appearance. It is supposed that in the colourless solution there is a molecular



compound (I); the appearance of the brown coloration is due to a kind of double decomposition, resulting in the formation of a halochromic complex (II), from which the removal of silver iodide gives stereoisomeric *acinitroethers*,  $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{O}\cdot\text{N}\cdot\text{OR}$  and  $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{RO}\cdot\text{N}\cdot\text{O}$ .

These are then stabilised, the former by isomerisation to the *C*-alkyl derivative, and the latter by "conjugation" (III) (Hantzsch and Voigt, *loc. cit.*).

*isoPropyl mercuriaci-nitroacetate anhydride*,  $\text{CO}_2\text{Pr}^\beta\cdot\text{C}\begin{array}{c} \text{NO} \\ \diagup \diagdown \\ \text{Hg} \end{array} \text{O}$ , is obtained by the addition of concentrated mercuric chloride solution to an aqueous solution containing sodium acetate and the *aciammonium* salt of *isopropyl* nitroacetate; the *isobutyl* and

isoamyl derivatives are prepared in a similar manner. These compounds resemble ethyl nitroacetate acimercurianhydride (cf. Prager, A., 1913, i, 5); they are white solids, which sublime when heated, and are soluble in dilute sodium hydroxide solution, potassium cyanide solution, or hydrochloric acid. The solution in alkali does not react with potassium iodide. The action of mercuric chloride on potassium or ammonium nitroacetate gives, apparently, a heterogeneous product, which does not sublime on being heated, but decomposes violently.

*Diammonium nitroacetate*,  $\text{NH}_4\text{O}\cdot\text{CO}\cdot\text{CH}\cdot\text{NO}_2\cdot\text{NH}_4$ , a white solid, is obtained from ammonia and nitroacetic acid in dry ethereal solution; the *disilver* salt is also prepared.

Condensation could not be effected between ethyl nitroacetate and benzaldehyde, piperonal, or anisaldehyde, using methylamine, ethylamine, amylamine, or piperidine as catalysts. W. S. N.

**The Formation of Ethyl Chloride from Ethylene and Hydrogen Chloride.** E. BERL and J. BITTER (*Ber.*, 1924, 57, [B], 95—99).—The union of ethylene with hydrogen chloride in the presence of aluminium chloride is effected most advantageously at 130—170°, but the slowness of the reaction renders prolonged contact with the catalyst necessary for the production of good yields of ethyl chloride; the latter substance is absorbed from the products of the reaction by active charcoal.

Ethyl chloride is analysed by passing it through a very narrow quartz tube heated at 900°, absorption of the hydrogen chloride by sodium hydroxide, and titration of the chloride by *N*/10-silver nitrate. The process is applicable to dichloroethylene, but not to chloroform or benzyl chloride. H. W.

**Chlorination of Carbon Chains. Chlorination of Normal Butyl Alcohol.** H. GAULT and R. GUILLEMET (*Bull. Soc. chim.*, 1923, 33, [iv], 1792—1801).—The chlorination, at definite temperatures in diffused daylight, of *n*-butyl alcohol has been studied, using iron (steel wire) as a catalyst, and different methods of procedure, viz., either bubbling chlorine through the alcohol, or (counter-current method) allowing the latter to run in a helical path down a vertical tube up which the chlorine passed. A comparative chlorination was carried out, in each case, in absence of the catalyst. The latter does not affect the yield of main product, but diminishes the amounts of by-products. These are produced in larger amount in cold than in hot chlorinations, owing to the formation of acetals in the latter case, and resulting restriction of action.

Chlorination, at temperatures not higher than 10°, by the bubbling method, gave, in presence of iron, a single product (corresponding with 18—20% of the alcohol used), shown to be the *dibutyl acetal* of a *chlorobutaldehyde*,  $\text{C}_4\text{H}_7\text{Cl}(\text{OBU})_2$ , a colourless liquid, b. p. 125°/15 mm. The latter in presence of hydrogen chloride in a closed tube at 120—130° was partly converted into an unstable liquid (b. p. 80—90°/15 mm., with loss of hydrogen

chloride) which reduced Fehling's solution and was converted by alcoholic hydrogen chloride into an *acetal*,  $\text{CHMeCl} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$  (?).

Chlorination by the bubbling method (using the catalyst) at 40–80° gave the *dibutyl acetal* of a *dichlorobutaldehyde* (yield, 50% of alcohol taken; b. p. 140–142°/15 mm.). This acetal, although unaffected by diluted mineral acids at the ordinary pressure, was partly converted, on heating at 125° in presence of hydrogen chloride, into a *liquid* (b. p. 105–110°/15 mm.) which reduced Fehling's solution, and lost hydrogen chloride on being distilled. The acetal, on being heated with acetic anhydride in a closed tube at 200°, was partly converted into *n*-butyl acetate and a *dichlorobutylidene diacetate* (b. p. 124–129°/15 mm.) (?), and with chromic acid yielded butyric acid and a *butyl dichlorobutyrate* (b. p. 210–215°).

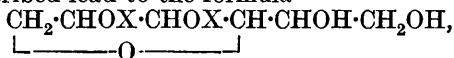
The counter-current method gives less homogeneous products than are given by the bubbling method. E. E. T.

**Oleic Alcohol.** Y. TOYAMA (*Chem. Umschau*, 1924, **31**, 13–16; cf. A., 1922, i, 895).—The acetyl ester of the oleic alcohol obtained from rabukazame oil gave on oxidation with potassium permanganate nonylic acid and acetylhydroxynonylic acid. This result, coupled with the previously established fact that the same substance gives the acetyl ester of normal octadecyl alcohol on hydrogenation, establishes the formula,  $\text{CH}_3 \cdot [\text{CH}_2]_7 \cdot \text{CH} : \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CH}_2 \cdot \text{OH}$ , for oleic alcohol. It is accordingly identical with the alcohol obtained from ethyl oleate. It has  $d_4^{15}$  0.8523,  $d_4^{20}$  0.8491,  $d_4^{40}$  0.8367;  $n_D^{15}$  1.4626,  $n_D^{20}$  1.4607,  $n_D^{40}$  1.4530, b. p. 333–335°/760 mm., 197°/10 mm., 209°/15 mm., 228°/30 mm. Elaidic alcohol has m. p. 35.0–35.5°,  $d_4^{40}$  0.8338,  $n_D^{40}$  1.4522, b. p. about 333°/760 mm., 198°/10 mm., 210°/15 mm., 229–230°/30 mm. These two isomeric alcohols are very stable and show no tendency to change into one another on heating or acetylation. They are sharply differentiated from one another by their melting points. H. C. R.

**Equilibria between some Glycols and their Acetone Compounds.** J. BÖESEKEN and P. H. HERMANS (*Rec. trav. chim.*, 1923, **42**, 1104–1110).—The authors have prepared the acetone derivatives [isopropylidene ethers] of ethylene glycol, propane- $\alpha\beta$ -diol, propane- $\alpha\gamma$ -diol, glycerol, and monochlorohydrin, 1 : 3-*cis*cyclopentanediol, and 1 : 2-*cis*cyclohexanediol. The method of preparation used was to heat suitable quantities of the glycol and acetone with sulphuric acid. The following new physical data are recorded: isopropylidene ether of ethyleneglycol, b. p. 92.5–92.7°,  $d_4^{17}$  0.9469,  $n_D^{17}$  1.40024, solubility in water, 1 vol. in  $3\frac{1}{2}$ –4 vols. at 18°; isopropylidene ether of propane- $\alpha\beta$ -diol, b. p. 98–99°,  $n_D^{15.5}$  1.40191,  $d_4^{18.5}$  0.9090, solubility in water, 1 vol. in 9–10 vols.; isopropylidene ether of propane- $\alpha\gamma$ -diol, b. p. 123–125°,  $n_D^{18.5}$  1.4252,  $d_4^{16.5}$  0.9587; isopropylidene ether of  $\alpha$ -monochlorohydrin, b. p. 116°/11 mm.,  $d_4^{17.5}$  1.322,  $n_D^{17.5}$  1.4820. The molecular weight of these compounds has been determined and is found to show no association of the molecules. The equilibrium constants of the reaction, acetone+

diol  $\rightleftharpoons$  isopropylidene ether + water, have been ascertained in each case, and the values compared with the difference in electrical conductivity of a 0.5 mol. solution of the diol containing 0.5 mol. of boric acid, and the sum of the electrical conductivities of a 0.5 mol. solution of boric acid and a 0.5 mol. solution of the diol. The two sets of figures are parallel, which is taken to indicate that the glycols combine with the same facility with acetone as they do with boric acid. A modification of the Le Bel-Henniger fractionating column was used in the purification of the materials, the bulbs of the original apparatus being connected with capillary tubes instead of the one opening; this causes the outside lateral tubes continuously to contain liquid. J. F. S.

**The Condensation of Mannitol with Olive Oil.** J. C. IRVINE and H. S. GILCHRIST (*J. Chem. Soc.*, 1924, **125**, 10—15).—"Mannitol fat" (cf. Lapworth and Pearson, A., 1919, i, 570), prepared by the interaction of mannitol and olive oil in the presence of sodium ethoxide, consists essentially of *mannitan dioleate*, which is formed by the dehydration of *mannitol dioleate*, the first product of the reaction. Further dehydration (at 200° under reduced pressure) results in the formation of *isomannide dioleate*. Treatment of *mannitan dioleate* with excess of methyl iodide and silver oxide results only in the formation of *monomethylmannitan dioleate*, together with a trace of *monomethylisomannide* ( $n_D$  1.4506), from *isomannide* originally present. On boiling with 0.5% alcoholic hydrogen chloride, *monomethylmannitan dioleate* gives ethyl oleate and *monomethylmannitan*, a viscous syrup. The latter was methylated to *trimethylmannitan*, a clear, mobile syrup, b. p. 115—120°/0.18 mm.,  $n_D$  1.4518. Structural considerations based on the reactions described lead to the formula



where X is the oleyl residue, for "mannitol fat." No more than two acyl groups can be introduced into the mannitol molecule.

F. G. W.

**The  $\alpha\gamma$ -Dichloropropyl Ethers and the Corresponding Acetals.** W. DULIÈRE (*Bull. Soc. chim.*, 1923, **33**, [iv], 1647—1654; cf. Wohl, A., 1898, i, 555).—The ethers were prepared by saturating an equimolecular mixture of acraldehyde and aliphatic alcohol with dry hydrogen chloride at  $-10^\circ$ , the products being purified by distillation under reduced pressure. They are colourless liquids of characteristic odour, decomposing with liberation of hydrogen chloride when heated at atmospheric pressure. They are not miscible with water, but react with it, hydrogen chloride being formed. With aliphatic alcohols, particularly those containing few carbon atoms, they readily produce acetals by reaction with the  $\alpha$ -chlorine atom, and with magnesium alkyl halides monochloroethers are obtained. The following are described: *methyl  $\alpha\gamma$ -dichloropropyl ether*, b. p. 45°/12 mm.,  $d^{20}$  1.187,  $n_D^{20}$  1.44777, yielding, with methyl alcohol, the acetal  *$\gamma$ -chloro- $\alpha\alpha$ -dimethoxy-*

propane, b. p.  $45^{\circ}/12$  mm.,  $d_{20}^{20}$  1.059,  $n_D^{20}$  1.41631; ethyl  $\alpha$ -dichloropropyl ether has b. p.  $56^{\circ}/12$  mm.,  $d_{20}^{20}$  1.122,  $n_D^{20}$  1.44235, and  $\gamma$ -chloro- $\alpha$ -diethoxypropane has  $d_{20}^{20}$  0.991 (cf. Wohl, *loc. cit.*); propyl  $\alpha$ -dichloropropyl ether, b. p.  $65^{\circ}/12$  mm.,  $d_{20}^{20}$  1.100,  $n_D^{20}$  1.44576, and  $\gamma$ -chloro- $\alpha$ -dipropoxypropane has b. p.  $87^{\circ}/20$  mm.,  $d_{20}^{20}$  0.972,  $n_D^{20}$  1.42871;  $\alpha$ -dichloropropyl isobutyl ether, b. p.  $89^{\circ}/21$  mm.,  $d_{20}^{20}$  1.067,  $n_D^{20}$  1.44305, and  $\gamma$ -chloro- $\alpha$ -diisobutoxypropane, b. p.  $105^{\circ}/12$  mm.,  $d_{20}^{20}$  0.936;  $\alpha$ -dipropyl isoamyl ether, b. p.  $103^{\circ}/20$  mm.,  $d_{20}^{20}$  1.027, turns brown and decomposes on being kept.

H. J. E.

**The Alkyl Titanates.** F. BISCHOFF and H. ADKINS (*J. Amer. Chem. Soc.*, 1924, **46**, 256—259).—Tetramethyl titanate, prepared from methyl alcohol, sodium, and titanium tetrachloride, crystallising point  $209$ — $210^{\circ}$ , b. p.  $243^{\circ}$ (corr.)/52 mm., is rapidly hydrolysed in air. Tetraethyl titanate, prepared similarly from ethyl alcohol, had b. p.  $205^{\circ}/156$  mm.,  $145^{\circ}/8.5$  mm.,  $d_{20}^{20}$  1.107. Tetraisopropyl titanate, obtained mixed with 4% of isopropyl alcohol as a constant-boiling mixture, has b. p.  $230^{\circ}/740$  mm. Tetra-*n*-butyl titanate has b. p.  $185$ — $187^{\circ}/16$  mm.,  $d_{20}^{20}$  0.993. On boiling the higher esters with methyl alcohol, a quantitative yield of the tetramethyl derivative is obtained. All these esters are colourless.

F. A. M.

**Octyl Mercaptan.** H. KAHN (*Bul. Soc. Chim. România*, 1923, **5**, 70—72).—Pure octane, obtained by the repeated fractionation of benzene from Ploesti and removal of aromatic hydrocarbons by repeated action of a mixture of nitric and sulphuric acids, is converted into octyl chloride, which, when treated with a saturated alcoholic solution of potassium hydrogen sulphide, yields octyl mercaptan, a colourless liquid of disagreeable odour, b. p.  $198$ — $200^{\circ}$ . When heated, it readily decomposes into octyl sulphide and hydrogen sulphide.

J. W. B.

**Valeric Acid.** S. KOIZUMI and H. ICHINOSE (*Japan. Pat.* 41910).—Valeric acid is prepared from amyl alcohol by electrolytic oxidation in 5—20% sulphuric acid solution at the ordinary temperature. Lead or lead peroxide is used as anode, and platinum, copper, iron, or nickel as cathode, without diaphragm. The addition of 1 g. of oxides of vanadium, chromium, or manganese to 1 litre of the sulphuric acid promotes the reaction. The electrolyte is vigorously agitated during the operation, the current density being 1—5 amp. per sq. dm. The product separates in a nearly pure state, the current yield being above 80%.

K. K.

**Palmitic and Stearic Anhydrides.** D. HOLDE, J. RIPPER, and F. ZADEK (*Ber.*, 1924, **57**, [B], 103—104).—Since the constants recorded in the literature for these substances are very discordant, they have been redetermined with material prepared by Albitzky's method as modified by Holde and Tacke (*A.*, 1920, i, 811). Palmitic anhydride has m. p.  $64^{\circ}$ ,  $d_4^{25}$  0.8383, whence  $d_4^{15}$  0.8832, and  $n_D^{100}$  1.4679. Stearic anhydride has m. p.  $72^{\circ}$ ,  $d_4^{25}$  0.855, whence  $d_4^{15}$  0.897, and  $n_D^{100}$  1.4284.

H. W.

**The Composition and Constitution of Elæostearic Acid.** L. MAQUENNE (*Bull. Soc. chim.*, 1923, **33**, [iv], 1654—1655).—The author claims priority over Vercruysse (A., 1923, i, 533) and refers to his own work (A., 1903, i, 62) in support of his view that the extreme readiness with which the acid undergoes oxidation has led to errors with regard to its formula and m. p., which are  $C_{18}H_{30}O_2$  and  $48^\circ$ , respectively. H. J. E.

**Elaidic Acid and its Anhydride.** D. HOLDE and K. RIETZ (*Ber.*, 1924, **57**, [B], 99—102).—Elaidic acid, obtained by the action of nitrous acid on oleic acid, crystallises in colourless, lustrous leaflets, m. p.  $44.4^\circ$  (corr.),  $n_D^{100}$  1.4308. Elaidic anhydride, prepared from the acid and acetic anhydride, has m. p.  $46.4^\circ$  (corr.),  $d_{15}^{25}$  0.8476,  $d_{15}^{25}$  0.8396,  $d_4^{100}$  0.8338,  $n_D^{100}$  1.4339.

The electrolytic conductivities of oleic and elaidic acids and their anhydrides in very highly purified acetone have been measured. Little differences are observed between the constants of the acids and their anhydrides, but those of elaidic acid and its anhydrides are somewhat higher than those of the oleic compounds. H. W.

**The Relative Solubilities of the Calcium and Magnesium Salts of the Higher Fatty Acids.** W. BILTZ and W. RÖHRS (*Z. angew. Chem.*, 1923, **36**, 609—611).—A study of the equilibria resulting from the action of solutions of calcium chloride on solid magnesium stearate and oleate. The mixture was heated for one hour, cooled, and filtered, the extent of double decomposition being found from analysis of the filtrate. When equimolecular proportions were used, the amounts of calcium stearate and oleate produced were 88% and 81%, respectively; these values increased to 98% and 90% on doubling the molecular ratio of calcium chloride. Fractional precipitation of a mixture of equivalent quantities of calcium and magnesium chlorides with potassium stearate and oleate yielded mainly calcium salt (Ca 6.54%, Mg 0.03%). Experiments on commercial soap are also described. The general conclusion is drawn that calcium stearate is considerably and calcium oleate appreciably less soluble than the corresponding magnesium salts. H. J. E.

**The Composition of Whale Oil.** C. H. MILLIGAN, C. A. KNUTH, and A. S. RICHARDSON (*J. Amer. Chem. Soc.*, 1924, **46**, 157—166).—Whale oil is shown to contain a complicated mixture of fatty acids having 14 to 22 carbon atoms, probably with a small amount of  $C_{24}$  acids. The highly unsaturated acids are chiefly those containing 20 and 22 carbon atoms. The percentage composition of the mixture of fatty acids is approximately: ( $C_{14}$ ) myristic 4.5; ( $C_{16}$ ) palmitic 11.5, palmitoleic 17.0; ( $C_{18}$ ) stearic 2.5, unsaturated (nearly all oleic) 36.5; ( $C_{20}$ ) unsaturated 16; ( $C_{22}$ ) unsaturated 10; ( $C_{24}$ ) unsaturated 1.5; unsaponifiable 0.7. F. A. M.

**The Catalytic Hydrogenation of some Unsaturated Compounds, especially Oils, by Means of Nickel at the Ordinary Temperature.** M. TANAKA (*Chem.-Ztg.*, 1924, **48**, 25—26).—The

author has extended the work of Kelber (A., 1916, ii, 309, 609) by using nickel, precipitated on kieselguhr, for reduction at the ordinary temperature of ethyl cinnamate, cinnamaldehyde, cinnamyl alcohol, azoxybenzene (to azobenzene, hydrazobenzene, and aniline), ricinostearol di-iodide, perilla oil, hemp-seed oil, chrysalis oil, and shark oil. Details of the amounts of hydrogen fixed are given and also of similar experiments carried out with a palladium catalyst for comparison. [Cf. B., Mar.] H. J. E.

**Reaction of Zinc on Mixtures of Ethyl  $\alpha$ -Bromoisobutyrate and Aldehydes or Ketones.** I. COUCOULESCO (*Bul. Soc. Chim. România*, 1923, 5, 63—70).—The action of zinc on mixtures of ethyl  $\alpha$ -bromoisobutyrate with isovaleraldehyde, isopropyl ketone, and acetophenone, respectively, has been studied. With isovaleraldehyde, the reaction takes the normal course and yields ethyl  $\beta$ -hydroxy- $\alpha\alpha$ -trimethylhexoate (b. p. 173—175°/140—145 mm.), which is hydrolysed to  $\beta$ -hydroxy- $\alpha\alpha$ -trimethylhexoic acid, colourless tetragonal or hexagonal crystals, m. p. 81°,  $\alpha=0.00147$ . The acid is soluble in alcohol and in ether. The barium, silver, potassium, zinc, and lead salts are described. The action either of dilute sulphuric acid (1:10) or of hydrogen iodide on this acid yields the  $\gamma$ -lactone,  $\text{CHMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}$ , b. p. 221—222°/742 mm., probably

$$\begin{array}{c} \text{O} \\ \text{—} \end{array}$$

owing to the initial formation of the  $\beta\gamma$ -unsaturated acid. Oxidation of the acid with potassium permanganate yields only unchanged material, carbon dioxide, and water.

With the two ketones, the main products isolated are ethyl isobutyrate, unchanged ketones, and a small quantity of oil, which is probably the expected ester of the hydroxy-acid. This on hydrolysis yielded an acid oil from which a pure substance could not be isolated. J. W. B.

**Synthesis of the Higher Monoalkylmalonic Acids.** (MRS.) G. M. ROBINSON (*J. Chem. Soc.*, 1924, 125, 226—231).—A method for the preparation of higher monoalkylmalonic acids, suitable for use with considerable quantities of material in one operation, and in which the formation of the corresponding dialkyl acids is minimal, is as follows. A mixture of the higher alkyl iodide (1 mol.), ethyl cyanoacetate (2 mols. or more), and potassium carbonate (1.5 mols.) is boiled under a reflux condenser and at a reduced pressure until the reaction is completed. The unchanged cyanoacetate is then recovered by distillation, the whole residue hydrolysed with hot 20% sodium hydroxide, and the product precipitated with dilute sulphuric acid. Under these conditions, the hydrolysis of  $\alpha$ -cyanocyclohexylacetic acid yielded only the malonamic acid,  $\text{CH}_2\langle\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{array}\rangle\text{CH}\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)\cdot\text{CO}_2\text{H}$ , a result ascribed to steric hindrance. The remaining cyanoacetic acids examined were completely hydrolysed to the corresponding malonic acids. cyclo-Hexylmalonamic acid, colourless needles, m. p. 184°, was unattacked on heating for four hours with alcoholic potassium hydroxide. k\*



Heated in a tube, it loses carbon dioxide and forms *cyclohexylacetamide*.

The preparation of *n*-heptylmalonic acid, *n*-octylmalonic acid, rhombic prisms, m. p. 115°, *n*-undecylmalonic acid, rectangular needles, m. p. 108°, and *n*-hexadecylmalonic acid, m. p. 119°, is described in detail.

*n*-Decyldimethylcarbinol, obtained from methyl undecate and magnesium methyl iodide, is a mobile liquid, b. p. 145°/10 mm.

F. G. W.

**The Chlorosulphides of Carbon. Decomposition in Presence of Iron.** M. DELÉPINE and J. GIRON (*Bull. Soc. chim.*, 1923, **33**, [iv], 1785—1792).—The chlorosulphides of carbon, when left in contact with metallic iron, are converted into sulphur and carbon tetrachloride. The action is catalytic, the iron suffering very little alteration. The chlorosulphides examined were: thio-carbonyl chloride, perchloromethyl mercaptan (also examined in presence of carbon disulphide and/or sulphur chloride), and the chlorosulphides represented by the formulæ: (1)  $\text{CCl}_3\cdot\text{S}\cdot\text{CS}\cdot\text{Cl}$ , (2)  $\text{CCl}_3\cdot\text{S}_3\cdot\text{CCl}_3$ , and (3)  $\text{C}_2\text{Cl}_6\text{S}_4$  (obtained from the residue in the distillation of perchloromethyl mercaptan, and having b. p. 150—154°/26 mm.).

E. E. T.

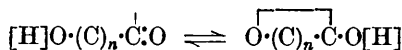
**Condensation of Citral with Ketones and Synthesis of some New Ionones.** H. HIBBERT and L. T. CANNON (*J. Amer. Chem. Soc.*, 1924, **46**, 119—129).—Citral, purified by a modification of Tiemann's method (A., 1899, i, 622), was condensed with acetone by means of sodium ethoxide, giving a 55% yield of pure  $\psi$ -ionone. The best condensing agent for converting  $\psi$ -ionone into  $\alpha$ -ionone was found to be 85% phosphoric acid.  $\psi$ -Ethylionone, prepared from citral and methyl propyl ketone, is a pale yellow oil, b. p. 155—158°/8 mm.; its structure is probably  $\text{Me}_2\text{C}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{Pr}$ . It is converted by means of 85% phosphoric acid into *ethylionone*, a pale yellow oil, b. p. 138—140°/8 mm., possessing a pleasant odour of violets.

Citral condenses with acetophenone, in presence of sodium ethoxide, to form *phenyl- $\psi$ -ionone*, an odourless, viscous, pale yellow oil, b. p. 182—185°/4 mm. *Phenylionone*, prepared from it by the action of 85% phosphoric acid, is a pale yellow, viscous oil, b. p. 172—175°/4.5 mm., with a very faint but rather disagreeable odour, the violet fragrance being almost entirely suppressed.

Attempts to condense citral with diethyl ketone or dipropyl ketone were unsuccessful.

F. A. M.

**Ring-chain Tautomerism. IX. The Mutarotation of the Sugars.** J. W. BAKER, C. K. INGOLD, and J. F. THORPE (*J. Chem. Soc.*, 1924, **125**, 268—291).—A proof, from a dynamical investigation and survey of structural evidence, supported by data from two series of crucial experiments, that the mutarotation of the sugars is a case of ring-chain tautomerism in the sense



on lines suggested by Jacobson and Stelzner (Meyer and Jacobson's "Organischen Chemie," 2 Aufl., 1, 2, 886, 910, 915, 927), and not dependent on the intermediate formation of hydrates as suggested by Lowry (T., 1903, **83**, 1316) and Armstrong (T., 1903, **83**, 1309). It is postulated that the phenomenon is of the same nature in all cases and not of varying kinds as suggested by Irvine and Steele (T., 1915, **107**, 1239—1240). The full mathematical derivation of the form and spacing of the mutarotation-time curves on the mutarotation-time-concentration diagram, according to the tautomeric-hydrogen theory, is given. It is deduced that whilst the form of the mutarotation-time curves can be accommodated by the intermediate-hydrate theory, the spacing of curves obtained from measurements of mutarotation in presence of varying initial concentrations of water is zero, in direct contradiction of the consequences of the hydrate theory, and in agreement with the experimental results. From structural considerations, it is pointed out that whilst *d*-fructose should not be capable of mutarotation according to Armstrong's theory, its mutarotation has actually been measured in water, pyridine, and formamide solutions, and that *d*-glucoseoxime, *d*-glucoseanilide, *d*-glucoseimine, *d*-glucose-phenylhydrazone, and ethylamino-*d*-glucose, all show mutarotation contrary to expectations based on Lowry's views. Also, no substance which, according to all three theories, should be incapable of mutarotation, has been found to exhibit this phenomenon, although interconversion of isomeric forms can sometimes be effected by reagents. This is shown to be at variance with Armstrong's views, and it is suggested that the mechanism of such conversions is fundamentally different from that of mutarotation. Experimentally, the mutarotation of tetra-acetyl-*d*-glucose in ethyl acetate solution at 44.8° was measured under conditions such that water was rigorously excluded, or present in small, accurately known concentrations of 0.025, 0.05, and 0.1%, respectively, these amounts being small in proportion to that possibly present in the dried materials. The velocity constants were, respectively, 0.0222, 0.0221, 0.0209, and 0.0208, *i.e.*, independent of the small initial concentration of water. The mutarotation of  $\alpha$ -*d*-glucose in methyl alcohol was also measured at the same temperature, first with dried materials, and then in presence of 0.5, 1.0, and 2.0%, respectively, of added water, these concentrations of water being relatively large in comparison with that which might have been present originally. The initial velocities were, respectively, 0.165, 0.178, 0.246, and 0.379. These values are not in proportion to the initial concentration of the water, as the hydrate theory demands.

F. G. W.

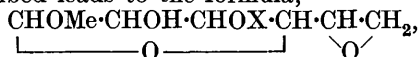
#### **Oxidation of Dextrose by Iodine in the Presence of Insulin.**

G. A. ALLES and H. M. WINEGARDEN (*J. Biol. Chem.*, 1923, **58**, 225—234).—The rate of oxidation of dextrose by iodine is not altered by the presence either of insulin alone or of insulin plus liver extract, blood-serum, or oxalated blood. Since the rates of oxidation of the various sugars differ greatly, it is evident that, under the conditions employed, insulin does not transform dextrose

into a more reactive form (cf. Winter and Smith, A., 1923, i, 513). E. S.

**A Quantitative Study of the Interaction of Dextrose and Phenylhydrazine.** E. KNECHT and F. P. THOMPSON (*J. Chem. Soc.*, 1924, **125**, 222—226).—In view of the strong reducing properties of phenylhydrazine and its resistance to reduction by titanous chloride, the reaction between phenylhydrazine and dextrose was studied to confirm quantitatively the formation of aniline and ammonia simultaneously with the osazone, and to discover the fate of the reactants in view of the low yields of osazone usually obtained. Pure dextrose (1 mol. : 3.6 g.) and phenylhydrazine (3 mols. : 6.48 g.) were dissolved in a mixture of water (190 c.c.) and glacial acetic acid (10 c.c.) and heated for three hours on the water-bath. A parallel experiment was made using *p*-nitrophenylhydrazine, but at twice the dilution of dextrose and phenylhydrazine. The osazone was filtered off and weighed. The unchanged phenylhydrazine was determined by boiling with Fehling's solution and measuring the nitrogen evolved, and the ammonia by a distillation during which tarring was avoided. The amount of ammonia produced in both cases was in agreement with that calculated from the weight of osazone obtained, in accordance with Fischer's equation, but it is inferred that a portion of the dextrose remains in solution as phenylhydrazone. The addition of aniline acetate or ammonium acetate to the reaction mixture increases the yield of osazone. By heating 3.6 g. of dextrose and 6.48 g. of phenylhydrazine with 20 c.c. of glacial acetic acid diluted to 100 c.c. with water, for three hours at water-bath temperature, a yield of osazone corresponding with 84% of the theoretical may be obtained. F. G. W.

**A Synthetic Fat containing a Methylglucoside Residue.** J. C. IRVINE and H. S. GILCHRIST (*J. Chem. Soc.*, 1924, **125**, 1—10).—When olive oil (1 mol.) is heated with  $\alpha$ -methylglucoside (3 mols.) in presence of sodium ethoxide at 140°, *methylglucoside mono-oleate* is formed, and this on further heating at 220°/12 mm. loses water and forms *anhydro-methylglucoside mono-oleate*, a viscous, yellow oil,  $[\alpha]_D^{25} + 38^\circ$  in chloroform. Attempts to introduce more than one oleyl residue failed. Treatment of the anhydro-mono-oleate with methyl iodide and silver oxide gave *monomethyl-anhydro-methylglucoside mono-oleate*, a mobile, yellow oil; this on boiling with methyl-alcoholic hydrogen chloride gave methyl oleate and *monomethyl-anhydro-methylglucoside*, a colourless, viscous syrup. The latter was further methylated to *dimethyl-anhydro-methylglucoside*, b. p. 115—120°/0.2 mm.,  $n_D^{20}$  1.4419, and hydrolysed with barium hydroxide to *monomethyl methylglucoside*, a colourless, viscous syrup. Further hydrolysis with 5% hydrochloric acid at 100° gave a syrupy monomethylglucose. Consideration of the reactions described leads to the formula,



where  $\text{X} = \text{CO} \cdot [\text{CH}_2]_7 \cdot \text{CH} \cdot \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CH}_3$ , for the methylglucoside fat. F. G. W.

**Fluoroacetyl Derivatives of Sugars. II. Optical Rotation and Atomic Dimension.** D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1923, **45**, 2381—2390).—In comparing the optical rotations of monohalogen-acetyl derivatives of dextrose, cellose, xylose, and lævulose, the differences F-Cl, Cl-Br, Br-I are found to be approximately proportional to the differences in atomic diameter. This simple relation holds for the specific, but not for the molecular rotation. *Fluorotetra-acetyl-lævulose* is obtained from  $\beta$ -penta-acetyl-lævulose. It is readily soluble in chloroform, and has m. p.  $112^\circ$ ,  $[\alpha]_D^{20} -90.43^\circ$  in chloroform. It is stable, colourless, and odourless. *Bromotetra-acetyl-lævulose* was prepared by the action of a solution of hydrogen bromide in glacial acetic acid on a solution of  $\beta$ -penta-acetyl-lævulose in the same solvent. It is a very unstable, crystalline solid,  $[\alpha]_D^{20} -189.1^\circ$  in chloroform, m. p.  $65^\circ$ . When preserved, it is transformed into  $\beta$ -tetra-acetyl-lævulose.  
F. G. P.

**Unsaturated Reduction Products of the Sugars and their Transformations. VIII.** M. BERGMANN [and, in part, H. SCHOTTE, E. RENNERT, S. LUDEWIG, and M. KOBEL] (*Annalen*, 1923, **434**, 79—110).—Fischer and Curme (A., 1914, i, 931) obtained a substance, which they described as lactal, by the hydrolysis of hexa-acetyl-lactal by means of barium hydroxide. This product had 1 mol. of water of crystallisation,  $[\alpha]_D +26.77^\circ$  to  $+26.95^\circ$ , m. p.  $184$ — $186^\circ$ , or, when anhydrous, m. p.  $165$ — $170^\circ$ . Lactal prepared by using methyl-alcoholic ammonia instead of barium hydroxide is anhydrous, and has  $[\alpha]_D^{16} +27.66^\circ$  to  $+27.67^\circ$ , m. p.  $192^\circ$  (corr.), decomp. about  $212^\circ$ . A sample so prepared is not changed on standing with barium hydroxide solution at  $37^\circ$  for two or three days. Lactal prepared by means of ammonia is reconverted by the action of acetic anhydride and pyridine into the hexa-acetate, m. p.  $114^\circ$ , but the product from "baryta-lactal" has m. p.  $108$ — $109^\circ$ . It is thought that Fischer and Curme's material was simply impure lactal.

When lactal is boiled with water, the product has m. p.  $198^\circ$  (corr.),  $[\alpha]_D^{17} +36.43^\circ$ , but the other properties are, in general, unchanged.

Hexa-acetyl-lactal is converted by boiling with water into  $\psi$ -lactal penta-acetate, a heavy, snow-white powder (flat tablets, small, thin prisms, or elongated, hexagonal crystals), m. p.  $123$ — $124^\circ$  (corr.) after previously softening, decomp.  $190^\circ$ . The structure of this compound is different from that of lactal or its hexa-acetate, because on treatment with acetic anhydride and pyridine it gives  $\psi$ -lactal hexa-acetate, aggregated prisms or needles, m. p.  $127$ — $128^\circ$  (corr.),  $[\alpha]_D^{18} +32.24^\circ$ , which is reconverted, by boiling with water, into the penta-acetate. Both the penta- and the hexa-acetate of  $\psi$ -lactal have a bitter taste; the hexa-acetate does not give the pine-shaving reaction, and does not react with bromine, but it reduces ammoniacal silver nitrate solution, and gradually gives a red coloration with magenta-sulphurous acid. In its sensitiveness to even dilute mineral acids it resembles lactal and the deoxy-sugars.

When  $\psi$ -lactal penta-acetate is treated successively with cold methyl-alcoholic hydrogen chloride, sodium hydroxide solution (with cooling), and sodium hydroxide and methyl sulphate, a yellow syrup is obtained, b. p.  $178-180^{\circ}/0.3-0.4$  mm.,  $n_D^{50}$  1.4661; this is the *pentamethyl ether of a compound*,  $C_{12}H_{20}O_9$ , isomeric with lactal. This series of reactions may involve a change of structure. When  $\psi$ -lactal penta-acetate is treated at  $0^{\circ}$  with a saturated solution of hydrogen bromide in glacial acetic acid, two molecular proportions of hydrogen bromide are taken up, giving a *dibromide*,  $C_{22}H_{30}O_{13}Br_2$ , small prisms or needles, m. p.  $124^{\circ}$  (corr.) (decomp.),  $[\alpha]_D^{23} +69.6^{\circ}$ . The latter is converted by means of silver carbonate in moist acetone solution into a *hydroxybromide*,  $C_{22}H_{30}O_{13}Br(OH)\frac{1}{2}H_2O$ , snow-white, glistening flakes, m. p.  $87-88^{\circ}$  after sintering at  $80^{\circ}$ , decomp.  $110^{\circ}$ . In dry methyl-alcoholic solution, the product is the corresponding *methoxybromide*, m. p.  $147-148^{\circ}$  (corr.), with subsequent decomposition, which is hydrolysed by means of methyl-alcoholic ammonia to the free *bromomethoxy-derivative*, snow-white, aggregated needles, m. p.  $119^{\circ}$  (decomp.).  $\psi$ -Lactal penta-acetate, which need not be isolated, is converted by the action of cold barium hydroxide solution into *isolactal*, short, slender needles, which is very difficult to purify. It has a vigorous reducing action on Fehling's solution, and gives a green coloration with a pine shaving. With warm alkali, it becomes yellow or brown, whilst concentrated mineral acids give a red solution; it is not attacked by perbenzoic acid. *isoLactal* has a slightly sweet taste, resembling that of lactose. The action of acetic anhydride and pyridine on *isolactal* gives *isolactal hexa-acetate*, rhombic prisms, or leaflets, m. p.  $166-167^{\circ}$  after sintering at  $163^{\circ}$ ,  $[\alpha]_D^{23} +55.30^{\circ}$ , which gives the pine-shaving test, and has an insipid taste. By the action of boiling water, one acetyl group is eliminated. *isoLactal* may be acetalised by means of methyl-alcoholic hydrogen chloride, or methylated by means of methyl sulphate; it is rapidly oxidised by means of aqueous bromine.

The action of perbenzoic acid, in warm ethyl acetate solution, on an aqueous solution of lactal gives *5-galactosidomannose*, needles, m. p.  $196-197^{\circ}$  (corr.), after slight softening. This compound has, initially,  $[\alpha]_D^{23} +23^{\circ}$  (about), rising to  $+30^{\circ}$  after eighty minutes. It reduces Fehling's solution immediately, and reacts gradually with ammoniacal silver nitrate solution or magenta and sulphurous acid. With phenylhydrazine, it gives lactosazone; it is decomposed by emulsin.

The diacetate, obtained by boiling triacetylglucal with water, is converted by heating with acetic anhydride and sodium acetate at  $100^{\circ}$  into  $\psi$ -glucal triacetate, a colourless liquid, b. p.  $150-165^{\circ}/0.2-0.3$  mm., which has a bitter taste and a pungent odour. It is reconverted by the action of boiling water into the diacetate, which is described as  $\psi$ -glucal diacetate. The triacetate is highly sensitive to the action of acids, and immediately becomes brownish-black when treated with cold alkali. It gives an intensely green

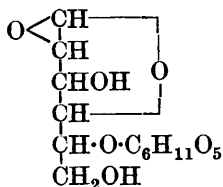
coloration with a pine shaving, and reacts with magenta-sulphurous acid, Fehling's solution, or ammoniacal silver nitrate. With bromine in chloroform solution at 18°, two atoms of halogen are absorbed, one of which may then be removed by boiling with silver carbonate and dry methyl alcohol. The action of 1% methyl-alcoholic hydrogen chloride on  $\psi$ -glucal diacetate gives a pale yellow syrup, from which the following fractions are isolated. (1) A colourless, mobile liquid, b. p. 68—69°/0.3 mm.,  $n_D^{20}$  1.4763,  $[\alpha]_D^{25} + 1.2^\circ$ , apparently  $C_7H_{10}O_3$ , and perhaps the methylcycloacetal of a hydroxyaldehyde, with two bonds, and a methylene group adjacent to the acetalised aldehyde group. (2) A viscous, slightly yellow oil, b. p. 88—90°/0.1 mm.,  $n_D^{20}$  1.4984,  $[\alpha]_D^{25} + 15.50 - + 16.1^\circ$ , evidently  $C_8H_{12}O_4$ . (3) A viscous, colourless liquid, apparently  $C_7H_{12}O_4$ , b. p. 120—121°/0.2 mm.,  $n_D^{20}$  1.4860,  $[\alpha]_D^{20} + 71.7 - + 72.2^\circ$ . Each of these fractions gives a green pine-shaving reaction, and is sensitive to acids; Fehling's solution is not reduced. The action of cold barium hydroxide solution on  $\psi$ -glucal diacetate gives *isoglucal*, a syrup, b. p. 120—130°/0.2—0.3 mm. (but sublimes at about 60° at this pressure),  $[\alpha]_D^{25} + 43.15^\circ$ , which is isolated as its *phenylbenzylhydrazone*, microscopic needles, m. p. 121—122°,  $[\alpha]_D^{25} - 22.38^\circ$ , from which it is regenerated by boiling with aqueous benzaldehyde or concentrated formaldehyde solution, the former being preferable. *isoGlucal* is readily decomposed by means of acids or of alkali. It gives a very pronounced green coloration with a pine shaving, and vigorously reduces Fehling's solution. On keeping the syrupy material in a vacuum, *crystals* are gradually deposited, m. p. 49—50°,  $[\alpha]_D^{18} + 45.6^\circ$ , which, in contrast with the original material, do not give a coloration with magenta-sulphurous acid. The syrupy *isoglucal* rapidly reacts with bromine, but in chloroform solution the reaction is apparently incomplete. Neutral or alkaline permanganate solution is immediately decolorised, but perbenzoic acid is not attacked.

Acetobromomaltose is reduced by means of zinc dust and 50% acetic acid, giving a poor yield (50%) of impure acetomaltal. The latter, when boiled with water, gives *penta-acetylmaltal hydrate*, needles, m. p. 173—174° (corr.); when acetylated, it gives a *hexa-acetate*, m. p. 155—157°. The elimination of the acetyl groups from acetomaltal, followed by oxidation using perbenzoic acid, gives a disaccharide containing mannose, perhaps 6-glucosidomannose (details will be given later).

When a solution of rhamnal in *N*-sulphuric acid is continuously extracted with ether at 35°, a yellow liquid is removed; the aqueous solution then contains *l-rhamnnodeose* (2-deoxy-*l-rhamnose*), a colourless liquid. This substance is very readily decomposed by the action of mineral acids. It gives the pine-shaving reaction, and reduces Fehling's solution. It is converted by keeping at 20° with methyl-alcoholic hydrogen chloride into its *methylcycloacetal*, b. p. 120—130°/0.2 mm., which undergoes fission when boiled with aqueous hydrochloric acid. When rhamnnodeose is oxidised by means of aqueous bromine solution, the product is *rhamnodesonic*

acid, which is isolated as its barium salt, colourless needles, or as the *phenylhydrazide*, m. p. 172—172.5° (corr.). Kiliani's digitoxose is therefore not identical with *l*-rhamnose.

It is proposed (cf. Bergmann, Schotte, and Lechinsky, A., 1922, i, 227) that, in naming a reducing disaccharide, the name of the sugar containing the intact aldehydic group should end in "ose," whilst the second constituent should be named as a glucosidic substituent, *e.g.*, 5-galactosidomannose. If both the reducing groups are glucosidically bound, as in trehalose, a name such as glucosido-glucoside is advocated. Thus sucrose becomes glucosidofructoside, or, alternatively, fructosidoglucoside, but raffinose is called galactosido-(glucosidofructoside). The terms anhydro-sugar, anhydrobiose, etc., are only employed when the aldehyde group, or its half-acetal form, is not involved in the anhydriation; otherwise, one speaks of monose-anhydride, disaccharide-anhydride, etc. The points of attachment of the oxygen bridge are indicated by means of bracketed numbers. Thus the substance having the



annexed formula is designated 5-galactosidomannose-anhydride [1 : 4] [1 : 2].

W. S. N.

**The Action of Iodine on Several Carbohydrates.** J. VINTILESCU and D. FALTIS (*Bul. Soc. Chim. România*, 1923, 5, 59—63).—When powdered iodine is heated (in a steam bath) in a sealed tube with solutions of sucrose, invert-sugar, dextrose, lævulose, lactose, dextrin, glycogen, or gum arabic, the iodine passes slowly into solution during the first period of heating, and is completely converted into hydriodic acid, the solution becoming colourless. On prolonged heating, decomposition of the carbohydrate occurs, with the formation of formaldehyde, formic acid, and a brown oxidation product of the sugar. The iodine is transformed more easily by sugars containing lævulose and progressively slowly by dextrose, lactose, dextrin, glycogen, and gum arabic; the period of heating necessary to cause the same amount of final decomposition follows the same order. The reaction is more rapid the greater the concentration of the sugar solution. The action of hydriodic acid on the carbohydrates is found to be similar, but the destruction of reducing sugars formed is slower than is the case when iodine is added directly. [Cf. B., 1924, 190.] J. W. B.

**Wood Cellulose.** E. HEUSER and S. S. AIYAR (*Z. angew. Chem.*, 1924, 37, 27—28).—The hypothesis of the identity of cellulose obtained from different sources is supported by experiments with cotton cellulose and wood cellulose. Both specimens give the same yield of pure cellulose triacetate on acetylation with glacial acetic acid, acetic anhydride, and sulphuryl chloride (cf. Barnett, A., 1921, i, 164), and on further treatment with methyl alcohol and hydrogen chloride (cf. Irvine and others, T., 1920, 117, 1489; 1922, 121, 1585) both triacetates give the same yield of the same  $\alpha$ -methyl-glucoside. Hydrolysis of both samples of cellulose with 72%

sulphuric acid (cf. Ost and Wilkening, A., 1910, i, 364) and recovery of the dextrose (cf. Monier-Williams, T., 1921, **119**, 803) gives the same yield of crystalline dextrose. W. T. K. B.

**The Constitution of Polysaccharides. VII. Esparto Cellulose.** J. C. IRVINE and E. L. HIRST (*J. Chem. Soc.*, 1924, **125**, 15—25).—The amount of furfuraldehyde produced by the action of hydrochloric acid on esparto cellulose corresponds with the presence of 18.5% of pentosan in the dry, bleached material. This pentosan can be completely extracted with boiling 12% sodium hydroxide, and was identified as xylan by hydrolysis, in 2% sulphuric acid at 90°, to xylose. The total yield of xylose, based on optical measurements, was 75%, and the nett yield of crystalline material 35—50%, m. p. 143—144°. The latter yielded on methylation the same trimethyl  $\beta$ -methylxyloside as has previously been obtained from xylose. The formation of furfuraldehyde during the hydrolysis of the xylan could not be prevented. The remaining 81.5% of the esparto cellulose, after complete extraction of the pentosan with alkali, gave on acetylation cellobiose octaacetate, and on methylation a trimethyl derivative from which 2:3:6-trimethylglucose was obtained on hydrolysis, thereby establishing the identity of the alkali-extracted material with cotton cellulose. The original esparto cellulose is more resistant to acetylation than cotton cellulose; the acetate was prepared by incorporating the material with glacial acetic acid containing a little chlorine, adding acetic anhydride, and then passing in a little sulphur dioxide and stirring, when a clear solution was obtained after twenty-four hours. The yield of acetate corresponds with 97.2% of the theoretical, assuming that the pentosan forms a diacetate and the remainder a triacetate. The acetate is softer and more sensitive to high temperature than that of cotton cellulose. On treatment with 1.5% methyl-alcoholic hydrogen chloride at 130° for 120 hours, the acetate yields a mixture of  $\alpha$ - and  $\beta$ -methylglucoside and  $\alpha$ - and  $\beta$ -methylxyloside, from which pure  $\alpha$ -methylglucoside was isolated by crystallisation from alcohol. It is concluded that esparto cellulose is a mixture of 81.5% of hexose cellulose and 18.5% of pentosan, probably in the form of a solid solution. F. G. W.

**Starch Iodide.** A. LOTTERMOSER (*Oesterr. Chem. Ztg.*, 1924, **27**, 13; cf. A., 1922, i, 10).—Experiments are mentioned on the adsorption of tri-iodion, iodion, and iodine by starch. The curves obtained are typical adsorption isotherms. In the reaction between starch and iodine in the presence of potassium iodide, there is probably an initial adsorption followed by a further slow combination. G. W. R.

**Lignosulphonic Acid and the Lactone of Waste Sulphite Liquors.** S. V. HINTIKKA (*Cellulosechemie*, 1923, **4**, 93—94).—Salts of  $\alpha$ -lignosulphonic acid with primary amines were prepared by separating the sodium lignosulphonate by salting out from waste sulphite liquors and precipitating the aqueous solution of

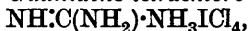


the product with  $\alpha$ -naphthylamine sulphate,  $\beta$ -naphthylamine hydrochloride, and *o*-toluidine salt. Klason (A., 1922, i, 324) has considered the  $\alpha$ -naphthylamine compound to be a normal ammonium salt of the sulphonic acid, and the  $\beta$ -naphthylamine compound a cyclic internal salt coupling the sulphonic acid and the aldehyde groups. The behaviour of these compounds towards 5% sodium hydroxide at 50° has been studied, the liberated amine being removed by extraction with ether and the lignosulphonic acid reprecipitated by acidification. No difference in the behaviour of these amine salts could be detected; the regenerated lignosulphonic acids were similar in appearance and contained only small residues of nitrogen. The crystalline substance isolated by Holmberg (A., 1921, i, 849) from waste sulphite liquors and described as a lactone has been further investigated. It occurs in the liquors from the digestion of spruce wood, but could not be detected in those from pine wood or from spruce bark. In the digestion of spruce wood, this lactone can be isolated in substantial quantity from the liquor in the early stages of digestion, but the quantity decreases towards the end of the process. J. F. B.

**Preparation of Methylamine.** M. SOMMELET (*Compt. rend.*, 1924, **178**, 217—219).—Methylamine hydrochloride, prepared by the methods of Brochet and Cambier or of Werner (cf. T., 1917, **111**, 844), is found to contain ammonium chloride and trimethyltrimethylenetriamine hydrochloride. It may be obtained pure by rendering alkaline, extracting with benzaldehyde, distilling the resulting benzylidenemethylamine (b. p. 180°), hydrolysing the latter with hydrochloric acid, washing the methylamine hydrochloride so obtained with alcohol to remove traces of the triamine salt, and finally crystallising twice from 88% alcohol. Pure methylamine hydrochloride has m. p. (in closed tube) 232—233·5° (corr.). E. E. T.

**Tetrachloro-iodides of Organic Bases.** F. D. CHATTAWAY and F. L. GARTON (*J. Chem. Soc.*, 1924, **125**, 183—188).—Stable tetrachloro-iodides of most organic bases can be prepared by dissolving the base in strong hydrochloric acid, adding an equivalent quantity of iodine, and passing excess of chlorine into the solution. The iodine gradually dissolves with evolution of heat and the tetrachloro-iodide separates either immediately or on allowing the solution to cool in a current of chlorine. The yields are generally quantitative. The tetrachloro-iodides are all golden-yellow, crystalline compounds, soluble in water with slight decomposition. They may be recrystallised from suitable solvents, to which the addition of a little iodine trichloride is sometimes necessary to prevent dissociation. They have sharp melting points, at which decomposition generally takes place, but appear to soften about 20° below the melting point. Heated at higher temperatures, they evolve chlorine, iodine monochloride, and iodine, and leave a residue of the chloride of the base. They can be stored unchanged for at least a month in dry air or in a vacuum over lime. The iodine atom appears to act as the central atom of the negative ion,

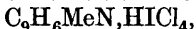
the four chlorine atoms being arranged tetrahedrally around it, the general formula thus becoming similar to that usually assigned to the chloroaurates. *Guanidine tetrachloro-iodide*,



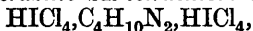
golden-yellow, flattened prisms, m. p.  $163^\circ$ . *Carbamide tetrachloro-iodide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}_3\cdot\text{I}\text{Cl}_4\cdot\text{H}_2\text{O}$ , long, pale yellow needles, m. p.  $73^\circ$ . The tetrachloro-iodides of pyridine, quinoline, etc., are so sparingly soluble that for their preparation it is necessary to dissolve the iodine in hydrochloric acid by means of a current of chlorine before adding the base. *Pyridinium tetrachloro-iodide*, pale yellow, flattened prisms, m. p.  $205^\circ$  (decomp.).  *$\alpha$ -Picolinium tetrachloro-iodide*, bright yellow, flattened prisms showing multiple twinning, m. p.  $166^\circ$  (decomp.). *Collidinium tetrachloro-iodide*,



orange-yellow, long, flat, rhombic prisms, m. p.  $94^\circ$ . *Quinolinium tetrachloro-iodide*,  $\text{C}_9\text{H}_7\text{N}\cdot\text{HICl}_4$ , pale yellow prisms, m. p.  $195^\circ$  (decomp.). *8-Methylquinolinium tetrachloro-iodide*,



long, pale yellow, hair-like crystals, m. p.  $152^\circ$  (decomp.). *6-Nitroquinolinium tetrachloro-iodide*,  $\text{NO}_2\cdot\text{C}_9\text{H}_6\text{N}\cdot\text{HICl}_4$ , dull yellow, elongated plates, m. p.  $131^\circ$  (decomp.). *2-Chloroquinolinium tetrachloro-iodide*,  $\text{C}_9\text{H}_6\text{ClN}\cdot\text{HICl}_4$ , pale yellow, flattened prisms, m. p.  $143^\circ$  (decomp.). *6-Chloroquinolinium tetrachloro-iodide*, dull yellow, crystalline powder, m. p.  $131^\circ$  (decomp.). *Quinaldinium tetrachloro-iodide*,  $\text{C}_9\text{H}_6\text{MeN}\cdot\text{HICl}_4$ , dull yellow, dendriform crystals, m. p.  $149^\circ$  (decomp.). *Caffeine tetrachloro-iodide*,  $\text{C}_8\text{H}_{12}\text{O}_2\text{N}_4\cdot\text{HICl}_4$ , pale yellow, crystalline powder, m. p.  $134^\circ$  (decomp.). *Piperidinium tetrachloro-iodide*,  $\text{C}_5\text{H}_{10}\text{NH}\cdot\text{HICl}_4$ , exists in two polymorphic forms; it crystallises from acetic acid in canary-yellow, fern-like crystals, which change on standing in contact with the mother-liquor into compact, six-sided, orange-yellow prisms. Both forms melt at  $102^\circ$  (decomp.). *Piperazine bis-tetrachloro-iodide*,



bright yellow, compact prisms with domed ends, darkens on heating above  $100^\circ$ , and loses iodine trichloride at  $160^\circ$ ; iodine is liberated at  $195^\circ$ , a black charred residue remaining. *Pyridine-betaine tetrachloro-iodide*,  $\text{C}_5\text{H}_5\text{N}(\text{ICl}_4)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , bright yellow, compact, six-sided prisms, m. p.  $133^\circ$  (decomp.). Semicarbazide does not form a tetrachloro-iodide, but is decomposed by a solution of  $\text{HICl}_4$  into nitrogen, carbon dioxide, and ammonium tetrachloro-iodide. *Methylammonium tetrachloro-iodide*,  $\text{CH}_3\cdot\text{NH}_2\cdot\text{HICl}_4$ , long, golden-yellow, hexagonal prisms with domed ends, m. p.  $96^\circ$  (decomp.). *Dimethylammonium tetrachloro-iodide*,  $(\text{CH}_3)_2\text{NH}\cdot\text{HICl}_4$ , compact, orange-yellow prisms, m. p.  $82^\circ$  (decomp.). *Trimethylammonium tetrachloro-iodide*, canary-yellow plates, m. p.  $182^\circ$  (decomp.). *Ethylammonium tetrachloro-iodide*,  $\text{C}_2\text{H}_5\cdot\text{NH}_2\cdot\text{HICl}_4$ , hygroscopic, orange-yellow, compact rhombs, m. p.  $45^\circ$ . *Diethylammonium tetrachloro-iodide*, thin, four-sided, pale yellow plates, m. p.  $79^\circ$  (decomp.). *Ethylenediammonium bis-tetrachloro-iodide*,  $\left. \begin{array}{l} \text{CH}_2\cdot\text{NH}_2\cdot\text{HICl}_4 \\ \text{CH}_2\cdot\text{NH}_2\cdot\text{HICl}_4 \end{array} \right\} 2\text{H}_2\text{O}$ , golden-yellow, long, hexagonal prisms,

m. p. 105° (decomp.). *Benzylammonium tetrachloro-iodide*,  $C_6H_5 \cdot CH_2 \cdot NH_2 \cdot HICl_4$ , flattened, yellow prisms, m. p. 97° (decomp.). *Dibenzylammonium tetrachloro-iodide*,  $(C_6H_5 \cdot CH_2)_2NH \cdot HICl_4$ , fine, yellow needles, m. p. 165°. *Tribenzylammonium tetrachloro-iodide*,  $(C_6H_5 \cdot CH_2)_3N \cdot HICl_4$ , yellow rhombs, m. p. 100° (decomp.).

F. G. W.

**The Constitution of Galegine.** G. BARGER and F. D. WHITE (*Biochem. J.*, 1923, **17**, 827—835).—The unsaturated amine,  $C_5H_{11}N$ , first obtained by Tanret by hydrolysis of galegine from the seeds of *Galega officinalis* (A., 1914, i, 721), gives Hofmann's carbylamine reaction, forms a toluenesulphonamide soluble in sodium hydroxide, and decolorises acid potassium permanganate. It has  $d_{18}^{25}$  0.779, and forms a *chloroplatinate*, m. p. 194—197°, a *chloroaurate*, m. p. 81°, and a *picrate*, m. p. 138.5—139.5°. It is identified as an aminoamylene. The urea obtained by Tanret from galegine arises from a guanidine residue. Galegine sulphate gives Weyl's reaction and the diacetyl reaction, and in the presence of a palladium catalyst takes up 1 mol. of hydrogen to give *dihydrogalegine sulphate*,  $(C_6H_{15}N_3)_2 \cdot H_2SO_4$ , colourless prisms, m. p. 270°. The *nitrate*, long needles, m. p. 75—76°, and the *picrate*, long, narrow plates, m. p. 172°, are also described. On distilling the sulphate with quicklime *isoamylamine* was obtained. Dihydrogalegine (*isoamylguanidine*) synthesised from cyanamide and *isoamylamine* gave the same salts as the product obtained by reduction of galegine from natural sources. The oxidation of galegine sulphate with barium permanganate yielded acetone and glycocyamine. On being boiled with dilute sulphuric acid, galegine takes up 1 mol. of water to form *hydroxydihydrogalegine sulphate*,  $(C_6H_{15}ON_3)_2 \cdot H_2SO_4$ , m. p. 205—206°, which yields on hydrolysis hydroxy*isoamylamine*. *Hydroxydihydrogalegine picrate*, rhomb-shaped crystals, has m. p. 153—154°. On the basis of these results, the formula  $Me_2C:CH \cdot CH_2 \cdot NH \cdot C(:NH) \cdot NH_2$  or  $CH_2:CMc \cdot CH_2 \cdot CH_2 \cdot NH \cdot C(:NH) \cdot NH_2$

is ascribed to galegine. The cyclic structures suggested by Tanret (*loc. cit.*) are therefore both incorrect. J. P.

**The Absorption Spectra of some Amino-acids. The Possible Ring Structure of Cystine.** F. W. WARD (*Biochem. J.*, 1923, **17**, 898—902).—Phenylalanine, tryptophane, and tyrosine show marked absorption bands, whereas alanine, histidine, glutamic acid, and cystine give general absorption. Cystine is the only amino-acid having any marked absorption in the region of the solar ultra-violet, and it shows absorption of greater intensity than that of the other aliphatic amino-acids examined, this being as strong as that of phenylalanine. A possible cyclic structure for cystine is suggested. J. P.

**The Reaction between Nitriles and Organo-magnesium Compounds. Ethyl Cyanoacetate.** R. BRECKPOT (*Bull. Soc. chim. Belg.*, 1923, **32**, 386—397).—The yield of ketone obtained from the reaction product of nitriles and the Grignard reagent is practically nil in the case of acetonitrile and phenylaceto-

nitrile. Bruylants (A., 1923, i, 310) postulates the existence of an equilibrium between the tautomeric forms of a nitrile  $\text{:CH}\cdot\text{CN} \rightleftharpoons \text{:C}\text{:C}\cdot\text{NH}$ , the normal form yielding a ketone by the Blaise reaction, the pseudo-acid form, on the other hand, yielding only condensation products. The formation of the condensation products is the result of the intermediate production of the derivative  $\text{:C}\text{:C}\cdot\text{NMgBr}$ . With ethyl cyanoacetate and ethyl magnesium bromide, a violent reaction takes place; a certain amount of the ketone is obtained, but the main portion of the reaction mixture consists of tarry products, whilst considerable quantities of gas (ethylene) are evolved. Using four molecular proportions of the Grignard reagent to one of ester, the amount of ethylene obtained shows that the ester contains two labile hydrogen atoms which are almost completely eliminated by the Grignard reagent. If the operation is carried out by adding the Grignard reagent to the nitrile, much ethylene is liberated until slightly more than one gram-molecular proportion has been added, when the reaction stops abruptly, owing to the formation of  $\text{CN}\cdot\text{CH}(\text{MgBr})\cdot\text{CO}_2\text{Et}$ . Addition of water to this compound regenerates the nitrile. The *ketimine* of ethyl propionylacetate,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{C}(\text{:NH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p.  $100\text{--}103^\circ/12\text{ mm.}$ , is a colourless liquid of musty odour,  $d_4^{20}$  1.0169,  $n_D^{20}$  1.4938. F. G. P.

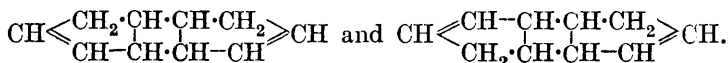
**The Relation between the Structure of Organic Halides and the Speed of their Reaction with Inorganic Iodides. I. The Problem of Alternating Polarity in Chain Compounds.** J. B. CONANT and W. R. KERNER (*J. Amer. Chem. Soc.*, 1924, **46**, 232—252).—A method has been developed for comparing the reactivities of the halogen atoms in organic compounds, consisting in measuring the rate of reaction between the organic halide and potassium iodide in acetone solution. The reactivity of the chlorine atom in three series of compounds of the type  $\text{A}(\text{CH}_2)_n\text{Cl}$  has been measured and compared with the reactivity of the chlorine atom in *n*-butyl chloride. The halogen atom is more reactive in the compounds  $\text{A}\cdot\text{CH}_2\text{Cl}$  than in  $\text{ACl}$  or  $\text{A}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$  in the three series studied, in which A is either benzoyl, phenyl, or carbethoxy. The influence of the group on the chlorine atom in the compounds of the type  $\text{A}\cdot\text{CH}_2\text{Cl}$  is roughly proportional to the effect of the same group on the activity of the hydrogen atom in the compounds of the type  $\text{A}\cdot\text{CH}_3$ . In the benzoyl series, the compound  $\text{A}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$  is eighty times more reactive than a simple normal alkyl chloride; in the phenyl and carbethoxy series, the activity of the corresponding compound is of the same order as that of the alkyl chlorides. The compounds  $\text{A}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$  in the benzoyl and phenyl series are more reactive than the compounds  $\text{A}\cdot\text{CH}_3\cdot\text{CH}_2\text{Cl}$ , this increase being large in the benzoyl series; in the carbethoxy series no such increase is apparent. The chlorine atom in the next higher homologue in the phenyl and carbethoxy series is only as reactive as that in butyl chloride; no higher homologues were available in the benzoyl series. Phenylamyl, phenylhexyl, and phenylheptyl chlorides do not differ significantly in their reactivity from one another or from *n*-butyl or *n*-amyl chlorides.

The preparation and properties of the following compounds are described:  $\beta$ -chloropropiophenone, from  $\beta$ -chloropropionyl chloride and benzene in presence of aluminium chloride, m. p. 49–50° (previous investigators have given it as 57–58°).  $\gamma$ -Chlorobutyrophenone, m. p. 19–20°.  $\beta$ -Phenylethyl chloride, from the corresponding alcohol and fuming hydrochloric acid at 140° for four to five hours, b. p. 68·5–69°/4 mm. Phenylpropyl chloride, from phenylpropyl alcohol and concentrated hydrochloric acid at 100°, b. p. 85–87°/9 mm.  $\delta$ -Phenylbutyl chloride, b. p. 100–101°/6 mm.  $\epsilon$ -Phenylamyl chloride, b. p. 111–112°/6 mm.  $\zeta$ -Phenylhexyl chloride, b. p. 115–116°/4 mm. Phenylheptyl chloride was obtained only about 88% pure, from the crude alcohol and hydrochloric acid, b. p. 120–140°/3 mm. F. A. M.

### Absorption of Ultra-violet Light by Organic Compounds.

II. L. MARCHLEWSKI and A. MOROZ (*Bull. Soc. chim.*, 1924, [iv], **35**, 37–40).—The results of studying the ultra-violet absorption spectra of alcoholic solutions of nitrobenzene, azoxybenzene, azobenzene, hydrazobenzene, and aniline are given in tables and curves. The extinction coefficients are calculated (cf. this vol., A., ii, 7). E. E. T.

**The Constitution of Dicyclopentadiene.** H. STAUDINGER and A. RHEINER (*Helv. Chim. Acta*, 1924, **7**, 23–31).—Commercial dicyclopentadiene can be separated by fractional distillation at a low pressure into two isomerides; the higher-boiling fraction, the  $\beta$ -form, has m. p. 19·5°, whilst the  $\alpha$ -form, the known dicyclopentadiene, has m. p. 32·5°. These two forms probably correspond with the formulæ



Each of these isomerides should exist in two stereoisomeric forms. The two isomerides which were isolated cannot be stereoisomerides, since by partial reduction they both give the same dihydrodicyclopentadiene, white crystals, m. p. 57°. This compound can be distilled at atmospheric pressure (b. p. 183·5–184·5°) and is therefore more stable than dicyclopentadiene, which, under these conditions, is completely depolymerised. Dihydrodicyclopentadiene is decomposed into cyclopentadiene and cyclopentene when its vapour is passed over a red-hot platinum spiral. Further reduction of dihydrodicyclopentadiene gives the known tetrahydrodicyclopentadiene, which is still more stable, and is with difficulty decomposed to cyclopentene. The disruption of the cyclobutane ring in dicyclopentadiene is attributed to the influence of the double bond in the  $\beta$ -position to the carbon linking. A similar cause is responsible for the ready decomposition of limonene, caoutchouc, and hexaphenylethane. Tricyclopentadiene is obtained when dicyclopentadiene is heated in a sealed tube at 170° for some hours. It forms colourless crystals, m. p. 60°, b. p. 90–92°/0·06 mm. It is more stable to heat than dicyclopentadiene or tetracyclopentadiene. The latter is obtained by heating dicyclopentadiene for a longer

time at  $180^{\circ}$ . It has m. p.  $188-190^{\circ}$ , and when heated at  $180-200^{\circ}$  decomposes smoothly into *cyclopentadiene*. When reduced with hydrogen and platinum black, it gives *tetrahydrotetracyclopentadiene*, m. p.  $200-202^{\circ}$ , which can be distilled unchanged. Still further polymerisation of *dicyclopentadiene* results in the production of *polycyclopentadiene*, an insoluble, infusible, white, crystalline powder, decomposing at  $285^{\circ}$ .  
E. H. R.

**The Constitution of the Disulphoxides.** I. S. SMILES and D. T. GIBSON (*J. Chem. Soc.*, 1924, **125**, 176—183).—The various formulæ given to the disulphoxides at different times are discussed, and an attempt is made to decide between the symmetrical and unsymmetrical formulæ,  $R\cdot SO_2\cdot SR$  and  $R\cdot SO\cdot SO\cdot R$ . Considered as a whole, the evidence at present available favours the unsymmetrical type. The reaction of mercaptans with disulphoxides is studied, and using a mercaptan  $R'\cdot SH$ , where  $R'$  is different from the group  $R$  in the disulphoxide it is found that high yields of the sulphinic acid,  $R\cdot SO_2H$ , are obtained with a mixed disulphide,  $R'S\cdot SR$ , but no sulphinic acid,  $R'\cdot SO_2H$ . 2 : 5-Dichlorobenzene-sulphinic acid,  $C_6H_3Cl_2\cdot SO_2H$ , forms crystals, m. p.  $122^{\circ}$ . 2 : 5 : 2' : 5'-Tetrachlorodiphenyl disulphoxide,  $(C_6H_2Cl_4)_2S_2O_2$ , crystallises in needles, m. p.  $128^{\circ}$ ; 3 : 3'-dicarboxydiphenyl disulphoxide,  $(C_6H_4\cdot CO_2H)_2S_2O_2$ , has m. p.  $229^{\circ}$ ; 2 : 5-dichloro-4'-methyl-diphenyl disulphide forms needles, m. p.  $71-72^{\circ}$ ; phenyl-2-naphthyl disulphide, m. p.  $74-75^{\circ}$ ; 2 : 5-dichloro-3'-nitrodiphenyl disulphide, needles, m. p.  $89-91^{\circ}$ ; 9-anthryl-4-tolyl disulphide, bright yellow needles, m. p.  $98-99^{\circ}$ ; 3-carboxyphenyl-4-tolyl disulphide, crystals, m. p.  $140^{\circ}$ .  
F. G. P.

**Preparation of Diphenyl.** C. H. LOWE and C. JAMES (*J. Amer. Chem. Soc.*, 1923, **45**, 2666—2669).—When using the apparatus previously described (*J. Amer. Chem. Soc.*, 1917, **39**, 933) for the preparation of diphenyl, difficulties arise owing to local heating and sagging of the filament of the heating element, with resulting short-circuiting. A filament support is now described in which these defects are eliminated. It is claimed that by maintaining the filament at a yellowish-red heat very good yields of diphenyl may be obtained from commercially pure benzene, which need not be anhydrous. The addition of more water does not hasten the reaction.  
W. S. N.

**Anthracenemonosulphonic Acids. Sulphonation of Hydrocarbons in a Basic or Neutral Medium.** M. BATTEGAY and P. BRANDT (*Bull. Soc. chim.*, 1923, **33**, [iv], 1667—1678; cf. A., 1922, i, 1001).—In the direct sulphonation of anthracene by means of fuming sulphuric acid or chlorosulphonic acid, the separation of the two isomeric anthracenemonosulphonic acids is effected by means of the barium in preference to the sodium salts. The position of the entering sulphonic group was determined by conversion of the acids into the corresponding  $\alpha$ - and  $\beta$ -chloroanthraquinones under the influence of nascent chlorine. The two acids are formed in almost equal proportions; elevation of temperature does not appear to favour a greater production of the  $\beta$ -isomeride,

as in the case of naphthalene (Fierz and Weissenbach, A., 1920, i, 430), although accurate observation is difficult by reason of the disulphonation of anthracene at temperatures above  $100^{\circ}$ . When, however, anthracene- $\alpha$ -sulphonic acid was heated in 96% sulphuric acid at temperatures ranging from  $150$ — $180^{\circ}$  and subsequently transformed into dichloroanthraquinone, the product appeared to consist wholly of the 1:5- and 1:8-isomerides, thus indicating that no shifting of the sulphonic group from the  $\alpha$ - to the  $\beta$ -position had occurred. Sulphonation in presence of mercury, mercurous sulphate, or mercurous oxide resulted in a slight increase in yield without any appreciable effect on the relative proportions of the isomerides. Attempts at sulphonation in a neutral or basic medium (cf. Battegay and Brandt, A., 1922, i, 1001) were made, pyridine being used as the medium in place of the acetic acid employed in the work described above. Experiments were carried out over a temperature range of  $95$ — $115^{\circ}$  and with varying proportions of the solvent. The best yields were obtained when a portion of the pyridine was replaced by a neutral solvent of higher b. p. In the presence of petroleum at  $165$ — $175^{\circ}$ , almost the whole of the resulting anthracenesulphonic acid is the  $\alpha$ -isomeride, and the addition of mercury compounds has no appreciable influence on the yield or the course of the reaction. When nitrobenzene is used, the yield is considerably smaller. A brief note on the application of Wagner's theory (A., 1886, 708) to the mechanism of the reaction is appended.

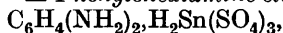
*Anthracene- $\alpha$ -sulphonic chloride*, m. p.  $90^{\circ}$ , was prepared, but probably in an impure condition; on being heated with alcoholic ammonia, it yields the corresponding *sulphonamide*, brown crystals, m. p.  $205^{\circ}$  (cf. Heffter, A., 1895, i, 671). H. J. E.

**Reactions of Strongly Electropositive Metals with Organic Substances in Liquid Ammonia Solution. IV. Action of the Alkali Metals on Triphenylmethyl and its Compounds.** C. A. KRAUS and T. KAWAMURA (*J. Amer. Chem. Soc.*, 1923, 45, 2756—2763).—The strongly electropositive metals react with triphenylmethyl chloride in liquid ammonia forming the compound of the metal with the triphenylmethyl group, e.g.,  $\text{CPh}_3\cdot\text{Na}$ . The sodium compound has been obtained in red needles. With ammonium chloride in liquid ammonia the sodium derivative gives an immediate pink precipitate which turns white on standing owing to production of triphenylmethane,  $\text{CPh}_3\cdot\text{Na} \rightarrow \text{CPh}_3\cdot\text{NH}_4 \rightarrow \text{CPh}_3\text{H} + \text{NH}_3$ . The sodium compound is unstable, but the *potassium* derivative is stable even at  $100^{\circ}$ . Triphenylmethyl is obtained by the action of triphenylmethyl chloride on sodium triphenylmethyl in the presence of toluene; this reaction does not take place if the sodium compound is replaced by the potassium derivative. Bromobenzene converts sodium triphenylmethyl into tetraphenylmethane. The mechanism of the reduction of organic halides by means of the alkali metals in liquid ammonia solution is discussed.

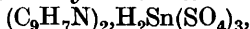
F. G. P.

**The Preparation and Properties of Organic Stannichlorides.**  
**VI. The Action of Sulphuric Acid on certain Stannichlorides.**

**The Formation of Stannisulphates.** J. G. F. DRUCE (*Chem. News*, 1924, **128**, 33—34; cf. A., 1922, i, 1206).—Stannisulphates of some organic bases can be obtained by the action of concentrated sulphuric acid on the corresponding stannichloride. The stannisulphate crystallises from the sulphuric acid after the addition of ether. *Aniline stannisulphate*,  $(\text{PhNH}_2)_2\text{H}_2\text{Sn}(\text{SO}_4)_3$ , forms grey, deliquescent crystals. *m-Phenylenediamine stannisulphate*,



does not melt below  $300^\circ$ . *Quinoline stannisulphate*,



forms colourless, deliquescent needles, m. p.  $124^\circ$ . Potassium and calcium stannisulphates can be prepared in the same way from the stannichlorides.

E. H. R.

**The Mechanism of the Hofmann Rearrangement of Methylaniline Hydrochloride.** J. W. HOWARD and C. G. DERICK (*J. Amer. Chem. Soc.*, 1924, **46**, 166—177).—The investigation was undertaken to confirm Hofmann's original views as to the nature of the change (*Ber.*, 1871, **4**, 742). It was found that in the rearrangement methyl chloride dissociates from the methylaniline hydrochloride and combines with a second molecule, forming phenyltrimethylammonium chloride; this compound then undergoes rearrangement. No rearrangement takes place at  $220$ — $250^\circ$  unless the heating is continued for ninety-six hours. At  $300^\circ$ , however, rearrangement takes place, and is somewhat affected by time, but temperature is the chief factor. Neither methylaniline nor dimethylaniline rearranges. A quantitative separation and determination of the three classes of amine by means of benzenesulphonyl chloride has been worked out.

F. A. M.

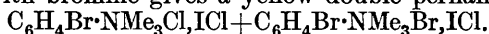
**p-Bromophenyltrimethylammonium Perhalides.** T. H. READE (*J. Chem. Soc.*, 1924, **125**, 148—157; cf. T., 1923, **123**, 141).—The degradation of perhalides by acetone has yielded analogous quaternary ammonium salts in the case of this series, the corresponding *p*-iodo series, and the simple phenyltrimethylammonium series itself, the part removed by acetone being either iodine chloride or bromide or chlorine. The points of difference between the *p*-bromo-series and the unsubstituted series are that *p*-bromophenyltrimethylammonium bromide di-iodide yielded the *p*-bromophenyltrimethylammonium bromide on treatment with acetone, whereas its analogue in the unsubstituted phenyl series was not attacked, and that well-defined double perhalides have been obtained in several reactions. Chlorine replaces *N*-halogen in iodides and periodides, replaces *N*-bromine only when iodine is also present, and replaces added halogens in perbromides. Both bromine and iodine replace *N*-chlorine to an appreciable extent, and iodine replaces *N*-bromine in one instance. *p*-Bromophenyltrimethylammonium methyl sulphate,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{NMe}_3\cdot\text{SO}_4\text{Me}$ , white crystals, m. p.  $208^\circ$ , when treated with bromine in hydrobromic



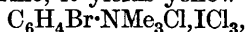
acid solution, gives the *perbromide*,  $C_6H_4Br \cdot NMe_3Br_3$ , orange-red leaflets, m. p.  $175^\circ$ . When warmed with acetone this perbromide yields the *bromide*,  $C_6H_4Br \cdot NMe_3Br$ , m. p.  $210^\circ$ . Iodine in acetic acid gave  $C_6H_4Br \cdot NMe_3Br \cdot IBr$ ; chlorine similarly yielded



lemon-yellow plates, m. p.  $158^\circ$ . The bromo-dichloride, the perbromide, and the bromodi-iodide are obtained by the action of halogens on the simple bromide of m. p.  $210^\circ$ . Chlorine with the *p*-bromophenyltrimethylammonium iodide gives the *chloride iodotrichloride*,  $C_6H_4Br \cdot NMe_3Cl \cdot ICl_3$ , m. p.  $187^\circ$ , bromine gives the *bromiodobromide*, m. p.  $185^\circ$ , iodine the *tri-iodide*, m. p.  $172^\circ$ . The *chloride iodochloride*,  $C_6H_4Br \cdot NMe_3Cl \cdot ICl$ , m. p.  $177^\circ$ , is obtained by the action of chlorine on the simple iodide, and on treatment with bromine gives a yellow double perhalide,



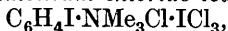
Acetone converts the chloride iodochloride into the simple *chloride*, m. p.  $199^\circ$ ; this with iodine gives the double compound,  $C_6H_4Br \cdot NMe_3I_3 + C_6H_4Br \cdot NMe_3I_5$ . The *bromide iodobromide*,  $C_6H_4Br \cdot NMe_3Br \cdot IBr$ , obtained by the action of bromine on the iodide, crystallises in orange plates, m. p.  $189^\circ$  (decomp.). With chlorine, it yields  $C_6H_4Br \cdot NMe_3Cl \cdot ICl_3$ ; bromine has no action, iodine gives a red double perhalide,  $C_6H_4Br \cdot NMe_3Br \cdot IBr + C_6H_4Br \cdot NMe_3Br \cdot I_2$ . The *bromide di-iodide*,  $C_6H_4Br \cdot NMe_3Br \cdot I_2$ , obtained by the action of iodine on the bromide, has m. p.  $172^\circ$  (decomp.). With chlorine, it yields yellow needles of



m. p.  $186^\circ$ , with bromine, the *bromide iodobromide*, m. p.  $189^\circ$ , and with iodine the tri-iodide. The *bromide iodochloride*,  $C_6H_4Br \cdot NMe_3Br \cdot ICl$ , is obtained by the action of iodine monochloride on the bromide, in the form of yellow crystals, m. p.  $178-179^\circ$ . With chlorine, it yields  $C_6H_4Br \cdot NMe_3Cl \cdot ICl_3$ , m. p.  $186^\circ$ ; with bromine a mixture of the bromide iodobromide and bromide iodochloride, and with iodine a mixture of bromide di-iodide and bromide iodochloride. The *bromide dichloride*,  $C_6H_4Br \cdot NMe_3Br \cdot Cl_2$ , results by the action of chlorine on the bromide. It forms greenish-yellow crystals, m. p.  $158^\circ$ . Neither chlorine nor bromine has any action on it; with iodine, it yields the *bromide iodochloride*, m. p.  $178^\circ$ .

‡ F. G. P.

***p*-Iodophenyltrimethylammonium Perhalides.** † T. H. READE and S. A. SIM (*J. Chem. Soc.*, 1924, **125**, 157—160).—Chlorine converts *p*-iodophenyltrimethylammonium iodide into the chloride iodotrichloride,  $C_6H_4I \cdot NMe_3Cl \cdot ICl_3$ , and this can be degraded by ethyl malonate, yielding the dichloro-iodide,  $C_6H_4I \cdot NMe_3Cl \cdot ICl$ . With hot glacial acetic acid, the dichloro-iodide yields a double perhalide,  $C_6H_4I \cdot NMe_3Cl_2I + C_6H_4I \cdot NMe_3ClI_2$ . *p*-Iodophenyltrimethylammonium chloride iodotrichloride,



crystallises in yellow needles, m. p.  $187^\circ$ ; on treatment with ethyl malonate under reduced pressure it gives the *chloride-iodochloride*, yellow crystals, m. p.  $184^\circ$ . The *tri-iodide* crystallises in brown

leaflets, m. p. 189°. A method for determining the ionisable halogen in the perhalides is given. F. G. P.

**Synthesis of Indanylamine and of its N-Substituted Derivatives.** C. COURTOT and A. DONDELINGER (*Compt. rend.*, 1924, **178**, 493—495; cf. A., 1923, i, 1090).—1-Chloroindane is converted by dry liquid ammonia in a closed vessel, at the ordinary temperature, into 1-indanylamine, b. p. 96—97°/8 mm., and a little di-indanylamine, m. p. 84—85°. Methyl-, dimethyl-, ethyl- and diethyl-amines similarly convert chloroindane into *methylindanylamine*, b. p. 106—107°/15 mm., *dimethylindanylamine*, b. p. 100°/10 mm., *ethylindanylamine*, b. p. 106—107°/7 mm., and *diethylindanylamine*, b. p. 112—113°/8 mm., respectively, all four amines being colourless liquids.

Indene, on hydrogenation in presence of platinum black, affords indane (in 97% yield), which does not react with magnesium ethyl bromide at 135° (cf. Grignard and Courtot, A., 1911, i, 193). The reactivity of the methylene group in indene is therefore due to the presence of unsaturation in the 5-membered ring. E. E. T.

**Preparation of 3 : 3'-Diaminodiphenylsulphone by Electrolytic Reduction of 3 : 3'-Dinitrodiphenylsulphone.** J. LACROIX (*Compt. rend.*, 1924, **178**, 483—486).—The electrolytic reduction of 3 : 3'-dinitrodiphenylsulphone to the diamino-derivative is best effected (yield, 94.5%) by the use of an alcoholic solution of the dinitro-compound acidified with hydrochloric acid as the cathode liquid, with a cathode consisting of nickel foil covered with spongy tin. The anode is of lead immersed in 10% sulphuric acid. The cathode liquid is maintained at a temperature of 68—72° and well agitated. A. B. H.

**Chloronitrobenzenes and Thiocarbamides.** J. TAYLOR and A. E. DIXON (*J. Chem. Soc.*, 1924, **125**, 243—250).—Neither *o*-nor *p*-chloronitrobenzene nor 2 : 5-dichloronitrobenzene combines with thiocarbamide. 1-Chloro-2 : 4-dinitrobenzene unites with thiocarbamide and with phenylthiocarbamide to form additive salts, from which alkali hydroxides eliminate hydrogen chloride, the dinitrophenyl residue breaking off as dinitrophenyl mercaptan. With thiocarbanilide, chlorodinitrobenzene gives mainly phenylthiocarbimide and dinitrodiphenylamine,  $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NHPh}$ . Picryl chloride unites with thiocarbamide to form an additive compound, from which a *picrate* and a *salicylate* were obtained. Phenylthiocarbamide gave little additive salt, thiocarbanilide none. The picryl compounds are unstable, decomposing readily into dipicryl sulphide and a dark-coloured powder. In no case was an *N*-substituted thiocarbamide obtained, the behaviour of dinitrochlorobenzene and picryl chloride thus more resembling that of an alkyl halide than of an acid chloride. The *picrates* of the compounds obtained from 1-chloro-2 : 4-dinitrobenzene with thiocarbamide and phenylthiocarbamide are yellow compounds, m. p. 192—193° and 160—161°, respectively. The *picrate* derived from picryl chloride and thiocarbamide has m. p. 149—150°, the *salicylate*, m. p. 76°. F. G. P.

**The Decomposition of Substituted Carbamyl Chlorides by Hydroxy-compounds. I. The Reaction between Phenylmethylcarbamyl Chloride and Ethyl Alcohol at Different Temperatures.** T. W. PRICE (*J. Chem. Soc.*, 1924, 125, 115—129).—The reaction between phenylmethylcarbamyl chloride (m. p. 87.5°) and alcohol is very slow at temperatures below the boiling point of alcohol, and was consequently studied in sealed tubes at 100°, 90°, 80°, and 70°. Under these conditions, the carbamyl chloride first reacts with the alcohol to form phenylmethylurethane together with hydrogen chloride, which then reacts further with alcohol to form ethyl chloride and water. The first reaction was studied separately by adding dimethylaniline to the reaction mixture to combine with the hydrogen chloride and prevent the formation of ethyl chloride. The velocity of the reaction between the alcohol and the carbamyl chloride was found to vary with the amount of dimethylaniline added, being slower in presence of more base. Three series of experiments were therefore made at 100° with different amounts of dimethylaniline, and the velocity constant of the reaction in absence of dimethylaniline was found by extrapolation to be  $k_1=0.0426$  at 100°. As this value was in good agreement with the value obtained by calculation from the study of the combined reaction, measurements in presence of varying quantities of dimethylaniline were omitted at the other temperatures. The position of the reaction under these conditions was determined by titration of the dimethylaniline hydrochloride present at any given moment, the initial concentration of the carbamyl chloride in the alcohol being in all cases  $N/2$ . The action of hydrogen chloride ( $N/2$ ) on ethyl alcohol was investigated separately. The velocity constant fell steadily at each temperature, the means of the first three values being  $k_2=0.0102$  at 100°, 0.00443 at 90°, 0.00162 at 80°, and 0.000521 at 70°.

The whole reaction was then studied by determining the amounts of carbamyl chloride, hydrogen chloride, and ethyl chloride present at any instant. The hydrogen chloride was determined by direct titration, and the carbamyl chloride by hydrolysis with excess of potassium hydroxide after removal of the ethyl chloride, followed by titration with silver nitrate. The velocity constants of the first reaction, calculated from the amounts of carbamyl chloride present, were  $k_1=0.0427$  at 100°, 0.0196 at 90°, 0.00873 at 80°, and 0.00329 at 70°. Expressions deduced for the amounts of the various reactants present at any time from the values of  $k_1$  and  $k_2$ , as well as for the maximum amount of hydrogen chloride present and the time taken for this maximum to be reached, gave satisfactory agreement with experimental results, and the variation of temperature coefficient for each reaction was shown to be in accordance with Lewis' deductions.

F. G. W.

**Esterification of cycloHexanol and of some of its Homologues.** (MLLE.) G. CAUQUIL (*Compt. rend.*, 1924, 178, 323—326).—cycloHexanol, 2-methylcyclohexanol, or 3 : 4-dimethylcyclohexanol was heated, at 95°; with an equivalent weight of acetic

acid until equilibrium was attained, when it was found that 55·6%, 49·8%, and 47·5% of the three alcohols, respectively, had undergone esterification. E. E. T.

**The Catalytic Hydrogenation of Organic Fluoro-derivatives.**

**III. The Hydrogenation of  $\omega$ -Trifluoro-*m*-cresol.** F. SWARTS (*Bull. Soc. chim. Belg.*, 1923, 32, 367—376; cf. A., 1921, i, 656).—The hydrogenation of  $\omega$ -trifluoro-*m*-cresol in the presence of platinum black proceeds in two directions, one resulting in the formation of  $\omega$ -trifluoromethylcyclohexanol, the other in the production of  $\omega$ -trifluoromethylcyclohexane and water, the group  $\text{CF}_3$ - being unaffected. The relative proportions of the cyclohydrocarbon and cycloalcohol are not constant, increase of temperature favouring the production of the hydrocarbon. In the case of  $\omega$ -trifluoro-*m*-cresol, a thermal coefficient of acceleration is observed, whilst the velocity of absorption of the hydrogen by the trifluoromethylcyclohexane varies little with the temperature. An attempt is made to deduce a formula by means of which the thermal coefficient of the reaction can be calculated.

*Trifluoromethylcyclohexan-3-ol*,  $\text{CF}_3\cdot\text{C}_6\text{H}_{10}\cdot\text{OH}$ , is a viscous liquid, b. p. 183—184°; its *benzoyl* derivative crystallises in prisms, m. p. 55°,  $d^{17}$  1·2611. The *acetyl* derivative has b. p. 192·5—194°. *Trifluoromethylcyclohexan-3-one* is obtained by oxidising the corresponding cyclohexane with chromic acid; it boils at 173—174°/746 mm.,  $d^{16}$  1·242. Its *semicarbazone* melts at 190°. F. G. P.

**The Lead Derivative of Trinitroresorcinol.** C. A. TAYLOR and W. H. RINKENBACH (*U.S. Bur. Mines, Repts. Investigations*, 1923, No. 2533).—The *lead* derivative of trinitroresorcinol is obtained in 94·4% yield, as fine, light orange-coloured crystals,  $d$  3·09, by mixing boiling solutions of lead nitrate, trinitroresorcinol, and sodium carbonate, to which glacial acetic acid has been added. Its explosion temperature is 293° and rate of detonation 2097—2209 m. per second.

CHEMICAL ABSTRACTS.

**The Influence of Hydrogen Concentration on the Auto-oxidation of Quinol. A Note on the Stability of the Quinhydrone Electrode.** V. K. LAMER and E. K. RIDEAL (*J. Amer. Chem. Soc.*, 1924, 46, 223—231).—The rate at which quinol reacts with molecular oxygen has been followed by shaking borate buffers, 0·01M with respect to quinol, with oxygen. The rate does not become appreciable until the solution is more alkaline than  $p_{\text{H}}$  7·3 or 7·8 for air. The rate of reaction is highly sensitive to further increase of  $p_{\text{H}}$  value, being proportional to  $[\text{H}^+]^{3/2}$ , where  $[\text{H}^+]$  is the hydrogen-ion concentration, for the region investigated. A mechanism involving complex formation of the primary and secondary ions is suggested to explain this relationship, such as:  $2\text{H}_2\text{C}_6\text{H}_3\text{O}_2 \rightarrow 3\text{H}^+ + \text{HC}_6\text{H}_4\text{O}^- + \text{C}_6\text{H}_4\text{O}^- \rightarrow \text{complex ion}$ ;  $\text{complex} + 2\text{O}_2 \rightarrow 2 \text{quinone} + \text{H}_2\text{O}_2$ . F. A. M.

**Arylazides. III. Quinol Ethers from *p*-Methylated Arylazides.** E. BAMBERGER and J. BRUN (*Helv. Chim. Acta*, 1924, 7, 112—122).—A detailed account of experiments the results of which have already been recorded (A., 1921, i, 721). E. H. R.

**Arylazides. IV. Iminoquinol Ethers from *p*-Methylated Arylazides.** E. BAMBERGER, J. BRUN, and A. HARTMANN (*Helv. Chim. Acta*, 1924, 7, 123—131).—A detailed account of work already published (A., 1921, i, 721). E. H. R.

**Electrochemical Oxidation of Alkyl Ethers of Phenol and of the Three Isomeric Dihydroxybenzenes.** F. FICHTER and W. DIETRICH (*Helv. Chim. Acta*, 1924, 7, 131—143).—Anodic oxidation of anisole in suspension in dilute sulphuric acid, using a lead peroxide anode, results in a high yield of benzoquinone, up to 71% of theory under favourable conditions. This result is obtained using a diaphragm; in absence of a diaphragm, a mixture of quinhydrone and quinol is obtained. Quinol monomethyl ether is probably formed as an intermediate product, since this is converted practically quantitatively into benzoquinone by anodic oxidation. The methyl group is oxidised to methyl alcohol. When a platinum anode is used the yield of benzoquinone is very small; some formaldehyde is formed but the principal product is carbon dioxide. Phenetole and phenyl *iso*amyl ether give smaller yields of benzoquinone, whilst the alkyl group is in each case oxidised to the corresponding acid. Quinol dimethyl ether gives benzoquinone, the best yield being 48.6% of theory.

By the oxidation of guaiacol, using a diaphragm, at first only fumaric acid could be obtained; this, in absence of a diaphragm, was reduced to succinic acid. By stopping the oxidation at an early stage, however, an oily product was obtained from which a diphenyl derivative, *diguaiacol*, was isolated. This is probably 4 : 4'-*dihydroxy-3 : 3'-dimethoxydiphenyl*; it crystallises in slender needles, m. p. 166°, and gives an orange colour with ferric chloride. Its *diacetyl* derivative crystallises in leaflets, m. p. 198°, and its *dibenzoyl* derivative in white needles, m. p. 203°. By demethylation, it gives a *tetrahydroxydiphenyl* (? 3 : 4 : 3' : 4'), needles, m. p. 134°, giving an emerald-green coloration with ferric chloride. Its *tetra-acetyl* derivative has m. p. 161°. Further methylation of *diguaiacol* converts it into *diveratrole*, or *tetramethoxydiphenyl*, colourless tablets or leaflets, m. p. 130°. Anodic oxidation of *veratrole* gives rise to some *diveratrole*, but in addition, partial demethylation occurs with formation of a *hydroxytrimethoxydiphenyl*, which gives an *acetyl* derivative, pale yellow leaflets, m. p. 116°. Anodic oxidation of resorcinol monomethyl ether gives an amorphous *dihydroxydimethoxydiphenyl* which, when demethylated, gives 2 : 4 : 2' : 4'-*tetrahydroxydiphenyl* (2 : 4 : 2' : 4'-*di*resorcinol). E. H. R.

**The Catalytic Condensation of Acetylene with Phenols.** H. H. WENZKE and J. A. NIEUWLAND (*J. Amer. Chem. Soc.*, 1924, 46, 177—181).—Acetylene condenses with phenols and cresols in 95% alcoholic solution, in presence of sulphuric acid and mercury salts, to form uncrystallisable resins. The di- and trihydroxybenzenes react even more readily. With  $\beta$ -naphthol, acetylene condenses to form an acetal and some ethyldenedi- $\beta$ -naphthol. Resorcinol condenses with acetylene to form ethyl-

idenediresorcinol (as-2:4:2':4'-tetrahydroxydiphenylethane), which loses water spontaneously to form 3:6-dihydroxy-9-methylxanthene, soluble in water and alkalis (decomp. 230—240°). On heating with stannic chloride at 160—180°, it oxidises to form 6-hydroxy-9-methylfluorone, the solutions of which resemble that of fluorescein.

The presence of nitro- and sulphonic groups prevents the absorption of acetylene by a phenolic compound. No cases have been noted where the acetylene substitutes in a meta-position to another group. Phenetole does not react with acetylene under the above conditions.

F. A. M.

**The Hydrobenzoin Rearrangement. I. Hydroanisoin.** M. TIFFENEAU and A. ORÉKHOFF (*Bull. Soc. chim.*, 1923, **33**, [iv], 1832—1838).—According to Russell (*Annalen*, 1869, **151**, 25), hydroanisoin, on dehydration, affords deoxyanisoin (m. p. 95°). Irvine and Moodie (T., 1907, **91**, 536) found for the latter compound the m. p. 108—109°. It is now shown that Russell's compound is *dianisylacetaldehyde*,  $(\text{OMe}\cdot\text{C}_6\text{H}_4)_2\text{CH}\cdot\text{CHO}$ , as would have been expected (cf. Orékhoff and Tiffeneau, A., 1921, i, 566). The aldehyde (needles, m. p. 104—105°; *semicarbazone*, m. p. 140—141°) is also obtained by treating magnesium *p*-anisyl bromide with ethyl ethoxyacetate, and the product of this interaction with formic acid. On oxidation, the aldehyde affords dianisyl ketone, and with magnesium phenyl bromide gives  $\alpha$ -phenyl- $\beta\beta$ -di-*p*-anisylethyl alcohol (needles, m. p. 139—140°). Hydroanisoin (m. p. 170—171°), on heating with 50% sulphuric acid, affords the above aldehyde, *isohydroanisoin* (m. p. 125—126°) behaving similarly.

Dianisyl ketone with magnesium methyl iodide is converted into *dianisylethylene*,  $(\text{OMe}\cdot\text{C}_6\text{H}_4)_2\text{C}:\text{CH}_2$  (m. p. 142—143°), the latter, when treated with mercuric oxide in presence of water and iodine, affording an iodohydrin (not isolated) which is converted by silver nitrate into deoxyanisoin.

E. E. T.

**Semi-pinacolic Transformation. Necessity for the Presence of the Phenyl Group in Semi-pinacolic Transformations.** (MLLE.) J. LÉVY (*Bull. Soc. chim.*, 1923, **33**, [iv], 1655—1666; cf. Tiffeneau and Lévy, A., 1923, i, 788, 789).—In the aromatic series, the stability of the secondary hydroxyl group in respect of semi-pinacolic transformations appears to be conditioned by the nature of the aryl group linked to the secondary carbon atom. The author has studied the dehydration of six tri-substituted glycols and draws the conclusion that in addition to transpositions involving only phenylic groups in which the shifting of a group occurs only when the group capable of migration is aryl, others take place only in the cyclic series, but this is limited to cases in which the aryl group occupies one definite position. In these cases, the migratory group may be either cyclic or acyclic. Experimental details of the dehydration of the glycols are given (cf. A., 1921, i, 860). The following substances are described:  $\beta\gamma$ -di-

*hydroxy- $\alpha$ -phenyl- $\gamma$ -methylbutane*, needles, m. p. 64—65°; *ethyl benzylglycollate*, b. p. 170—173°/30 mm.; *benzyl isopropyl ketone*, b. p. 234—235°; *semicarbazone*, m. p. 140—141°;  *$\alpha$ -phenyl- $\gamma$ -ethyl-pentane- $\beta\gamma$ -diol*, small needles, m. p. 79—80°, yielding on dehydration by means of sulphuric acid an oil, b. p. 160—170°/50 mm., which forms a semicarbazone, m. p. 160—161°;  *$\alpha\delta$ -diphenyl- $\gamma$ -benzyl-butane- $\beta\gamma$ -diol*, crystals, transformed by concentrated sulphuric acid into a substance,  $C_{23}H_{20}$ , m. p. 94—95°, of unknown constitution;  *$\alpha$ -methylhexane- $\beta$ -ol*, b. p. 140—142°/760 mm., prepared by the action of magnesium butyl bromide on acetone, yields on dehydration a *methyl- $\Delta^8$ -hexene*, b. p. 95—98°/760 mm., which on treatment with hypoiodous acid yields an *iodohydrin*; this is converted into a ketone on treatment with silver nitrate without undergoing any transposition.

H. J. E.

### 3 : 4-Dihydroxyphenylmethylaminoethanol (Adrenaline).

I. HOSHINO and DAICHI SEIYAKU KABUSHIKI KAISHA (Japan. Pat. 42351).—Adrenaline is prepared from methylaminoacetyl-3 : 4-dihydroxybenzene by reducing with hydrogen, using as a catalyst colloidal solutions of metals of the platinum group, the finely powdered metals, or nickel or carbon bearing these metals. The product is purer than that obtained by Stolz's method and the yield almost theoretical.

K. K.

### Cyclic Trimethylene [*cycloPropane*] Compounds. P.

BRUYLANTS (*Bull. Soc. chim. Belg.*, 1923, **32**, 358—367).—Bromination (in direct sunlight) of *cyclopropane-1-carboxylic chloride*, until the liquid boils at 135—140°, followed by treatment of the product with methyl alcohol, gives a mixture of methyl *cyclopropane-1-carboxylate*, *methyl 1-bromocyclopropane-1-carboxylate* (a colourless, mobile liquid, b. p. 168°/702 mm.,  $d_4^{20}$  1.545,  $n_D^{20}$  1.4784), and *methyl  $\alpha\gamma$ -dibromobutyrate*. The latter (b. p. 113—114°/14 mm.) is the only product of bromination in the dark, and was identified by conversion into  *$\alpha\gamma$ -dibromobutyramide* (m. p. 80—82°). *cyclo-Propane-1-carboxylic anhydride*, which, on bromination, gives only open-chain derivatives, is a colourless liquid, b. p. 232°/752 mm.,  $d_4^{20}$  1.1132,  $n_D^{20}$  1.4628. The corresponding *ethyl ester* has b. p. 178°/758 mm.,  $d_4^{20}$  1.428,  $n_D^{20}$  1.4678. The esters are converted by ammonia into the *amide* (needles, m. p. 108°), and by concentrated sodium hydroxide into the *acid*, m. p. 77°. Magnesium methyl bromide converts the methyl ester into the *bromohydrin* (b. p. 171—172°/762 mm.), the latter with acetic anhydride giving the *bromo-acetin* (b. p. 180—182°,  $d_4^{20}$  1.327,  $n_D^{20}$  1.4731), and with alkali hydroxide the *oxide*,  $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{C} - \text{CMe}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$ , b. p. 121—125°,  $d_4^{20}$  0.886,  $n_D^{20}$  1.419. Digestion of the oxide with dilute sulphuric acid, followed by addition of semicarbazide, gives a *semicarbazone* (?), m. p. 115—140° (very indefinite). Electrolysis of potassium *cyclopropane-carboxylate* yields the free acid and a little *cyclopropane*.

F. G. P.

**Preparation and Properties of some Organic Uranyl Salts and, in particular, of Uranyl Benzoates and Salicylates.** G. COURTOIS (*Bull. Soc. chim.*, 1923, **33**, [iv], 1761—1773).—A continuation of previous work (A., 1914, i, 799, 802). When the hydroxide,  $\text{UO}_3 \cdot \text{H}_2\text{O}$ , is dissolved in a hot aqueous solution of benzoic acid, and the solution evaporated, *uranyl benzoate*,  $(\text{Ph} \cdot \text{CO}_2)_2\text{UO}_2$  (yellow crystals, stable at  $100^\circ$ ), separates, together with benzoic acid, which may be extracted with benzene. On further evaporation, the *acid salt*,  $(\text{Ph} \cdot \text{CO}_2)_2\text{UO}_2 \cdot \text{Ph} \cdot \text{CO}_2\text{H}$ , separates, the latter salt also being obtained if uranyl hydroxide is dissolved in boiling benzoic acid. Uranyl benzoate is sparingly soluble in water, the solution depositing a basic salt on standing. Below  $5^\circ$ , the saturated aqueous solution deposits the *dihydrate*, which becomes anhydrous on keeping at the ordinary temperature, and dissolves in ether to give a solution which rapidly deposits a yellow, crystalline compound,  $(\text{Ph} \cdot \text{CO}_2)_2\text{UO}_2 \cdot 2\text{Et}_2\text{O}$ . The latter is also formed when a concentrated aqueous solution of the benzoate is shaken with ether, and slowly loses ether of crystallisation on keeping (rapidly at  $100^\circ$ ).

Uranyl hydroxide dissolves in a hot alcoholic solution of benzoic acid, the *compound*,  $(\text{Ph} \cdot \text{CO}_2)_2\text{UO}_2 \cdot \text{EtOH}$  (pale yellow crystals, from which ether displaces the alcohol of crystallisation), separating on cooling. This salt, on crystallisation from water or from chloroform, or on heating at  $100^\circ$ , loses its alcohol of crystallisation.

When aqueous solutions of uranyl benzoate are concentrated by protracted (hot) evaporation, a yellow, crystalline, *basic salt*,  $(\text{PhCO}_2)_2\text{UO}_2 \cdot \text{UO}_3 \cdot \text{H}_2\text{O}$ , separates, and may be freed from accompanying uranyl benzoate by extracting the latter with alcohol. Prolonged heating with water converts the basic salt into uranyl hydroxide.

Aqueous solutions of uranyl benzoate are unaffected by sunlight, whilst alcoholic solutions afford a violet precipitate of uranoso-uranic oxide, the latter becoming yellow on washing with water containing dissolved air.

*Uranyl salicylate*,  $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2)_2\text{UO}_2$ , separates as orange-yellow crystals, readily soluble in methyl or ethyl alcohol, from the warm solution obtained by heating uranyl hydroxide with aqueous salicylic acid. The mother-liquors, on cooling, deposit the *dihydrate* of the above salt in the form of yellow crystals, giving red solutions in methyl or ethyl alcohol and becoming anhydrous at  $140$ — $150^\circ$ , with slight decomposition. Aqueous solutions of uranyl salicylate, on boiling, acquire a red colour. Neither aqueous nor alcoholic solutions of the salt are affected by sunlight, a fact that distinguishes the salt from all other uranyl salts studied. E. E. T.

**Stability of Solutions of some Organic Uranyl Salts in Absence or in Presence of Light.** G. COURTOIS (*Bull. Soc. chim.*, 1923, **33**, [iv], 1773—1785).—Previous results (A., 1914, i, 799 and 802; and preceding abstract) are re-stated and slightly extended. It is shown that saturated aqueous solutions of the



following uranyl salts are unstable even in absence of light, giving crystalline basic salts (already described): Formate, acetate, benzoate, glycollate, and citrate. The other uranyl salts examined (propionate, butyrate, lactate, quinate, salicylate, oxalate, and tartrate) are stable in the dark in aqueous solution.

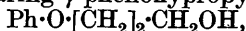
Sunlight, in absence of air, causes the reduction of all the above salts, with the exception of the benzoate and salicylate. The stability of the latter may be due to the "antioxygen" property of the salicylate residue. Contrary to the view of Aloy and Rodier (A., 1920, ii, 182), decomposition by sunlight does not depend on the hydroxylic character of the salt, as in the case of the tartrate, since uranyl propionate, butyrate, etc., are decomposed in aqueous solution under the influence of sunlight. In these cases, the violet hydrated uranoso-uranic oxide (converted by washing with water into the oxide,  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ ), is precipitated. Alcohol (or ether) accelerates these decompositions, but does not initiate them. In the decomposition of uranyl salts of monobasic aliphatic acids, carbon dioxide and a hydrocarbon result (the formate giving carbon monoxide and dioxide). The other salts examined give rise to carbon dioxide, except the oxalate, which also affords the monoxide. In the case of the glycollate (lactate), formic acid and formaldehyde (acetaldehyde) are first formed. E. E. T.

**The Isoelectric Point of *m*-Aminobenzoic Acid and its Equilibrium with Water, Acetic Acid, and Sodium Acetate.** J. BARBAUDY (*Bull. Soc. chim.*, 1924, [iv], 35, 31—37).—The equilibria in the systems: (1) *m*-aminobenzoic acid, acetic acid, and water, and (2) *m*-aminobenzoic acid, acetic acid, sodium acetate, and water have been studied at 25°, by determinations of hydrogen ion concentration, density, and viscosity in addition to solubility. From the solubility of *m*-aminobenzoic acid in pure water, the  $p_H$  of the isoelectric point for this acid is found to be 3.886. System (1) gave concordance between calculated and found isoelectric points, whilst in system (2) concordance was less good. [Cf. Michaelis and Davidsohn, A., 1911, ii, 192.] E. E. T.

**Preparation of Benzyl Diphenylalkylacetates and the Corresponding Acids by Means of Sodamide and Alkyl Iodides.** (MME.) P. RAMART (*Compt. rend.*, 1924, 178, 396—397; cf. this vol., i, 171).—Benzyl diphenylacetate was dissolved in ether and heated with powdered sodamide for several hours, an alkyl halide then being added and so on. The following new compounds (in addition to some previously known) have been prepared by this method: *Benzyl  $\alpha$ -diphenylpropionate*, prisms, m. p. 71—72°, b. p. 230—233°/10 mm.; *benzyl  $\alpha$ -diphenyl- $\beta$ -methylbutyrate*, m. p. 73—74°, b. p. 225°/2 mm.;  *$\alpha$ -diphenyl- $\Delta^7$ -penteonic acid*, prisms, m. p. 142° (*benzyl ester*, b. p. 240—242°/10 mm.; *amide*, m. p. 90—92°). E. E. T.

**The Methods of Preparation of 6-Chloro-3-hydroxybenzoic Acid.** V. I. MINAEV and K. M. RIPPER (*J. Russ. Phys. Chem. Soc.*, 1924, 54, 673—679).—A further account of work already published (A., 1922, i, 162). G. A. R. K.

**$\beta$ -Phenoxypropionic Acid and some of its Derivatives.**  
**Chromanone.** S. G. POWELL (*J. Amer. Chem. Soc.*, 1923, **45**, 2708—2711).—In preparing  $\gamma$ -phenoxypropyl alcohol,



(Rindfusz, A., 1919, i, 342), an aqueous solution of sodium phenoxide, in which trimethylenechlorohydrin is completely soluble, may be used in place of an absolute-alcoholic solution; in fact, a slightly better yield (80%) is actually obtained by this method.  $\beta$ -Phenoxypropionic acid,  $\text{Ph}\cdot\text{O}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ , may be obtained in yield varying between 32% and 45% by the gradual addition of potassium permanganate solution to a suspension of  $\beta$ -phenoxypropyl alcohol in a solution of magnesium sulphate. Its *ethyl* ester, a colourless oil, has b. p.  $170^\circ/40$  mm. The acid *chloride*, a liquid of irritating odour, is obtained when the acid is gently warmed for a few seconds with only a slight excess of thionyl chloride; it reacts with aqueous ammonia, giving the *amide*, glistening needles, m. p.  $119^\circ$ . The action of phosphoric oxide in boiling benzene solution on the acid gives *chromanone*,  $\text{C}_6\text{H}_4\begin{smallmatrix} \diagup \text{O}-\text{CH}_2 \\ \diagdown \text{CO}-\text{CH}_2 \end{smallmatrix}$ , a colourless, highly refracting liquid, b. p.  $160^\circ/50$  mm., with a pleasant, lemon-like odour; it solidifies on keeping to a mass of crystals, m. p.  $38\cdot5^\circ$ . Chromanone is also formed, together with a fraction of b. p.  $237^\circ/50$  mm. (which is free from halogen), by the prolonged action of an excess of thionyl chloride on  $\beta$ -phenoxypropionic acid. Chromanone forms an *oxime*, glistening needles, m. p.  $140^\circ$ , and a *benzylidene* derivative, long, yellow needles, m. p.  $112^\circ$ . W. S. N.

**The Isomeric Esters of *p*-Methoxybenzoylacrylic Acid.**  
 G. P. RICE (*J. Amer. Chem. Soc.*, 1924, **46**, 214—223; cf. A., 1923, i, 218).—In continuation of previous work on the isomeric esters of benzoylacrylic acid, the isomeric methyl and ethyl esters of *p*-methoxybenzoylacrylic acid have been examined. The stable yellow forms when exposed to sunlight in benzene solution are converted into colourless isomerides, the reverse change taking place on exposing solutions of the colourless solids, containing a crystal of iodine, to sunlight. *p*-Methoxybenzoylacrylic acid itself is transformed by sunlight to a polymeric acid. The yellow unsaturated esters are much more readily hydrolysed by sodium carbonate than the colourless isomerides, the product being methoxybenzoylacrylic acid. With cold concentrated or boiling dilute hydrochloric acid, both isomeric esters give a mixture of unsaturated acid and  $\alpha$ -hydroxy-*p*-methoxybenzoylacrylic acid.

The esters of the *p*-methoxy-acid do not behave in the same way as the esters of the unsubstituted acid on treatment with semicarbazide. *p*-Methoxybenzoylacrylic acid itself yields a semicarbazone; the colourless esters react with semicarbazide to form additive products and semicarbazones of these additive products.

*Methyl p-methoxybenzoylacrylate*, yellow needles, m. p.  $71-72^\circ$ ; *colourless isomeride*, needles, m. p.  $62^\circ$ . *Ethyl p-methoxybenzoylacrylate*, large, yellow crystals, m. p.  $42-43^\circ$ , b. p.  $210-215^\circ/11$  mm.; *colourless isomeride*, m. p.  $46-47^\circ$ . *Methyl  $\alpha\beta$ -dibromo-*

*p*-methoxybenzoylpropionate from the yellow ester, m. p. 115°. Ethyl  $\alpha\beta$ -dibromo-*p*-methoxybenzoylpropionate from the yellow ester, 1st isomeride, m. p. 51°; 2nd isomeride, m. p. 66°.

Bromination of *p*-methoxybenzoylacrylic acid yielded two isomeric forms of  $\alpha\beta$ -dibromo-*p*-methoxybenzoylpropionic acid, m. p. 140° and 164°, respectively. The polymeric acid,  $C_{20}H_{20}O_8$ , from *p*-methoxybenzoylacrylic acid, has m. p. 180°.

$\alpha$ -Hydroxy-*p*-methoxybenzoylacrylic acid (from hydrolysis of unsaturated acid) has m. p. 122°.

The yellow methyl *p*-methoxybenzoylacrylate reacts with 1 mol. of semicarbazide and yields two isomeric semicarbazones, yellow needles, m. p. 165°, and colourless plates, m. p. 178°. The same yellow methyl ester on treatment with two molecular proportions of semicarbazide yields the semicarbazone of methyl  $\alpha$ -semicarbazido-*p*-methoxybenzoylpropionate, m. p. 178° (decomp.). Methyl  $\alpha$ -semicarbazido-*p*-methoxybenzoylpropionate, m. p. 161—162°, is obtained as a by-product in preparation of the semicarbazone, m. p. 178°, and also by treating the semicarbazone of methyl  $\alpha$ -semicarbazido-*p*-methoxybenzoylpropionate with concentrated hydrochloric acid.

Treatment of the solid, m. p. 161°, with nitrous acid gave methyl nitroso- $\alpha$ -semicarbazido-*p*-methoxybenzoylpropionate, m. p. 132° (decomp.).

In a similar manner, the yellow ethyl ester of *p*-methoxybenzoylacrylic acid yields two isomeric semicarbazones, colourless crystals, m. p. 165°, and yellow crystals, m. p. 124°.

The semicarbazone of ethyl  $\alpha$ -semicarbazido-*p*-methoxybenzoylpropionate, m. p. 182° (decomp.), and ethyl  $\alpha$ -semicarbazido-*p*-methoxybenzoylpropionate, m. p. 173°, and the nitroso-compound, m. p. 124—125° (decomp.), are described.

Methoxybenzoylacrylic acid itself yields a semicarbazone, pale yellow solid, m. p. 216° (decomp.). F. A. M.

**Constitution of Phthalonic Acid.** CORNILLOT (*Compt. rend.*, 1924, 178, 490—492).—Phthalonic anhydride is rapidly converted by acetic acid at 100° into the acetyl- $\psi$ -phthalonic acid described by Kuroda and Perkin (T., 1923, 123, 2094), who concluded that phthalonic acid has the phthalide structure. With this conclusion the author disagrees, since the anhydride possesses the normal structure. Acetyl chloride or acetic anhydride converts phthalonic acid into a mixture of phthalonic anhydride and acetyl- $\psi$ -phthalonic acid, the proportions of the two products varying with the conditions of experiment. In boiling ethyl acetate solution (with acetic anhydride) or in suspension in acetyl chloride, almost pure phthalonic anhydride results, whilst the latter, on boiling for an hour with acetic anhydride, is entirely converted into the acetyl- $\psi$ -acid. In any case (as in the work of Kuroda and Perkin), the secondary reaction is responsible for the production of the acetyl- $\psi$ -acid. [See also Tcherniac, T., 1916, 109, 1236.] E. E. T.

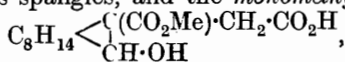
**Condensations of Aldehydes with Resorcinol and some other Aromatic Hydroxy Compounds.** R. N. SEN and N. N. SINHA (*J. Amer. Chem. Soc.*, 1923, 45, 2984—2996).—The benzein

type of compound has been prepared by condensing aldehydes with resorcinol and similar substances in the presence of concentrated sulphuric acid at 100—130°. The intensity of the fluorescence of alkali solutions of these compounds varies with the number and the position of hydroxyl and carboxyl groups, the influence of hydroxyl groups being greater when they occur in the benzene nuclei associated with the pyrone ring than when they occur in the phenyl residue, whereas the opposite is the case with the carboxyl group. *Resorcinol-1'-hydroxybenzein*,  $C_{19}H_{12}O_4$ , has m. p. above 260°. Its *tetrabromo-derivative* forms red crystals. *Resorcinol-2'-methoxy-3'-hydroxybenzein*,  $C_{20}H_{14}O_5$ , is obtained from vanillin and resorcinol as a greyish-black powder, m. p. above 295°. *Gallic acid benzein*,  $C_{21}H_{12}O_6$ , from gallic acid and benzaldehyde, is a green, microcrystalline powder. *Resorcinothein*,  $C_{14}H_{10}O_3$ , from resorcinol and paraldehyde, is a black, microcrystalline powder, m. p. above 290°. *Resorcinolphenetoleazobenzeinsulphonic acid*,  $C_{27}H_{20}O_7N_2S$ , from phenetoleazobenzaldehydesulphonic acid and resorcinol, does not fluoresce. *Resorcinol-p-hydroxybenzein-m-carboxylic acid*,  $C_{20}H_{12}O_6$ , is a yellow powder, m. p. above 295°.  $\beta$ -*Resorcyllic acid benzein*,  $C_{21}H_{12}O_7$ , from  $\beta$ -resorcyllic acid and benzaldehyde, is a yellow powder. *Resorcinol-3'-methoxybenzein*,  $C_{20}H_{14}O_4$ , from anisaldehyde and resorcinol, gives a red *tetrabromo-derivative*, decomposing at 200°.

F. G. P.

### Reduction Products of some Acids Derived from Camphor.

L. PALFRAY (*Ann. Chim.*, 1923, 20, [ix], 297—385).—A republication of work previously described (A., 1921, i, 418; 1922, i, 548; also Haller and Palfray, A., 1923, i, 577) with additional matter. Reduction of the dimethyl ester of carboxycamphoracetic acid by means of sodium and absolute alcohol resulted in the formation of a mixture of borneol, *camphoracetic glycol*,  $C_8H_{14}$   $\begin{matrix} \diagup CH \cdot CH_2 \cdot CH_2OH \\ \diagdown CH \cdot OH \end{matrix}$ , an oil, b. p. 195—198°/14 mm.,  $\alpha_D^{15} +19^\circ 57'$ , yielding a *phenyl-urethane*, colourless spangles, and the *monomethyl ester*,



$\alpha_D^{20} +49^\circ 22'$ . Similar reduction of the diethyl ester also yields borneol, the same glycol, and a substance of the formula  $C_{15}H_{23}O_3$ , probably a lactone, crystals, m. p. 50—51°,  $\alpha_D^{15} +62^\circ 22'$ . A discussion on the molecular refraction of the substances dealt with is appended. The following additional data are given. Ethyl hydrogen camphorate has m. p. 56—56.5°; the diethyl ester of carboxycamphoracetic acid has b. p. 202—204°/18 mm.,  $d_4^{24.9}$  1.09635,  $n_D^{24}$  1.47354,  $n_D^{24}$  1.47595,  $n_D^{24}$  1.48708; the dimethyl ester  $d_4^{25.1}$  1.14245,  $n_D^{25.1}$  1.48086,  $n_D^{25.1}$  1.48347,  $n_D^{25.1}$  1.49440. To obtain any considerable yield of reduction products from cyanocamphoric and homocamphoric esters, the reaction should be carried out at a temperature approaching 150°. This is also the case with the esters of carboxycamphoracetic acid, but only the ketonic group and the  $\alpha$ -carbalkoxy-group are completely hydrogenated, the final product being the glycol.

H. J. E.

**Derivatives of Camphoronic Acid.** W. F. GOEBEL and W. A. NOYES (*J. Amer. Chem. Soc.*, 1923, **45**, 3064—3070).—The investigation was undertaken in order to establish the structure of the various derivatives of camphoronic acid. The attempts to prepare either a dibasic amide or an anhydro-amide which would react with sodium hypobromite failed. Isomeric imide-amides were, however, obtained from the corresponding imides and have been found to react with sodium hypobromite.  $\beta$ -Anhydrocamphoronyl chloride reacts with ammonia to give transparent crystals of an *imide*,  $C_9H_{13}O_4N$ , m. p. 234.5—235°,  $[\alpha]_D^{20} -5.40^\circ$ . A *bromo-imide*, m. p. 220°, is similarly obtained from  $\alpha$ -anhydrobromocamphoronyl chloride.  $\alpha$ -Camphoronamide-imide is obtained by the action of phosphorus pentachloride and then anhydrous ammonia on  $\alpha$ -camphoronimide. It forms transparent crystals, m. p. 235—236°,  $[\alpha]_{5416}^{28} +11.87^\circ$ . The *acid chloride* of  $\beta$ -camphoronimide is obtained from the imide and phosphorus pentachloride. It is a crystalline solid, m. p. 175.5—176.5°  $[\alpha]_{5416}^{26} -18.32^\circ$ .  $\beta$ -Camphoronimide-amide obtained by the action of ammonia on the  $\beta$ -imide chloride, is a crystalline solid, m. p. 205°,  $[\alpha]_{5416}^{28} -13.73^\circ$ . It reacts readily with sodium hypobromite. Potassium hydroxide fails to open the ring of either  $\alpha$ - or  $\beta$ -camphoronimide, partial hydrolysis to the parent acid being the only reaction involved. F. G. P.

**Oxidations with Ozone. I. The Preparation of Vanillin.** E. BRINER, R. PATRY, and E. DE LUSERNA (*Helv. Chim. Acta*, 1924, **7**, 62—74).—The possibility of utilising ozone for technical oxidations is discussed, and experiments on the oxidation of *isoeugenol* to vanillin are recorded. The oxidations were carried out by conducting a current of ozonised air at varying concentrations of ozone (5% to 19%) into a solution of *isoeugenol* in carbon tetrachloride, at temperatures from  $-15^\circ$  to  $+50^\circ$ . The highest oxidation efficiency obtained, in terms of ozone consumed, was 20%, at the lowest temperature. At higher temperatures, the efficiency falls off rapidly and the quantity of resinous by-product formed increases. [Cf. *B.*, Apr.] E. H. R.

**Phthalaldehyde. II.** L. SEEKLES (*Rec. trav. chim.*, 1924, **43**, 93—102; cf. *A.*, 1923, i, 931).—Attempts were made unsuccessfully to utilise the blue colour obtained by the reaction between phthalaldehyde, ammonia, and acetic acid for the determination of small quantities of ammonia. The reaction product appears to contain at least three different coloured substances, and the tint produced varies with the proportions of the reactants.

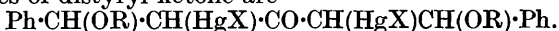
The dioxime of phthalaldehyde has not hitherto been prepared. It is now obtained in small yield by the action of hydroxylamine on phthalaldehyde in cold alcohol. *Phthalaldioxime* forms light yellow crystals containing  $2H_2O$ , m. p. 105° (indistinct), decomposing at 150°. The *di-p-nitrophenylhydrazone* of phthalaldehyde forms an orange precipitate ( $\alpha$ -form), m. p. 244—245° (decomp.). By treatment with gaseous hydrogen chloride in chloroform solution it is converted into a red *isomeride* ( $\beta$ -form), decomposing violently at

208°. Attempts to prepare *isoquinoline* by the interaction of methylamine and phthalaldehyde were not successful. E. H. R.

**Amino- and Oximo-derivatives of Thymoquinone.** R. M. HIXON (*J. Amer. Chem. Soc.*, 1923, **45**, 2333—2341).—It is pointed out that quinones may be expected to add ammonia (or an amine), (a) at the carbonyl group, by analogy with the formation of aldehyde-ammonia, or (b) at the ethylenic bond, as do certain unsaturated aliphatic acids, and that actually both reactions probably occur with the quinones. The intermediate additive compound, derived from an amine and a quinone, is structurally analogous to an ammonium salt; this undergoes rearrangement, the amine becoming attached in either of the two ways mentioned. Such an intermediate complex, if formed from a tertiary amine, would be incapable of rearrangement. Actually Jackson and Clarke (A., 1905, i, 908) have reported that dimethylaniline yields coloured additive products with quinones. This is now qualitatively confirmed, since an additive compound appears to be formed when thymoquinone is dissolved in dimethylaniline (2 mols.). This is apparently stable when air and solvents are excluded, but otherwise a purple tar is produced, which, on hydrolysis by means of 50% sulphuric acid, gives both mono- and di-hydroxythymoquinone. This indicates to some extent that tertiary amines may react with quinones just as do primary and secondary amines.

Directions are given for the purification of nitrosothymol and of nitrosocarvacrol. Their benzoates are, in effect, hydrolysed when treated in dry heptane solution with dry methylamine gas. The reaction, which cannot be an ordinary hydrolysis, is explained by assuming the formation of an intermediate compound, structurally similar to aldehyde-ammonia, which undergoes rearrangement to give the nitroso-derivative and *N*-methylbenzamide. These benzoates form unstable *additive* compounds with concentrated nitric acid, having the formulæ and m. p., respectively,  $C_{17}H_{17}O_2N, 3HNO_3$ , 53°, and  $C_{17}H_{17}O_2N, 2HNO_3$ , 65°. Thymoquinone dioxime may be prepared more conveniently by the action of hydroxylamine hydrochloride on nitrosocarvacrol, yield 70%, than by using nitrosothymol, yield 6—10%. It forms a *dibenzoate*, colourless needles, m. p. 199—200° (becomes discoloured at 170°). W. S. N.

**The Addition of Mercuric Salts to  $\alpha\beta$ -Unsaturated Ketones.** E. B. MIDDLETON (*J. Amer. Chem. Soc.*, 1923, **45**, 2763—2769).— $\alpha\beta$ -Unsaturated ketones such as benzylideneacetophenone (phenyl styryl ketone) react with but one molecule of mercuric acetate, whilst dibenzylideneacetone (distyryl ketone) containing two double linkages reacts with 2 mols. of mercuric acetate. The products obtained in alcoholic solution show that the groups  $\cdot OR$  and  $HgOCOCH_3$  have been added. The reactions of the additive compounds show that the mercury compounds of phenyl styryl ketone have the structure  $Ph\cdot CH(OR)\cdot CH(HgX)\cdot CPh$ , whilst the derivatives of distyryl ketone are



Substitution in the nuclei does not affect the reaction of the

unsaturated ketones with mercuric acetate. Ketones of the *cyclopropane* series do not yield additive compounds. A comparison is made between the mercuric acetate additive compounds and the compounds obtained by Vorländer and Eichwald (A., 1923, i, 684), using the mercury halides.  $\alpha$ -Acetoxymercuri- $\beta$ -methoxy- $\beta$ -phenylpropio-phenone,  $C_{18}H_{18}O_4Hg$ , obtained by the action of mercuric acetate on phenyl styryl ketone in methyl alcohol, has m. p.  $115^\circ$ . The corresponding *ethoxy*-derivative has m. p.  $134^\circ$ .  $\alpha$ -Bromomercuri- $\beta$ -methoxy- $\beta$ -phenylpropio-phenone,  $C_{16}H_{15}O_2BrHg$ , m. p.  $141^\circ$ , is prepared by the action of potassium bromide on the acetoxy-compound. The *ethoxy*-compound has m. p.  $138^\circ$ .  $\alpha$ -Bromo- $\beta$ -methoxy- $\beta$ -phenylpropio-phenone, m. p.  $76^\circ$ , is obtained by adding bromine to the acetoxymercuric-methoxy-derivative of phenyl styryl ketone. The *ethoxy*-compound has m. p.  $60$ — $61^\circ$  and the corresponding *iodo*-compounds  $96^\circ$  and  $75$ — $76^\circ$ . Sodium methoxide converts  $\alpha$ -bromo- $\beta$ -methoxy- $\beta$ -phenylpropio-phenone into an oil, b. p.  $200$ — $205^\circ/6$  mm., addition of mercuric acetate to the oil yielding diacetoxymercuridibenzoylmethane,  $C_{19}H_{16}O_6Hg_2$ , m. p.  $237^\circ$ . The bromomethoxyphenylpropio-phenone reacts with ethyl magnesium bromide to yield  $\beta$ -phenylvalerophenone,  $C_{17}H_{18}O$ , m. p.  $63^\circ$ . Distyryl ketone reacts with mercuric acetate to form the dimercurated compound containing two methoxy- and two mercuri-groups, m. p.  $183^\circ$ .  $\alpha$ -Acetoxymercuri- $\beta$ -methoxy- $\beta$ -phenyl-*p*-chloropropio-phenone, m. p.  $124^\circ$ , is obtained from mercuric acetate and *p*-chlorophenyl styryl ketone in methyl alcohol solution. F. G. P.

**Preparation of 2:4:2':4'-Tetrahydroxybenzophenone.** J. B. SHOESMITH and J. HALDANE (*J. Chem. Soc.*, 1924, 125, 113—115).—2:4-Diacetoxybenzonitrile is condensed with resorcinol by means of zinc chloride and dry hydrogen chloride, the resulting imine hydrochloride,  $(AcO)_2C_6H_3:C(NH_2Cl)C_6H_3(OH)_2$ , being readily hydrolysed to the required benzophenone in acid solution. A certain amount of resacetophenone and of  $\beta$ -resorcylamide may be recovered from the reaction mixture. 2:4-Diacetoxy-2':4'-dihydroxybenzophenoneimine hydrochloride gives crystals decomposing at  $195^\circ$ . F. G. P.

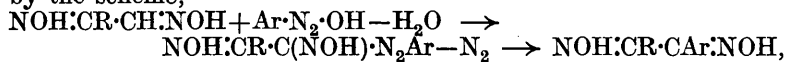
**The Benzil Rearrangement. V. Cannizzaro's Reaction.** A. LACHMAN (*J. Amer. Chem. Soc.*, 1923, 45, 2356—2363).—In the Cannizzaro reaction, benzyl benzoate is formed from benzaldehyde, even in the presence of water, provided an excess of alkali is avoided and any considerable rise in temperature is prevented. It is suggested that dihydroxydibenzyl ether,  $[CHPh(OH)]_2O$ , is formed as an intermediate stage, and by a glycol rearrangement is converted into the benzoate. In the course of the investigation it was shown that by heating benzyl alcohol in a sealed tube at  $210$ — $215^\circ$ , dibenzyl ether is obtained, and that bromine reacts with dibenzyl ether to produce benzyl bromide and benzoyl bromide. F. G. P.

**The Isomerism of the Oximes. XV. The Alleged Fourth Benzildioxime.** O. L. BRADY and F. P. DUNN (*J. Chem. Soc.*, 1924, 125, 291—296).—The work of Atack and Whinyates (T.,

1921, 119, 1184) has been repeated, but the authors have been unable to confirm the results, no evidence of the existence of the fourth dioxime being obtained. The purely structural theory of the isomerism of the oximes suggested by Atack is criticised and the principal objections to it are stated, particularly the existence of two *O*-ethers.

F. G. P.

**Dioximes. XVI.** G. PONZIO and V. BERNARDI (*Gazzetta*, 1923, 53, 813—817; cf. this vol., i, 54, 56).—The formation of the two benzildioximes from the two forms of phenylglyoxime by the action of phenyldiazonium chloride (A., 1923, i, 856) proves to be a reaction of general application constituting a new method of synthesising symmetrical and unsymmetrical, disubstituted glyoximes. Not only a glyoxime of the type  $\text{NOH}\cdot\text{C}\cdot\text{Ar}\cdot\text{CH}\cdot\text{NOH}$ , in which Ar is an aryl radical, but also methylglyoxime, reacts with many aryldiazonium chlorides with liberation of nitrogen and formation of the glyoximes,  $\text{NOH}\cdot\text{CR}\cdot\text{CR}_1\cdot\text{NOH}$ . This reaction, which gives a yield of about 45%, is not so simple as is represented by the scheme,



since there is entire lack of experimental evidence of the formation of an intermediate unstable compound with the  $\text{N}_2\text{Ar}$  group in direct union with a carbon atom. Participation in the reaction of the oximino-groups may, however, be excluded, since these pass with unaltered properties into the final products. Of special interest is the behaviour of methylglyoxime, which yields only the  $\beta$ -forms of glyoximes,  $\text{NOH}\cdot\text{CMe}\cdot\text{C}\cdot\text{Ar}\cdot\text{NOH}$ ; the conclusion that it is a  $\beta$ -modification is thus confirmed. Thus,  $\beta$ -phenylmethylglyoxime (A., 1922, i, 17) may be obtained by the action of phenyldiazonium chloride on methylglyoxime in 10% sodium hydroxide solution cooled with ice.

$\beta$ -*o*-Tolylmethylglyoxime,  $\text{NOH}\cdot\text{CMe}\cdot\text{C}(\text{NOH})\cdot\text{C}_6\text{H}_4\text{Me}$ , prepared from methylglyoxime and *o*-tolyldiazonium chloride, crystallises in white needles, m. p.  $236^\circ$  (slight decomp., and sublimation); its nickel salt,  $(\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}_2)_2\text{Ni}$ , forms red prisms, m. p.  $222^\circ$ , and its dibenzoyl derivative,  $\text{C}_{24}\text{H}_{20}\text{O}_4\text{N}_2$ , prisms, m. p.  $144^\circ$ .

$\beta$ -*p*-Tolylmethylglyoxime crystallises in white laminae, m. p.  $234$ — $235^\circ$ ; Borsche (A., 1907, i, 326) gave m. p. above  $230^\circ$  (decomp.). Its nickel salt,  $(\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}_2)_2\text{Ni}$ , forms blood-red prisms, m. p.  $250$ — $251^\circ$  (decomp.), with previous browning, and its dibenzoyl compound, white needles, m. p.  $148.5$ — $149.5^\circ$ .

$\beta$ -*p*-Anisylmethylglyoxime, prepared from *p*-methoxyphenyldiazonium chloride and methylglyoxime, forms white prisms, m. p.  $213^\circ$  (slight decomp.). Boeris (A., 1894, i, 72) gave m. p.  $206^\circ$ , and Tschugaev (A., 1908, i, 554), m. p.  $207^\circ$ ; cf. also Wieland (A., 1903, i, 837). Its nickel salt,  $\text{C}_{20}\text{H}_{22}\text{O}_6\text{N}_4\text{Ni}$ , crystallises in scarlet needles, m. p.  $224^\circ$  (cf. Tschugaev, *loc. cit.*), and its dibenzoyl derivative in needles, m. p.  $148.5^\circ$ .

$\beta$ -Phenyl-*p*-tolylglyoxime,  $\text{NOH}\cdot\text{CPh}\cdot\text{C}(\text{NOH})\cdot\text{C}_6\text{H}_4\text{Me}$ , prepared by the interaction either of *p*-tolyldiazonium chloride and  $\beta$ -phenyl-



glyoxime, or of phenyldiazonium chloride and  $\beta$ -*p*-tolylglyoxime, crystallises in lustrous laminae, m. p. 223—224° (partial sublimation). Its *nickel* salt,  $(C_{15}H_{13}O_2N_2)_2Ni$ , forms microscopic, brick-red needles, m. p. 295—297° (decomp.), and its *dibenzoyl* derivative, laminae, m. p. 184° (slight decomp.).

$\beta$ -*Phenyl-p-anisylglyoxime*,  $C_{15}H_{14}O_3N_2$ , prepared similarly, crystallises in white laminae, m. p. 223° (slight decomp.). Its *nickel* salt forms a microcrystalline, blood-red powder, m. p. 264° (decomp.), and its *dibenzoyl* derivative, laminae, m. p. 162°.

T. H. P.

**Dioximes. XVIII.** L. AVOGADRO (*Gazzetta*, 1923, **53**, 824—828).—The dehydrogenating action of nitrogen tetroxide on the  $\alpha$ -modifications of arylglyoximes proceeds similarly to that of the same reagent on  $\alpha$ -phenylglyoxime (A., 1923, i, 1019, 1137). Thus,  $\alpha$ -*p*-tolylglyoxime yields a compound which must be regarded as the oxide of *p*-toluoyl cyanide oxime since (1) with acetic anhydride it yields a monoacetyl derivative, (2) it is reduced by means of zinc and acetic acid, giving *p*-toluoyl cyanide oxime, (3) when heated with xylene it undergoes isomerisation to 5-hydroxy-3-*p*-tolyl-1:2:4-oxadiazole, (4) it unites with a molecule of ammonia to form amino- $\alpha$ -*p*-tolylglyoxime, and (5) it reacts with magnesium methyl iodide to form *p*-tolylmethylglyoxime.

The *oxide* of *p*-toluoyl cyanide oxime,  $NOH:C(C_6H_4Me) \cdot C \leq \begin{smallmatrix} O \\ N \end{smallmatrix}$ , or  $NOH:C(C_6H_4Me) \cdot C:N:O$ , crystallises in silky, white needles, m. p. 108° with previous softening, and is highly stable towards acids, but is readily decomposed by bases or even by boiling water, giving *p*-toluonitrile and substances having the odour of carbylamine. Its *acetyl* derivative forms white prisms, m. p. 157—158°.

*Amino- $\alpha$ -p-tolylglyoxime*,  $C_6H_4Me \cdot C:(NOH) \cdot C:(NOH) \cdot NH_2$ , crystallises in white laminae, m. p. 173—174°, and, when treated in aqueous alcoholic solution with nickel acetate, gives a greyish-green precipitate soluble in dilute acetic acid. When boiled with dilute acetic acid it slowly undergoes isomerisation into amino- $\beta$ -*p*-tolylglyoxime, which has not been investigated further. T. H. P.

**Ketens. XLVII.** The Constitution of Dimeric Ketens, a Contribution to the Valency Problem of Organic Chemistry. H. STAUDINGER (*Helv. Chim. Acta*, 1924, **7**, 3—8).—A reply to Schroeter (A., 1920, i, 852), who criticises the author's conception of the dimeric ketens as *cyclobutan*-1:3-diones or 1:3-*cyclobutenolones*, and considers them to be molecular compounds. The conception of dimeric aldoketens as 1:3-*cyclobutenolone* derivatives is supported by their physical properties and absorption spectra. Schroeter considers the more stable dimeric ketens to be true *cyclobutandiones*, the less stable to be molecular compounds, but it is pointed out that *cyclobutane* derivatives differ much in their stability to heat; substitution, including the keto-group, weakens the ring, and heavily substituted compounds such as ethyl diethyl-*cyclobutandionedicarboxylate* are especially labile. The author's

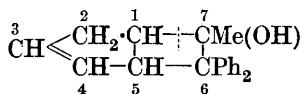
view is also supported by preparation of *cyclobutane* derivatives by the combination of diphenylketen with ethylenic compounds (A., 1920, i, 556, and following abstract). E. H. R.

**Ketens. XLVIII. *cyclo*Butane Derivatives from Diphenylketen and Ethylenic Compounds.** H. STAUDINGER and A. RHEINER (*Helv. Chim. Acta*, 1924, 7, 8—18).—The compound formed by diphenylketen with styrene is now found to be 1 : 1 : 4-*triphenylcyclobutan-2-one*,  $\begin{array}{c} \text{CHPh} \cdot \text{CPh}_2 \\ | \\ \text{CH}_2 - \text{CO} \end{array}$ , instead of the 1 : 1 : 3-

compound as previously stated (Staudinger and Suter, A., 1920, i, 556). It follows that the acid obtained by treating it with sodium hydroxide in alcoholic solution is  $\alpha\beta$ -*triphenyl-n-butyric acid* instead of the  $\alpha\gamma$ -compound. Evidence for the constitution of the triphenyl*cyclobutanone* was obtained through the action of methyl magnesium iodide, by means of which the tertiary alcohol, 1-*methyl-2 : 2 : 3-triphenylcyclobutan-1-ol* was obtained, colourless crystals, m. p. 132°; the yield was 87% of the theoretical. When rapidly distilled at the ordinary pressure, the tertiary alcohol decomposes to the extent of 80% into *as*-diphenylacetone and styrene and 20% into acetone and triphenylethylene. These products establish its constitution. When distillation is carried out in a high vacuum, decomposition does not take place, but an *isomeride* is formed, m. p. 137°; in all probability the ring has opened with formation of a triphenyl-*n*-propyl methyl ketone. By the action of phenyl magnesium bromide on the triphenyl*cyclobutanone* there is obtained, not the expected tertiary alcohol, but *benzylidenediphenylacetone*,  $\text{CHPh}_2 \cdot \text{CO} \cdot \text{CH} : \text{CHPh}$  [*benzhydryl styryl ketone*], m. p. 112°, b. p. 250°/18 mm. The same compound was synthesised from diphenylacetone and benzaldehyde (cf. Rack, A., 1923, i, 681).

As previously described (*loc. cit.*), diphenylketen combines with *cyclopentadiene* to form a compound, which can be reduced to a saturated compound, for which the formula  $\text{CH}_2 < \begin{array}{c} \text{CH}_2 \cdot \text{CH} - \text{CO} \\ | \\ \text{CH}_2 \cdot \text{CH} - \text{CPh}_2 \end{array}$ ,

is now proposed. When this is submitted to prolonged boiling with sodium hydroxide, hydrolysis takes place at the dotted line with formation of *diphenylcyclopentylacetic acid*, m. p. 85°; *anilide*, m. p. 139°. The compound of diphenylketen with *cyclopentadiene*



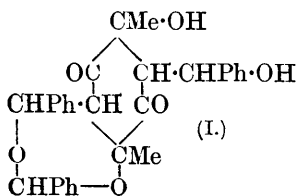
reacts with methyl magnesium iodide to give the tertiary alcohol having the annexed formula, designated 6 : 6-*diphenyl-7-methyl-0 : 2 : 3-bicyclo-3 : 4 (?) -hepten-7-ol*, m. p. 130°. When boiled

with alcoholic potassium hydroxide the heptane ring opens, probably at the dotted line, forming a *ketone*; its semicarbazone has m. p. 115°. By treatment with hydrogen and platinum black, the above heptenol is reduced to the corresponding *heptanol*, m. p. 99°. By the action of phenyl magnesium iodide on the diphenylketen-*cyclopentadiene* compound, a *substance* was obtained, m. p. 214°, having the same empirical composition as the original compound. It may be a

dimeride. Diphenylketen and dicyclopentadiene form a *compound*, m. p. 95°. E. H. R.

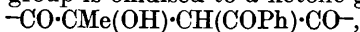
**Ketens. XLIX. cycloButane Derivatives from Dimethylketen and Ethylenic Compounds.** H. STAUDINGER and P. J. MEYER (*Helv. Chim. Acta*, 1924, 7, 19—22).—Dimethylketen combines less readily with ethylenic compounds than diphenylketen, but the compounds when formed are more stable than those from diphenylketen. The four-membered ring is relatively stable and the ketonic group has normal properties. Dimethylketen does not combine with styrene, but with vinyl ethyl ether it forms 3(or 4)-ethoxy-1:1-dimethylcyclobutan-2-one, a colourless oil, b. p. 166—169°; the phenylhydrazone forms white needles, m. p. 70°, and quickly decomposes in the air. With cyclopentadiene, dimethylketen forms a *compound* probably having the formula  $\text{CH} \begin{smallmatrix} \swarrow \text{CH}_2 \cdot \text{CH} \cdot \text{CO} \\ \searrow \text{CH} \cdot \text{CH} \cdot \text{CMe}_2 \end{smallmatrix}$ , but the position of the double bond is uncertain; it is an oil with a camphor-like odour, b. p. 175—178°; when superheated it decomposes into dimethylketen and cyclopentadiene. Its *semicarbazone* has m. p. 215°. When reduced with hydrogen and platinum black it gives the saturated compound, 6:6-dimethyl-0:2:3-bicycloheptan-7-one, also having the odour of camphor, b. p. 176—178°; it gives dimethylketen when superheated. Its *semicarbazone* has m. p. 224°. E. H. R.

**Reaction Products from Aldehydes and 1:2-Diketones.** O. DIELS [with R. W. POINDEXTER, K. ILBERG, and W. GÄDKE] (*Annalen*, 1923, 434, 1—20).—When a mixture of benzaldehyde and diacetyl is treated at  $-10^\circ$  with 25% methyl-alcoholic potassium hydroxide solution, the diketone first polymerises to its dimeride, 1:4-dihydroxy-1:4-dimethylcyclohexan-3:6-dione (Diels, Blanchard, and v. d. Heyden, A., 1914, i, 1052); this then undergoes condensation with the aldehyde (3 mols.), 1 mol. of water being eliminated, with the formation of the same *compound* (I), slender, white needles, m. p. 198° (decomp.), which is obtained if the dimeride itself is used. The structure of this substance is evident from the

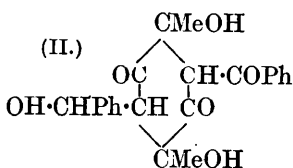


following reactions. Although, probably owing to steric hindrance, the ketone groups are not reactive, the hydroxyl group next to the phenyl radical can be esterified. The *benzoate* forms thick, transparent prisms, m. p. 192°; the *acetate*, four-sided tablets or prisms, has m. p. 197—198°. But if, in preparing the acetate, the action of acetic anhydride is continued, water is eliminated, with the production of the unsaturated *acetate*,  $-\text{OC} \cdot \text{CMe} \cdot \text{C}(\text{CHPh} \cdot \text{OAc}) \cdot \text{CO}-$ , m. p. 237°. This compound reacts immediately with potassium permanganate in glacial acetic acid solution, or with bromine in cold chloroform solution; the subsequent spontaneous elimination of hydrogen bromide from the dibromide produced in the latter reaction gives two *bromo-derivatives*,  $\text{C}_{31}\text{H}_{27}\text{O}_6\text{Br}$ , (*a*) colourless needles, or

small, elongated plates, m. p. 193°, (b) small, transparent prisms, m. p. 210°. The action of phenylhydrazine in methyl-alcoholic glacial acetic acid solution at 65° on the unsaturated acetate gives the corresponding unsaturated *alcohol*, m. p. 198—203°, +xEtOH, long prisms, which is readily converted into the compound (I) by boiling with hydrochloric, acetic, or propionic acid, and gives the saturated *methyl ether*,  $-\text{OC}\cdot\text{CMe}(\text{OMe})\cdot\text{CH}(\text{CHPh}\cdot\text{OH})\cdot\text{CO}-$  (felted needles, m. p. 240°, after decomposing at 218°), when boiled with methyl alcohol containing a trace of hydrochloric acid. Similarly, the action of acids on the unsaturated acetate gives the saturated acetate, which, like the analogous benzoate, is readily hydrolysed to the compound (I) by means of boiling alcoholic potassium hydroxide solution. By the action of a boiling mixture of glacial acetic acid and concentrated nitric acid on the compound (I), the secondary alcohol group is oxidised to a ketone group,

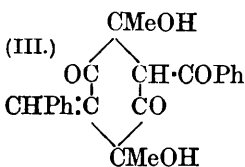


with the formation of a *compound*, m. p. 203—204° (decomp.), which crystallises from acetonitrile with 1MeCN, in rhombic crystals, readily soluble in alkali. In 25% methyl-alcoholic potassium hydroxide solution, benzaldehyde is rapidly eliminated, with the



production of the *compound* (II), thin, felted needles, m. p. 151—153° after sintering at about 146°. The latter is soluble in aqueous alkali, but soon resinifies, more rapidly on warming, with the elimination of benzaldehyde.

It is converted by the action of methyl alcohol containing hydrogen chloride into its *methyl ether*, compact, snow-white crystals, m. p. 169—171° (slight decomp.); methyl hydrazinecarboxylate gives a *salt*, felted needles, m. p. 130—132° (decomp.), in the formation of which, presumably, the benzoyl group has taken part in its enolic form. The ketonic groups are not reactive. The compound (II) forms an additive *compound* with cold formic acid, but the boiling, anhydrous reagent causes the elimination of water, to give 2-benzoyl-1:4-dihydroxy-5-benzylidene-1:4-dimethylcyclohexan-3:6-dione (III), a bright sulphur-yellow compound, m. p. 238—243°, one



of the ketone groups of which is reactive; the *oxime*, m. p. 221—222°, *semicarbazone*, long, colourless needles, decomp. about 235°, m. p. 245—248°, and the *carbomethoxyhydrazone*, long, colourless prisms, decomp. 220°, m. p. 240—243°, are described. The compound (III) is decomposed at 250—270° into benzoyldiacetyl and benzylidenediacetyl.

*Compounds* are also prepared by condensing diacetyl with furfural and anisaldehyde. The first forms thick, colourless needles, m. p. 203° (decomp.) after sintering at 180°; the second forms small needles, and has m. p. 203—205° (decomp.). With concentrated sulphuric acid they give, respectively, a dark reddish-purple color-

ation, which changes to brown, and an intense carmine coloration, which persists during twenty-four hours. W. S. N.

**Trihydroxymethylanthraquinones.** I. G. D. GRAVES and R. ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 2439—2455).—3 : 6-Dimethoxyphthalic anhydride is prepared by the action of boiling 98% sulphuric acid on the dimethyl ether of 2 : 3-dicyanoquinol, which is obtained by the action of potassium hydroxide solution and methyl sulphate on 2 : 3-dicyanoquinol.

The action of an excess of *p*-cresol on 3 : 6-dimethoxyphthalic anhydride in the presence of aluminium chloride at 70° gives 3 : 6-dimethoxy-2-(2'-hydroxy-5'-methylbenzoyl)benzoic acid, white plates, m. p. 218° (corr.), together with 12 : 15-dimethoxy-2 : 7-dimethylfluoran, white crystals, m. p. 290° (corr.). When the benzoic acid derivative is boiled with potassium hydroxide solution and methyl sulphate, the product is 3 : 6-dimethoxy-2-(2'-methoxy-5'-methylbenzoyl)benzoic acid, white needles, or colourless, truncated prisms, m. p. 203—204° (corr.), which is identical with the product from 3 : 6-dimethoxyphthalic anhydride and *p*-cresyl methyl ether (cf. following abstract). When the substituted benzoic acid and concentrated sulphuric acid are heated at 100° with a small quantity of boric acid, the colour changes from green to bluish-red, owing to the formation of 1-hydroxy-5 : 8-dimethoxy-4-methylanthraquinone, red needles, m. p. 224° (corr.). The latter is demethylated by boiling with glacial acetic acid and hydrobromic acid (constant-boiling), giving 1 : 5 : 8-trihydroxy-4-methylanthraquinone. When 3 : 6-dimethoxyphthalic anhydride is heated at 75° with an excess of *o*-cresol in the presence of aluminium chloride, the products are 3 : 6-dimethoxy-2-(2'-hydroxy-3'-methylbenzoyl)benzoic acid, white needles, m. p. 194° (corr.), and *o*-cresol-3 : 6-dimethoxyphthalein, white needles, m. p. 258° (corr.). The latter is an indicator, changing from colourless to red at  $p_H$  9.1. The methylation of the benzoic acid gives 3 : 6-dimethoxy-2-(2'-methoxy-3'-methylbenzoyl)benzoic acid, white needles, m. p. 178° (corr.), which is not identical with the acid formed by condensing 3 : 6-dimethoxyphthalic anhydride with *o*-cresyl methyl ether; in the latter reaction, there is also formed the dimethyl ether of *o*-cresol-3 : 6-dimethoxyphthalein, white needles, m. p. 202° (corr.), which is likewise produced by the methylation of the phthalein. The action of sulphuric acid, containing boric acid, on the benzoic acid derivative, gives 1-hydroxy-5 : 8-dimethoxy-2-methylanthraquinone, red needles, m. p. 165° (corr.), which may be demethylated to give 1 : 5 : 8-trihydroxy-2-methylanthraquinone, red needles, which sublime at 250—260°. When *o*-cresol-3 : 6-dimethoxyphthalein and 3 : 6-dimethoxyphthalic anhydride are heated at 125° with concentrated sulphuric acid, the product is 2 : 5 : 8-trihydroxy-1-methylanthraquinone, dark red needles, m. p. 270° (corr.), which is identical with the product obtained by condensing 3 : 6-dimethoxyphthalic anhydride with *o*-cresyl methyl ether, dehydrating the benzoylbenzoic acid thus obtained, and hydrolysing the resulting anthraquinone. The interaction of 3 : 6-dimethoxyphthalic anhydride and *m*-cresol at

75° in the presence of aluminium chloride gives 3 : 6-dimethoxy-2-(2'-hydroxy-4'-methylbenzoyl)benzoic acid, white needles, m. p. 233° (corr.), and 3-hydroxy-6-methoxy-2-(2'-hydroxy-4'-methylbenzoyl)benzoic acid, white needles, m. p. 189° (corr.). A third substance formed in the above reaction is *m*-cresol-3 : 6-dimethoxyphthalein, white needles, m. p. 271° (corr.), a solution of which changes from colourless to red at  $p_H$  9.8. The conversion of 3 : 6-dimethoxy-2-(2'-hydroxy-4'-methylbenzoyl)benzoic acid into 1-hydroxy-5 : 8-dimethoxy-3-methylanthraquinone, red needles, m. p. 172° (corr.), can only be accomplished by the use of fuming sulphuric acid at 100° in the presence of boric acid. The demethylation of this dimethoxyanthraquinone by means of glacial acetic acid and hydrobromic acid gives 1 : 5 : 8-trihydroxy-3-methylanthraquinone, red needles, m. p. 227° (corr.).

The condensation of 3 : 5-dimethoxyphthalic anhydride with *m*-cresol by heating with aluminium chloride at 70° gives 3 : 5-dimethoxy-2-(2'-hydroxy-4'-methylbenzoyl)benzoic acid, white needles, m. p. 233° (corr.), and *m*-cresol-3 : 5-dimethoxyphthalein, which cannot be purified. The former gives, on methylation, 3 : 5-dimethoxy-2-(2'-methoxy-4'-methylbenzoyl)benzoic acid, white needles, m. p. 219° (corr.), whereas the condensation of 3 : 5-dimethoxyphthalic anhydride with *m*-cresyl methyl ether gives 3 : 5-dimethoxy-2-(4'-methoxy-2'-methylbenzoyl)benzoic acid, m. p. 233° (corr.). The action of fuming sulphuric acid and boric acid at 100° on 3 : 5-dimethoxy-2-(2'-hydroxy-4'-methylbenzoyl)benzoic acid leads to sulphonation, a poor yield of the expected anthraquinone, yellow needles, m. p. about 185°, being obtained. This substance gives a red solution in alkali, which reacts with methyl sulphate at 100° to give a trimethoxy compound, yellow needles, m. p. about 175—180°, which gives a red solution in concentrated sulphuric acid, and should be the trimethyl ether of emodin, if the latter has the structure suggested (*Arch. Pharm.*, 1912, **250**, 301). The action of concentrated nitric acid in glacial acetic acid solution at 50—60° on 3 : 5-dimethoxy-2-(2'-hydroxy-4'-methylbenzoyl)benzoic acid gives the 5'-nitro-derivative, pale yellow needles, m. p. 241° (corr.), but the product of the condensation of 3 : 5-dimethoxyphthalic anhydride and *o*-nitro-*m*-cresol is 3 : 5-dimethoxy-2-(4'-hydroxy-5'-nitro-2'-methylbenzoyl)benzoic acid, white needles, m. p. 181° (corr.).

3 : 5-Dimethoxyphthalic acid is obtained by the action of cold, alkaline, potassium permanganate solution on 3 : 5-dimethoxyphthalide, which is prepared by heating its carboxylic acid. The latter is made by the action of warm sodium hydroxide solution on 3 : 5-dimethoxytrichloromethylphthalide, which is formed when a mixture of chloral hydrate and ethyl 3 : 5-dimethoxybenzoate is treated with somewhat concentrated sulphuric acid. W. S. N.

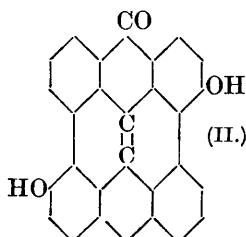
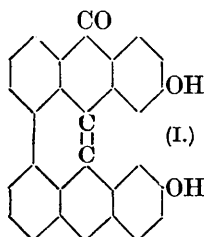
**Trihydroxymethylanthraquinones.** II. J. H. GARDNER and R. ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 2455—2462; cf. preceding abstract).—The action of an excess of *p*-cresyl methyl ether on 3 : 6-dimethoxyphthalic anhydride at 70° in the presence of

aluminium chloride gives 3 : 6-dimethoxy-2-(2'-methoxy-5'-methylbenzoyl)benzoic acid, together with the *dimethyl ether* of *p*-cresol-3 : 6-dimethoxyphthalein, colourless needles, m. p. 187.5° (corr.). When the trimethoxybenzoic acid is rapidly heated with concentrated sulphuric acid at 150°, and then cooled, the products are 1-hydroxy-5 : 8-dimethoxy-4-methylanthraquinone and 1 : 5 : 8-trihydroxy-4-methylanthraquinone, slender, red needles, m. p. 276—278° (corr.) (with sublimation); the latter is the sole product if the reaction mixture is kept at 145—155° for twenty minutes. When a mixture of 3 : 6-dimethoxyphthalic anhydride and an excess of *o*-cresyl methyl ether is treated at 65° with aluminium chloride, there are formed 3 : 6-dimethoxy-2-(4'-methoxy-5'-methylbenzoyl)benzoic acid, a white powder, m. p. 192° (corr.), and the *dimethyl ether* of *o*-cresol-3 : 6-dimethoxyphthalein, colourless needles, m. p. 202—203° (corr.). When the acid is rapidly heated with concentrated sulphuric acid at 150°, and immediately cooled, the chief product is 5 : 8-dihydroxy-2-methoxy-1-methylanthraquinone, dark red needles, m. p. 249—249.5° (corr.), which is accompanied by a small quantity of 2 : 5 : 8-trihydroxy-1-methylanthraquinone. The latter may more conveniently be prepared by heating a mixture of concentrated sulphuric acid, 3 : 6-dimethoxyphthalic anhydride, and *o*-cresol-3 : 6-dimethoxyphthalein, or its dimethyl ether, at 125°. The structure of the original benzoic acid is proved by distilling the trihydroxyanthraquinone with zinc dust, the resulting methylanthracene being then oxidised to 1-methylanthraquinone. 3-Hydroxy-6-methoxy-2-(4'-methoxy-1'-methylbenzoyl)benzoic acid, colourless prisms, m. p. 194—195° (corr.), and not the dimethoxyacid, is obtained when 3 : 6-dimethoxyphthalic anhydride is treated with an excess of *m*-cresyl methyl ether and aluminium chloride at 75°; a phthalein is not produced. A pure derivative of anthraquinone has not been obtained by the dehydration of this acid.

W. S. N.

### Reduction Products of the Hydroxyanthraquinones. IV.

J. W. E. HALLER and A. G. PERKIN (*J. Chem. Soc.*, 1924, 125, 231—239).—Reduction of 2-hydroxyanthraquinone with glucose and alkali in the presence of sodium nitrate yields 2-hydroxybenzanthrone-



carboxylic acid, and two compounds which are now shown to be a 3 : 6'-dihydroxyhelianthrone,  $C_{28}H_{14}O_4$  (I), and 3 : 6'-dihydroxy-mesonaphthadanthrone,  $C_{26}H_{12}O_4$  (II). Better yields of (I) are obtained by the oxidation

of dihydroxydianthrone with potassium ferricyanide. (II) may be obtained by exposing the diacetyl derivative of (I) (in benzene or acetic acid solution) to sunlight for some weeks, when an almost quantitative yield of the diacetoxynaphthadanthrone

results. Oxidation of the acetyl compound of (I) with chromic acid yields *diacetoxy-1:1'-dianthraquinonyl*,  $C_{28}H_{12}O_6Ac_2$ , small plates, m. p.  $277^\circ$ . The corresponding *dihydroxy* compound crystallises in prisms or leaflets, m. p.  $>350^\circ$ . The *dimethyl ether*,  $C_{30}H_{18}O_6$ , crystallises in yellow prisms, m. p.  $343-344^\circ$ . With iodine in pyridine solution, (I) yields *5-iodo-3:6'-diacetoxyhelianthrone*,  $C_{32}H_{17}O_6I$ , yellow needles, m. p.  $282^\circ$ , and from this by hydrolysis the *dihydroxy* compound is obtained in the form of scarlet needles, m. p.  $>350^\circ$ . *3:6'-Dihydroxynaphthodianthrone*,  $C_{28}H_{12}O_4$ , is an orange-brown powder, m. p.  $>350^\circ$ . Its *diacetyl* derivative crystallises in yellow needles.

F. G. P.

### Camphorylcarbamates and their Physiological Action.

H. E. FIERZ-DAVID and W. MÜLLER (*J. Chem. Soc.*, 1924, 125, 26—27).—Camphorylcarbamates may be obtained in almost quantitative yield by the interaction of aminocamphor and alkyl chloroformates. Their pronounced poisonous action renders them unsuitable for practical application. *isoAmyl* and *allyl camphorylcarbamates* are viscous, oily liquids, b. p.  $199^\circ/11$  mm., and  $186^\circ/10$  mm., respectively, with  $[\alpha]_D +34.2^\circ$ , and  $+34.3^\circ$ . *Methyl camphorylcarbamate*, m. p.  $110^\circ$ , b. p.  $169^\circ/11$  mm.,  $[\alpha]_D +39.4^\circ$ . The *ethyl*, *isopropyl*, and *isobutyl* derivatives have, respectively, m. p.  $88^\circ$ ,  $73^\circ$ ,  $83^\circ$ ; b. p.  $178^\circ/13$  mm.,  $170^\circ/10$  mm.,  $184^\circ/11$  mm., with  $[\alpha]_D +35.1^\circ$ ,  $35.3^\circ$ , and  $33.9^\circ$ .

F. G. P.

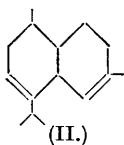
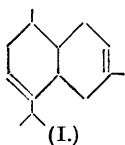
### Piperitone. VII. The Constitution of Piperitone. J.

READ, H. G. SMITH, and R. S. HUGHESDON (*J. Chem. Soc.*, 1924, 125, 129—137).—Benzyl-*dl*-isomenthone, obtained by hydrogenation of benzylidene-*dl*-piperitone, is distinct from 2-benzyl-*dl*-isomenthone obtained, from *dl*-piperitone. It is concluded from this observation that piperitone is  $\Delta^1$ -*p*-menthen-3-one, and benzylidene-piperitone is 6-benzylidene- $\Delta^1$ -*p*-menthen-3-one. 6-Benzyl-*dl*-isomenthone reacts with benzaldehyde to yield 2-benzylidene-6-benzyl-*dl*-isomenthone, and it also forms a semicarbazone, whilst 2-benzyl-*dl*-isomenthone is incapable of so reacting. 2-Benzylidene-*dl*-isomenthone hydrochloride forms colourless needles, m. p.  $108-110^\circ$ . 2-Benzyl-*dl*-isomenthol,  $C_{10}H_{19}O \cdot CH_2Ph$ , is a colourless, viscid liquid, b. p.  $194-196^\circ/20$  mm. Its *phenylurethane* melts at  $153-154^\circ$ . 2-Benzylidene-*dl*-isomenthone,  $C_{10}H_{16}O \cdot CHPh$ , is a colourless liquid, b. p.  $193-195^\circ/15$  mm. The corresponding benzyl compound,  $C_{10}H_{17}O \cdot CH_2Ph$ , is a colourless, viscid liquid, b. p.  $195-197^\circ/20$  mm.,  $d_4^{20}$  0.9957,  $n_D^{20}$  1.5230, and  $[R_L]_D$  74.92. 6-Benzyl-*dl*-isomenthone,  $C_{10}H_{17}O \cdot CH_2Ph$ , is a colourless, viscid liquid, b. p.  $202-203^\circ/14$  mm.,  $d_4^{20}$  0.9884,  $n_D^{20}$  1.5176, and  $[R_L]_D$  74.84. Its *semicarbazone* crystallises in colourless prisms, m. p.  $170-171^\circ$ . 6-Benzyl-*dl*-isomenthone distils at  $213-220^\circ/20$  mm., and has  $d_4^{20}$  0.9905,  $n_D^{20}$  1.5239, and  $[R_L]_D$  75.42. Its *semicarbazone* has m. p.  $170-171^\circ$ . 6-Benzyl-2-benzylidene-*dl*-isomenthone is a yellow, mobile oil, b. p.  $218-225^\circ/15$  mm. Reduction of this yields 2:6-dibenzyl-*dl*-isomenthol, a pale yellow, viscid liquid, b. p.  $282-287^\circ/23$  mm. 6-Benzyl-*dl*-isomenthol,  $C_{10}H_{19}O \cdot CH_2Ph$ , distils at  $203-207^\circ/16$  mm. Its *phenylurethane* crystallises in needles and

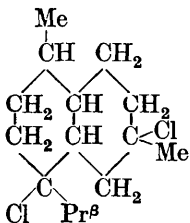


has m. p. 138—139°. A crystalline variety of the *isomenthol*, m. p. 66—68°, has also been obtained. F. G. P.

**Higher Terpene Compounds. XVIII. The Constitution of Cadinene.** L. RUZICKA and M. STOLL (*Helv. Chim. Acta*, 1924, 7, 84—94).—The carbon framework of cadinene has already been established by its dehydrogenation with sulphur to cadaline (Ruzicka and Meyer, A., 1921, i, 573). This result has now been confirmed by the catalytic dehydrogenation of cadinene with platinum black in a high vacuum at 300°. It remains therefore to determine the positions of the two double bonds. That one of these is probably adjacent to the *isopropyl* group has already been shown (Ruzicka and Seidel, A., 1922, i, 562). It is now shown, by a variety of arguments, that cadinene is probably to be represented by one or both of the two annexed formulæ.



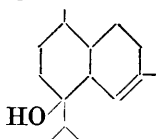
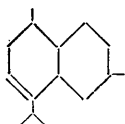
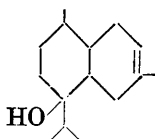
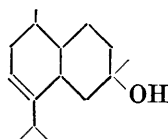
The products obtained by the action of ozone on cadinene, followed by decomposition of the ozonide first formed, render it extremely improbable that both double bonds are contained in the same ring. Although great difficulty was experienced in obtaining any identifiable products from this reaction, an *ethyl dicarboxylate* was obtained, b. p. 190—200°/0.2 mm., having the composition  $C_{19}H_{30}O_5$  or  $C_{19}H_{32}O_6$ , in which all the carbon atoms of cadinene are intact. The absence of conjugated double bonds in cadinene is shown by the failure of attempts at reduction with sodium and amyl alcohol. The oxidation of cadinene with manganese dioxide and sulphuric acid as described by Ruzicka, Schinz, and Meyer (this vol., i, 171) resulted in the formation of trimellitic acid and mellophanic acid as primary products, and benzenepentacarboxylic acid as a secondary product. Cadinene dihydrochloride can be definitely stated to have the annexed formula.



E. H. R.

**Higher Terpene Compounds. XIX. Cadinol from Galbanum Oil.** L. RUZICKA and M. STOLL (*Helv. Chim. Acta*, 1924, 7, 94—105).—A sesquiterpene alcohol, cadinol,  $C_{15}H_{26}O$ , which by loss of a molecule of water gives cadinene, was discovered by Semmler and Jonas in galbanum resin (A., 1915, i, 573). Having elucidated the constitution of cadinene (preceding abstract), the authors now attempt to discover that of cadinol. The compound does not react at a high temperature with phthalic anhydride, and must therefore be a tertiary alcohol. To determine the position of the double bond and of the hydroxyl group, the action of ozone was studied on cadinol itself and on the dihydrocadinene obtained by hydrogenating cadinol and then removing water. An attempt to reduce cadinol to a dihydrocadinene by heating with zinc dust was unsuccessful; only cadinene was obtained, by dehydration of the cadinol. Reduction of cadinol to *dihydrocadinol* was effected

with some difficulty by hydrogen and platinum black; it is a colourless oil, b. p. 150—153°/12 mm.,  $[\alpha]_D +23^\circ$ ,  $n_D^{16} 1.4948$ ,  $d_4^{16} 0.9579$ . By boiling with 90% formic acid, dihydrocadinol is converted into *dihydrocadinene* (annexed formula), a colourless oil, b. p. 129—131°/12 mm.,  $[\alpha]_D +19.8^\circ$ ,  $n_D^{18} 1.4952$ ,  $d_4^{18} 0.8999$ . By the action of ozone on this compound and decomposition of the ozonide there were obtained a keto-aldehyde and a keto-acid by the disruption of the hydrocarbon at the double bond; neither, however, was obtained in a pure condition. By ozonisation of cadinol itself there was obtained a neutral product,  $C_{15}H_{24}O_2$ , probably a *ketone-alcohol*, b. p. 180—184°/12 mm.; it contains one double bond. In addition a doubly unsaturated *ketone*,  $C_{15}H_{22}O$ , probably formed from the previous compound by loss of water, was obtained, b. p. 140—145°/12 mm. Oxidation of this ketone with manganese dioxide and sulphuric acid gave only mellophanic acid. The higher-boiling fractions of the neutral products from the ozonisation of cadinol gave, besides mellophanic acid, trimellitic acid. These observations can be explained on the assumption that cadinol consists of at least two forms,  $\alpha$  and  $\beta$ , with probably a small proportion of a third form,  $\gamma$ , having the formulæ:

 $\alpha$ -Cadinol. $\beta$ -Cadinol. $\gamma$ -Cadinol.

Structural formulæ are suggested for the products obtained by the ozonisation of cadinol, based on the above formulæ for cadinol. The cause of the formation of trimellitic acid by oxidation of higher fractions of these products is traced back to the small proportion of  $\gamma$ -cadinol probably present in the cadinol. E. H. R.

**The Chlorohydrins of  $\beta$ -Pinene.** G. G. HENDERSON and C. A. KERR (*J. Chem. Soc.*, 1924, 125, 102—106).— $\beta$ -Pinene, on treatment with a very dilute aqueous solution of hypochlorous acid, gives mainly a mixture of three isomeric crystalline *dichlorohydrins*,  $C_{10}H_{18}O_2Cl_2$ , of m. p. 135°, 166°, and 131°, respectively. They are isomeric but not identical with the corresponding compounds prepared from  $\alpha$ -pinene. The dichlorohydrin of m. p. 135° is converted into a *monochlorohydrin*,  $C_{10}H_{17}O_2Cl$ , m. p. 128—129°, by the action of dilute potassium hydroxide solution; this is an isomeride of pinol glycol chlorohydrin. Further action of caustic alkali converts it into an oily liquid which is apparently somewhat similar to pinol oxide in properties. The dichlorohydrin, m. p. 166°, also yields an oily liquid on treatment with caustic alkali, but a solid monochlorohydrin could not be obtained in this case. The third dichlorohydrin, m. p. 131°, is unaffected by caustic alkali in the cold. F. G. P.

**Some Oxidation Products of  $\beta$ -Pinene.** G. G. HENDERSON and D. CHISHOLM (*J. Chem. Soc.*, 1924, **125**, 107—113).— $\beta$ -Pinene unites with chromyl chloride to form a solid compound,  $C_{10}H_{16} \cdot 2CrO_2Cl_2$ , which on decomposition by water yields as chief product the ketone  $C_{10}H_{14}O$ , previously prepared in a similar fashion from  $\alpha$ -pinene. A trace of an aldehyde and a small quantity of the inactive form of *trans*-pinol glycol were also obtained. Oxidation of  $\beta$ -pinene in glacial acetic acid solution by hydrogen peroxide gives a mixture of volatile and non-volatile products, the chief constituents of the volatile portion being borneol and a little fenchyl alcohol. The non-volatile portion could not be obtained sufficiently pure for identification.  
F. G. P.

**Diacetyl Compound of Desmotropo-Artemisin.** P. BERTOLO (*Gazzetta*, 1923, **53**, 867—869).—It is now found that desmotropo-artemisin forms a diacetyl derivative, so that, in the transformation of artemisin into desmotropo-artemisin, the fourth oxygen atom retains its alcoholic character (cf. A., 1923, i, 1108).

*Diacetyldesmotropo-artemisin*,  $C_{19}H_{22}O_6$ , crystallises in hard, lustrous, white needles, often grouped in radiating masses, m. p. 149—150°,  $[\alpha]_D^{25} -50.75^\circ$  (in alcohol). When hydrolysed by means of alcoholic potassium hydroxide, it yields, not artemisin, but a moderately stable, acid compound, m. p. above 200°, which is apparently identical with that obtained by hydrolysis of the acetyl derivative of artemisin (*loc. cit.*).  
T. H. P.

**The Formation of Free Radicals by Reduction with Vanadous Chloride.** J. B. CONANT and A. W. SLOAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2466—2472).—The addition of vanadous chloride solution to a solution of triphenylpyrylium chloride, or of its ferric chloride double salt, in the absence of air, causes the formation of a red precipitate, which is thought to be a *free radical*. With chloroform or benzene, it gives a red solution, the colour of which disappears when it is shaken with air. The substance is reoxidised to the pyrylium salt when it is treated in aqueous suspension with a solution of a ferric salt; if this process is conducted in the absence of oxygen, using freshly prepared material, a maximum of 1 mol. of ferric salt is required, but much less than this is needed if the compound, which is evidently unstable, has been kept for a few hours, even in an atmosphere of carbon dioxide.

The action of an excess of vanadous chloride on 9-phenylxanthylum chloride, in hydrochloric acid solution, in the absence of air, gives Gomberg and Cone's free radical, phenylxanthyl, which is identified by conversion into its peroxide.

Triphenylcarbinol, in concentrated hydrochloric acid or concentrated sulphuric acid solution, is reduced by means of vanadous chloride in an atmosphere of carbon dioxide to triphenylmethyl, which is likewise identified by means of the peroxide.

The action of vanadous chloride on a very dilute solution of xanthylum chloride in concentrated hydrochloric acid gives a pink solid, which may be kept for a few hours in air at the ordinary

temperature, but gradually changes to the colourless dixanthyl. Attempts to dry it in an atmosphere of nitrogen without loss of colour have been unsuccessful. When the bright pink solid is washed with water, drained, and dissolved in chloroform in an atmosphere of nitrogen, the solution is momentarily red; this colour disappears in the course of a few seconds. It is evident, from the last experiment, that polymerisation, and not oxidation, causes the change to dixanthyl. There is therefore strong evidence that the pink solid is the free radical, *xanthyl*.

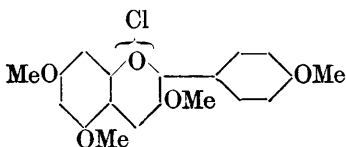
The addition of vanadous chloride to an aqueous solution of benzylpyridinium chloride does not cause the formation of a precipitate, although the first portions of vanadous chloride undergo a change of colour; after making the solution alkaline, however, *N:N'*-dibenzyltetrahydrodipyridyl may be extracted from the solution by means of ether.

W. S. N.

**Chloro- and Amino-anthracoumarins.** V. I. MINAEV (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 680—684).—A short abstract of this work has already appeared (*A.*, 1922, i, 162); the preparation of the following additional compounds is now described: *8-amino-anthracoumarin*, from *m*-aminocinnamic and *m*-hydroxybenzoic acid, silvery crystals resembling  $\beta$ -naphthol, softens at 285°, carbonises at about 300°; *8-chloroanthracoumarin*, obtained in a similar way from *m*-chlorocinnamic acid, forms brown crystals, m. p. 241°; gives on sublimation golden-yellow needles, m. p. 329°; *9-aminoanthracoumarin*, obtained by condensing *p*-aminocinnamic acid and *m*-hydroxybenzoic acid, and the corresponding *chloro*-compound, were also prepared, but their properties are not recorded.

G. A. R. K.

**A Synthesis of Pyrylium Salts of Anthocyanidin Type.**  
**III. A New Synthesis of Pelargonidin Chloride.** D. D. PRATT and R. ROBINSON (*J. Chem. Soc.*, 1924, **125**, 188—199).—Phloroglucinol dimethyl ether on treatment with formanilide and phosphoryl chloride, followed by subsequent decomposition, yields 2-hydroxy-4:6-dimethoxybenzaldehyde and a smaller relative amount of 4-hydroxy-2:6-dimethoxybenzaldehyde. When hydrogen chloride is passed into a cold solution of the 2-hydroxy-compound in the presence of  $\omega$ -4-dimethoxyacetophenone, a good yield of tetramethylpelargonidin chloride (annexed formula) is obtained.



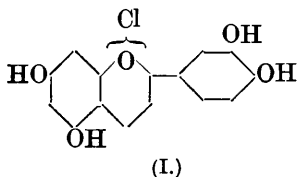
On demethylation, pelargonidin chloride is produced. 4-Hydroxy-2:6-dimethoxybenzaldehyde on similar treatment gives a trimethylpelargonidin chloride. It is suggested that the blue coloration characteristic of pelargonidin and other anthocyanidins is dependent

on the presence of at least four hydroxyl groups, as well as on their positions. 3:7-Dihydroxy-2-phenylbenzopyrylium chloride crystallises in orange-brown prisms, decomposing at 184°. 3:7:4'-Trihydroxy-2-phenylbenzopyrylium chloride,  $C_{15}H_{11}O_4Cl \cdot H_2O$ , crystallises

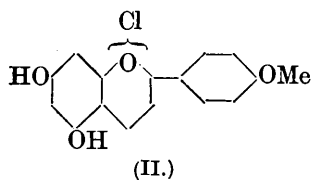
in needles, and decomposes at  $262^{\circ}$ . 4-Hydroxy-2:6-dimethoxybenzaldehyde crystallises in colourless prisms, m. p.  $190^{\circ}$ . Trimethylgalangidin ferrichloride (3:5:7-trimethoxy-2-phenylbenzopyrylium ferrichloride) forms yellowish-brown prisms, m. p.  $174^{\circ}$ . The trimethylgalangidin chloride crystallises in orange-red needles. F. G. P.

#### A Synthesis of Pyrylium Salts of Anthocyanidin Type. IV. Flavylum Salts related to Chrysin, Apigenin, and Luteolin.

D. D. PRATT, R. ROBINSON, and P. N. WILLIAMS (*J. Chem. Soc.*, 1924, 125, 199—207; cf. previous abstract).—A series of compounds related to the flavones has been obtained and a system of nomenclature based on names suggesting their relationship to particular flavones and having the termination *-idin* suggested. Thus (I) is luteolidin chloride. The dimethyl ether of chrysinidin chloride is obtained by the action of hydrogen chloride on acetophenone in the presence of 2-hydroxy-4:6-dimethoxybenzaldehyde, and has been isolated as a ferrichloride. With

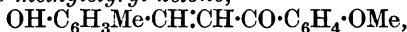


phloroglucinol, *p*-anisyl  $\beta$ -hydroxyvinyl ketone reacts in the presence of hydrogen chloride to give acacetidin chloride (II). Trimethyl-



apigenidin ferrichloride has been prepared from 2-hydroxy-4:6-dimethoxybenzaldehyde and acetyl-anisole. Dimethylchrysinidin ferrichloride,  $C_{17}H_{15}O_3Cl_4Fe$ , crystallises in reddish-brown prisms, m. p.  $178^{\circ}$ . *p*-Anisyl  $\beta$ -hydroxyvinyl ketone,  $OMe \cdot C_6H_4 \cdot CO \cdot CH:CH \cdot OH$ , can be isolated as a copper salt, green prisms, m. p.  $206-207^{\circ}$ . 7-Hydroxy-4'-methoxy-2-phenylbenzopyrylium chloride,  $C_{16}H_{13}O_3Cl \cdot 2H_2O$ , brownish-orange needles, decomposes at  $182-183^{\circ}$ ; its picrate melts at  $219-221^{\circ}$ . Acacetidin chloride forms brown prisms, m. p.  $>360^{\circ}$ ; trimethylapigenidin ferrichloride, orange needles; 2-hydroxy-4:6-dimethoxystyryl 3:4-dimethoxyphenyl ketone, yellow prisms, m. p.  $178-179^{\circ}$ ; tetramethyl-luteolidin ferrichloride, salmon-red needles, m. p.  $206-207^{\circ}$ . F. G. P.

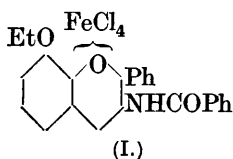
**Some Derivatives of Benzopyrylium.** R. ROBINSON and (in part) H. G. CRABTREE, C. R. DAS, W. LAWSON, R. W. LUNT, B. H. ROBERTS, and P. N. WILLIAMS (*J. Chem. Soc.*, 1924, 125, 207—214).—The oxonium salts described have been prepared by the method of synthesis, which depends on the condensation of a derivative of salicylaldehyde and a substance containing the group  $-CO \cdot CH_2-$ , under the influence of hydrogen chloride. 4-Methoxyphenyl 2-hydroxy-5-methylstyryl ketone,



forms yellow plates, m. p.  $151-152^{\circ}$ ; 4'-methoxy-2-phenyl-6-methyl-

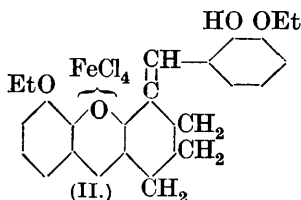
*benzopyrylium ferrichloride*,  $C_{17}H_{15}O_2Cl_4Fe$ , obtained from the ketone, crystallises in crimson needles, m. p. 165—166°. *Phenyl 2-hydroxy-3-methoxystyryl ketone*,  $MeO \cdot C_6H_3(OH) \cdot CH:CH \cdot C(=O)Ph$ , crystallises in yellow prisms, m. p. 112°. *8-Methoxy-2-phenylbenzopyrylium ferrichloride*, from the ketone, crystallises in reddish-brown needles, m. p. 157°. *8:4'-Dimethoxy-2-phenylbenzopyrylium ferrichloride*, obtained from *o*-vanillin and *p*-methoxyacetophenone, crystallises in brown needles, m. p. 180°. *2:3:4-Trimethoxyphenyl 2-hydroxy-3-methoxystyryl ketone*, obtained from *o*-vanillin and gallacetophenone trimethyl ether, forms bright yellow needles, m. p. 145°. *2'-Hydroxy-8:3':4'-trimethoxy-2-phenylbenzopyrylium ferrichloride* forms dark red needles, m. p. 194°; the *picrate*, red prisms, m. p. 164°; the *periodide*, purple needles, m. p. 133°; the *mercurichloride*, yellow needles, m. p. 143°. *2-Phenyl-3:4'-dimethylbenzopyrylium ferrichloride*, from salicylaldehyde and *p*-tolyl ethyl ketone, forms yellow needles, m. p. 165—166°. *8-Methoxy-2-phenyl-3:4'-dimethylbenzopyrylium ferrichloride* from *o*-vanillin and *p*-tolyl ethyl ketone, forms orange-brown needles, m. p. 172°; *8-methoxy-2- $\alpha$ -naphthylbenzopyrylium ferrichloride*, from *o*-vanillin and  $\alpha$ -naphthyl methyl ketone, brownish-red needles, m. p. 230°; *2'-hydroxy-3'-methoxy-2-benzylidene-1-hydrindone*, from *o*-vanillin and  $\alpha$ -hydrindone, yellow needles, m. p. 198°; *8-methoxy-2:3-indeno-(1:2)-benzopyrylium ferrichloride*, red needles, m. p. 187—188°. F. G. P.

**Some Benzopyrylium Salts.** L. R. RIDGWAY and R. ROBINSON (*J. Chem. Soc.*, 1924, 125, 214—222).—Attempts to prepare a benzopyrylium salt in which a halogen atom occurs in position 3 have not so far succeeded. The attachment of nitrogen to the pyrylium nucleus has been successful, and 3-benzoylamino-8-ethoxy-2-phenylbenzopyrylium ferrichloride (I) has been prepared from 2-hydroxy-3-ethoxybenzaldehyde and  $\omega$ -benzoylaminoacetophenone. The removal of the benzoyl group from this salt was not possible. An account is included of some compounds which have been prepared in order to throw light on the property of fluorescence in relation to structure in this

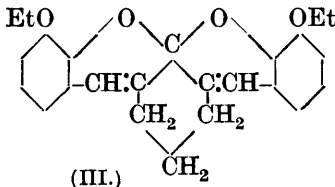


group. *8-Ethoxy-2-phenylbenzopyrylium ferrichloride*,  $C_{17}H_{15}O_2Cl_4Fe$ , forms brown plates, m. p. 139—140°; *3-benzoylamino-8-ethoxy-2-phenylbenzopyrylium ferrichloride* (I), orange-red needles, m. p. 198°; *3-benzoylamino-4'-methoxy-8-ethoxy-2-phenylbenzopyrylium ferrichloride*,  $C_{25}H_{22}O_4NCl_4Fe$ , reddish-brown plates, m. p. 201°. *5-Ethoxy-4-(2-hydroxy-3-ethoxybenzylidene)-1:2:3:4-tetrahydroxanthylum ferrichloride* (II) is obtained from cyclohexanone and 2-hydroxy-3-ethoxybenzaldehyde. It is a chocolate-coloured powder, m. p. 197°.

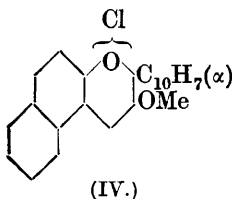
The chloride obtained from this when boiled with water containing a



little hydrochloric acid is converted into *diethoxytrimethylenedibenzo-spiropyran* (III), colourless needles, m. p. 155°. *α-Naphthylmethoxymethyl ketone*,  $C_{10}H_7 \cdot CO \cdot CH_2 \cdot OMe$ , is obtained from methoxyacetonitrile and magnesium *α*-naphthyl bromide. It is a pale yellow, viscid oil, b. p. 184—186°/13 mm. It condenses with 2-hydroxy-5-methyl-



benzaldehyde to 3-methoxy-2-*α*-naphthyl-6-methylbenzopyrylium chloride,  $C_{21}H_{17}O_2Cl \cdot 3H_2O$ , orange needles, m. p. 84°. The ferrichloride crystallises in plates, m. p. 184°. With 2-hydroxy-3-ethoxybenzaldehyde the above ketone yields 3-methoxy-8-ethoxy-2-*α*-naphthylbenzopyrylium chloride,  $C_{22}H_{18}O_3Cl \cdot 2H_2O$ , orange-red plates, m. p. 115—116°, whilst with *β*-hydroxy-*α*-naphthaldehyde, 3-methoxy-2-*α*-naphthyl-naphtha-(2:1)-pyrylium chloride (IV) is obtained in red, microscopic plates, m. p. 94°. The ferrichloride forms bright red plates, m. p. 183°. 6:4'-Dimethoxy-2-phenylbenzopyrylium chloride forms orange-red plates, m. p. 135°; the ferrichloride crystallises in brownish-red plates, m. p. 192—193°. 8-Methoxy-*β*-naphthacoumarono-(*β*:*α*-2:3)-benzopyrylium chloride (V) is prepared from *o*-vanillin and *β*-naphthacoumaranone. It crystallises in green prisms, m. p. 236—240°. When warmed with ethyl alcohol and a trace of sodium acetate, it is decolorised and the colourless



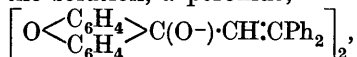
ethyl ether of the pyranol is obtained in the form of needles, m. p. 165°. F. G. P.

**"Tervalent" Carbon. I. The Tetra-arylallyl Radicals and their Derivatives.** K. ZIEGLER [with G. BREMER, F. THIEL, and F. THIELMANN] (*Annalen*, 1923, **434**, 34—78; cf. A., 1922, i, 1047).—This investigation was undertaken to determine the factors responsible for the dissociation of poly-substituted ethane derivatives. For this purpose, compounds of the type of octaphenyldiallyl were studied. Assuming that the theoretical considerations developed by Thiele and Werner are correct, the unsaturated *ββ*-diphenylvinyl group would possess a markedly higher degree of "valency requirement" than the relatively saturated phenyl residue. Comparison of the dissociation capacity of the diallyl derivatives with that of the hexaphenylethanes provides a test for the accuracy of the theoretical considerations advanced by various authors. The first results of the work are given in an earlier paper (*loc. cit.*). 9-*ββ*-Diphenylvinylxanthenol,  $O < C_6H_4 > C < \begin{smallmatrix} OH \\ CH:CPH_2 \end{smallmatrix}$ , has now been obtained in needles which on heating lose water and pass into the allene derivative. Characteristic salts are obtained, particularly

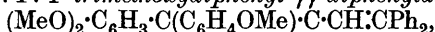
the *perchlorate*, as well as acid halogenides such as the *chloride-hydrochloride*,  $\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{C}(\text{Cl}, \text{HCl}) \cdot \text{CH} \cdot \text{CPh}_2$ , red needles, m. p. 156—157°, and the *bromide hydrobromide*, m. p. 130—131°; perhalogenides, namely, the *chloride tetrabromide* and *bromide tetrabromide*, reddish-brown powders, decomp. 123—124°, and 128—129°, respectively. Double salts of the xanthyl chloride are obtained by addition of heavy metal salts to solutions of the chloride hydrochloride in glacial acetic acid. The *zinc chloride* salt is a red, crystalline solid, decomposing at 165—166°. Hydrolysis of the salts regenerates the xanthenol, whilst tertiary amines such as pyridine and dimethylaniline convert them into the allene derivatives. Methyl and ethyl alcohols convert the hydrohalogenides into 9-methoxy- and 9-ethoxy-9- $\beta\beta$ -diphenylvinylxanthen, crystallising in needles, m. p. 133—134° and 136—137°, respectively. These ethers are readily decomposed by acids into alcohol and the coloured salts. The salts, particularly the chloride hydrochloride, dissolve in saturated alcoholic hydrogen chloride unaltered, and on reduction by zinc the parent substance, 9- $\beta\beta$ -diphenylvinylxanthen, has been obtained in large, colourless crystals, m. p. 164—165°. This has also been obtained from 9-xanthylacetic acid by the Grignard reaction. Aryl and alkyl derivatives of 9- $\beta\beta$ -diphenylvinylxanthen are obtained by the action of the Grignard reagent on the xanthyl salts, particularly on the perchlorate. The xanthen and its alkyl and aryl derivatives are easily reduced by hydriodic acid, the  $\beta\beta$ -diphenylvinyl group probably being eliminated as  $\alpha\alpha$ -diphenylethane. 9-Ethyl-9- $\beta\beta$ -diphenylvinylxanthen crystallises in colourless crusts, m. p. 129—130°. These xanthenes, when acted on by bromine, yield perbromides such as  $\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{C}(\text{Br} \cdot \text{Br}_2)\text{H}$ , and brominated compounds of the type of  $\alpha\beta\beta$ -tribromo- $\alpha\alpha$ -diphenylethane,  $\text{Ph}_2\text{CBr} \cdot \text{CHBr}_2$ , m. p. 88—89°. Di-*p*-anisyl ketone and 2:4:4'-trimethoxybenzophenone, on treatment with the magnesium compound of  $\beta\beta$ -diphenylvinyl bromide, yield alcohols,  $(\text{MeO} \cdot \text{C}_6\text{H}_4)_2\text{CR} \cdot \text{CH} \cdot \text{CPh}_2$  and  $(\text{MeO})_2\text{C}_6\text{H}_3(\text{MeO} \cdot \text{C}_6\text{H}_4) \cdot \text{CR} \cdot \text{CH} \cdot \text{CPh}_2$ , from which crystalline perchlorates may be prepared. The trimethoxy-compound forms fine red crystals yielding violet-red solutions. Pyridine converts it into 2:4:4'-trimethoxydiphenyl- $\gamma\gamma$ -diphenylallene,  $(\text{MeO})_2\text{C}_6\text{H}_3 \cdot \text{C}(\text{C}_6\text{H}_4\text{OMe}) \cdot \text{C} \cdot \text{CPh}_2$ , colourless crystals, m. p. 134—135°. Tetraphenylpropene derivatives have been prepared,  $\alpha\alpha\gamma\gamma$ -tetraphenylallyl ethyl ether,  $\text{Ph}_2\text{C}(\text{OEt}) \cdot \text{CH} \cdot \text{CPh}_2$ , resulting from the action of alcoholic sulphuric acid on the corresponding alcohol. It forms colourless crystals, m. p. 106—107°. Tetraphenylallyl perchlorate, obtained from tetraphenylallyl alcohol, is an unstable, chocolate-brown powder, decomposing at 63—64°. On keeping, it is converted into the colourless 1:1:3-triphenylindene. Results show that the coloured compounds of the substituted tetra-allylallenes are true tetra-aryllallyl salts, that tetra-aryllallyl alcohols are pseudo-bases; the chlorides were not isolated, losing hydrogen chloride and giving tetra-allylallenes; these allenes readily add acid so as to form salts. Magnesium aryl



haloids convert the xanthen perchlorate into the free *di*-9- $\beta\beta$ -*diphenylvinylxanthyl*,  $O\langle\text{C}_6\text{H}_4\rangle\text{C}\cdot\text{CH}\cdot\text{CPh}_2$ , a colourless, crystalline powder, m. p. 144—145°, sparingly soluble in most reagents. This dissolves in benzene with a yellow colour, the solution becoming brown on warming, turning yellow again on cooling. Air completely decolorises the solution, a peroxide,



being obtained. Bromine converts the coloured solution into 9- $\beta\beta$ -*diphenylvinylxanthyl* bromide tetrabromide. Hydrazobenzene reduces it to 9- $\beta\beta$ -*diphenylvinylxanthen* (cf. triphenylmethyl). Sodium and potassium give coloured metal derivatives, the potassium derivative crystallising in the form of a copper-red sludge. Dry air decolorises the solutions of the alkali metal derivatives, water also decomposes them with production of the xanthen, whilst ethyl bromide converts them into the ethylxanthen. Tetraphenylhydrazine converts the free radical into 9- $\beta\beta$ -*diphenylvinylxanthyl**diphenylamine*,  $O\langle\text{C}_6\text{H}_4\rangle\text{C}(\text{NPh}_2)\cdot\text{CH}\cdot\text{CPh}_2$ , crystallising in colourless plates, m. p. 194—196° (cf. triphenylmethyl). These analogies with hexaphenylethane show that the xanthyl compound in solution exhibits radical dissociation. Molecular-weight determinations in naphthalene show that the xanthyl is decomposed to the extent of about 60% into 2 mols. of radical-like form. The free tetra-arylallyl radicals are also obtained by the decomposition of the corresponding perchlorates with the Grignard reagent. *Dianisyl**diphenylallyl*,  $(\text{MeO}\cdot\text{C}_6\text{H}_4)_2\cdot\text{C}\cdot\text{CH}\cdot\text{CPh}_2$ , crystallises in dark green plates, 2 : 4 : 4'-*trimethoxydiphenyl- $\gamma\gamma$ -diphenylallyl*,



is similar, but the colour is deeper.  $\alpha\alpha\gamma\gamma$ -*Tetraphenylallyl*, the parent substance, is a green, crystalline powder, molecular-weight determinations in benzene showing a degree of dissociation of 80%. These three compounds are exceedingly stable. The corresponding peroxides are very unstable. The sodium compounds of the allyl radicals are readily converted into the corresponding propenes. In the triarylmethyl series, the union of the two benzene nuclei through oxygen opposes the association of the radicals, for 9-phenylxanthyl in naphthalene is present to the extent of about 50—70% in the unimolecular form and about 30—50% in the bimolecular form, whilst hexaphenylethane under like conditions is only dissociated to the extent of 15—25%. Tetraphenylallyl, on the other hand, in benzene solution at 4°, is present in the bimolecular form to the extent of at most 20%, whilst 9- $\beta\beta$ -*diphenylvinylxanthyl* in naphthalene at 80° is present perhaps to the extent of 40%; at 4°, therefore, it is still more strongly associated. If, according to Thiele and Werner, the high valency requirement of a residue is explained by its unsaturated character, based on the principle of a distribution of affinity, the existence of tetra-arylallyl radicals is a weighty argument in favour of this principle.  $\alpha\alpha$ -*Diphenylethylene* is essentially more unsaturated than benzene, so that it must be

assumed that the  $\beta\beta$ -diphenylvinyl residue requires more valency than the phenyl residue, and in agreement with this it is found that on replacing two phenyl residues in hexaphenylethane by two such residues the tendency to dissociate is very much increased.

F. G. P.

**Atropine Phosphates.** L. DEBUCQUET (*J. Pharm. Chim.*, 1924, 29, 15—22).—The salt  $C_{17}H_{23}O_3N, H_3PO_4$  is obtained in 92% yield when an alcoholic solution containing equimolecular quantities of atropine and phosphoric acid is heated for half an hour in a water-bath at 90—95°, and then left to crystallise. Small, lustrous crystals (m. p. 196°) are obtained which are soluble in rather less than five times their weight of water (giving a solution acid to litmus), sparingly soluble in cold alcohol and almost insoluble in ether and chloroform. Attempts to prepare the salt,  $(C_{17}H_{23}O_3N)_2, H_3PO_4$ , gave only the monobasic phosphate (in diminished yield) and unchanged atropine.

W. T. K. B.

**Stereoisomerism and Local Anæsthetic Action in the  $\beta$ -Eucaine Group. Resolution of  $\beta$ - and *iso*- $\beta$ -Eucaine.** H. KING (*J. Chem. Soc.*, 1924, 125, 41—57).—On benzylation,  $\alpha$ - and  $\beta$ -vinylldiacetonalkamines yield *O*-benzoyl derivatives and for convenience the name of *iso*- $\beta$ -eucaine is proposed for the derivative of the  $\beta$ -compound.  $\beta$ -Eucaine has been resolved by means of camphorsulphonic acid. With *d*-camphor-10-sulphonic acid, the partial racemate, *dl*- $\beta$ -eucaine *d*-camphor-10-sulphonate, was obtained, working between the ordinary temperature and zero, and it has been found possible to resolve this salt by means of the more soluble active forms which are unstable in respect of the partial racemate, a total yield of 54% of *l*- $\beta$ -eucaine *d*-camphor-sulphonate being obtained. Owing to the formation of a continuous series of mixed crystals between the two active salts, the more soluble *d*- $\beta$ -eucaine *d*-camphorsulphonate could not be isolated, but the isolation of *d*- $\beta$ -eucaine *l*-camphorsulphonate was finally accomplished by the use of *l*-camphor-10-sulphonic acid. *iso*- $\beta$ -Eucaine was resolved by the use of *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonic acid. In this case the salts, being of approximately equal solubility, separate alternately from the solution on fractional crystallisation. On the rabbit's cornea *r*- $\beta$ -eucaine, *r*-*iso*- $\beta$ -eucaine and their optically active components have approximately equal local anæsthetic action; on the sciatic nerve of the frog, however,  $\beta$ -eucaine is a more powerful anæsthetic than *iso*- $\beta$ -eucaine. *dl*- $\beta$ -Eucaine *d*-camphorate forms plates, m. p. 211—212°; the *l*-malate has m. p. 212—213° and  $[\alpha]_D -2.6^\circ$ ; the *d*-tartrate crystallises in tablets which have m. p. 257° and  $[\alpha]_D +10.1^\circ$ . The *d*-camphor-10-sulphonate (mono-alcoholate) forms tablets, m. p. 228—229°,  $[\alpha]_D +10.3^\circ$  (anhydrous salt). *l*- $\beta$ -Eucaine *d*-camphorsulphonate forms leaflets, m. p. 248—249°,  $[\alpha]_D 4.78^\circ$  and  $4.83^\circ$ , whence the *l*- $\beta$ -eucainium-ion has  $[\alpha]_D -11^\circ$ . *d*- $\beta$ -Eucaine *l*-camphorsulphonate has  $[\alpha]_D -5.09^\circ$ , whence the *d*- $\beta$ -eucainium-ion has  $[\alpha]_D +10.6^\circ$ . *l*- $\beta$ -Eucaine forms prisms, m. p. 57—58°. The *hydrochloride* forms

plates (m. p. 244—245°,  $[\alpha]_D -11.3^\circ$ ), the *picrate* (small prisms) having m. p. 198—199°. *d*- $\beta$ -*Eucaïne* has m. p. 57—58°, the *hydrochloride* having  $[\alpha]_D +11.5^\circ$ . *r*- $\beta$ -*Eucaïne hydrochloride* forms tablets, m. p. 277—279°; the free base has m. p. 70—71°; the *picrate* (plates), has m. p. 230.5—231.5°. *d*- $\alpha$ -*Vinyldiacetonalkamine hydrochloride* (tablets, m. p. above 300°), has  $[\alpha]_D +13.3^\circ$ ; the *l*-*hydrochloride* has m. p. above 300° and  $[\alpha]_{5461} -18.5^\circ$ . The *l*-base forms prisms, m. p. 79—81° (*picrate*, needles, m. p. 242—244°). *N*-*Benzoyl*- $\beta$ -*vinyldiacetonalkamine*, obtained by benzoylation of the  $\beta$ -alkamine base, forms leaflets, m. p. 121—122°; the *O*-*benzoyl* derivative, obtained by benzoylating the *hydrochloride*, forms needles or plates, m. p. 269—271°. Its *picrate* has m. p. 256—258°. *l*-*iso*- $\beta$ -*Eucaïne d*- $\alpha$ -*bromocamphor*- $\pi$ -*sulphonate* forms needles, m. p. 236—238°, and has  $[\alpha]_{5461} +52.1^\circ$ , and  $[M]_{5461} +290.9^\circ$ , whence  $[M]_{5461}$  for the *l*-*iso*- $\beta$ -*eucainium-ion* is  $-55.6^\circ$ . *d*-*iso*- $\beta$ -*Eucaïne d*- $\alpha$ -*bromocamphor*- $\pi$ -*sulphonate* forms needles containing 0.5—1 mol.  $H_2O$ , the anhydrous salt having  $[\alpha]_{5461} +70^\circ$ ,  $[M]_{5461} +390^\circ$ , whence the *d*-*iso*- $\beta$ -*eucainium-ion* has  $[\alpha]_{5461} +17.8^\circ$ . *d*-*iso*- $\beta$ -*Eucaïne hydrochloride* forms needles, m. p. 271—273°,  $[\alpha]_{5461} +14.9^\circ$ . The *l*-*hydrochloride* has m. p. 271—273°, and  $[\alpha]_{5461} -14.25^\circ$ . The *l*-*picrate* forms needles, m. p. 280°. *d*- $\beta$ -*Vinyldiacetonalkamine hydrochloride*, tablets, has m. p. 217—219°,  $[\alpha]_{5461} +22.85^\circ$ . The base has m. p. 121—123°; the *picrate* (needles) has m. p. 181—182°. *ON*-*Dibenzoyl*- $\alpha$ -*vinyldiacetonalkamine*, obtained by benzoylation of  $\beta$ -*eucaine* base, crystallises in plates, m. p. 142—143°. The similar *dibenzoyl* derivative from the *iso*- $\beta$ -*eucaine* base forms prisms, m. p. 114—115°. F. G. P.

**Complex Thiocyanates of Tervalent Metals. III.** G. SCAGLIARINI and G. TARTARINI (*Gazzetta*, 1923, 53, 876—878).—Unlike vanadium (A., 1923, i, 547, 1225), molybdenum forms complex thiocyanates which are highly stable and resemble, indeed, those of chromium.

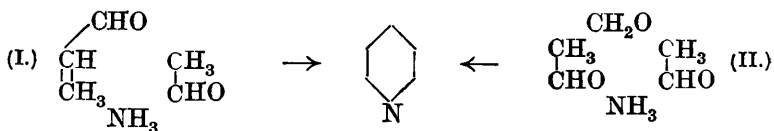
*Piperidine vanadihexathiocyanate*,  $(C_5H_{11}N \cdot H)_3[V(SCN)_6]$ , forms deep red acicular crystals; *basic pyridine vanaditetra-thiocyanate*,  $(C_5H_5N \cdot H)_3[V(SCN)_4(OH)_2]$ , small, brick-red crystals; *hexamethylene-tetramine molybdihexathiocyanate*,  $(C_6H_{12}N_4 \cdot H)_3[Mo(SCN)_6]$ , straw-yellow crystals; *basic pyridine molybdipentathiocyanate*,  $(C_5H_5N \cdot H)_3[Mo(SCN)_5OH]$ , orange-yellow crystals; and *basic piperidine molybdipentathiocyanate*,  $(C_5H_{11}N \cdot H)_3[Mo(SCN)_5OH]$ , brick-red crystals.

T. H. P.

**Galegine.** BARGER and WHITE.—(See i, 272.)

**The Synthesis of Pyridine from Aldehydes and Ammonia.** A. E. TSCHITSCHIBABIN and (MLLE.) M. P. OPARINA (*J. Russ. Phys. Chem. Soc.*, 1924, 54, 601—606; cf. A., 1923, i, 1121 *et seq.*).—Pyridine can theoretically be formed by the interaction of ammonia either with one molecule of acetaldehyde and one of acetaldehyde

(scheme I) or with two molecules of acetaldehyde and one of formaldehyde (scheme II), thus :



Either scheme would account for the formation of small quantities of pyridine in the experiments of Stöhr (A., 1891, 579; 1892, 628), because it is well known that acraldehyde is formed from formaldehyde and acetaldehyde and that the process is reversible.

It is now shown that mixtures of acraldehyde and acetaldehyde or of acetaldehyde and ethylal can be made to react with ammonia under the influence of alumina (*loc. cit.*), yielding pyridine as the main product. In the former case, some  $\beta$ -picoline and a small quantity of  $\alpha$ -picoline were also obtained, whilst in the second case  $\alpha$ -,  $\beta$ -, and  $\gamma$ -picoline and 3 : 5-dimethylpyridine were isolated in small quantities. The formation of  $\beta$ -picoline from ethylal, acetaldehyde, and ammonia is doubtless due to the intermediate formation of acraldehyde, which then reacts with ammonia, whilst pyridine can be produced according to either scheme (I) or (II).

G. A. R. K.

**4-Methyl-2-ethylpyridine.** A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 607—610).—Pure  $\gamma$ -picoline, regenerated from its picrate, was heated with ethyl iodide in sealed tubes at 310—325° and the new base isolated in the form of its *picrate*, short yellow prisms, m. p. 120—121°; the *base*, regenerated from this *picrate*, boiled at 172° and was characterised by the formation of the *chloroplatinate*, short, sparkling, orange prisms, m. p. 176° (decomp.), and the *chloroaurate*, yellow prisms, m. p. 80°. The synthesis of 4-methyl-2-ethylpyridine has since been described by Eckert and Loria (A., 1918, i, 79), but the properties of the derivatives prepared by them differ somewhat from those given above.

G. A. R. K.

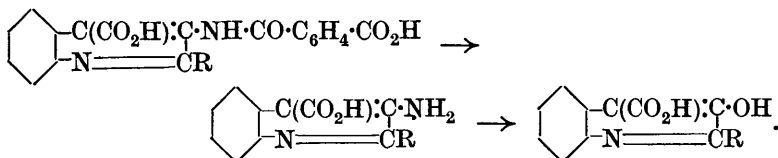
**The Condensation of Acetylene with Ammonia in the Presence of Alumina.** A. E. TSCHITSCHIBABIN and P. A. MOSCHKIN (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 611—624).—A preliminary account of this work has already been published (A., 1915, i, 638); a detailed description is now given of the method of synthesis and of the separation of the pyridine bases formed by the fractional precipitation of their picrates. Pyrrole bases were found to be present; of the crude condensation product, some 30% consisted of picolines, which were isolated in the form of their picrates and, by crystallising the latter from acetone, were shown to consist of the  $\alpha$ -compound with small quantities of the  $\gamma$ -isomeride. The collidine fraction constituted about 10% of the original mixture. The separation was again effected through the picrates, which were crystallised from ethyl acetate. The presence

of  $\beta$ -collidine (4-methyl-3-ethylpyridine, chloroaurate, m. p. 140—141°, chloroplatinate, m. p. 215° [decomp.], picrate, m. p. 149°), identical with that obtained from cinchonine, and 2-methyl-5-ethylpyridine (picrate, m. p. 164°, chloroaurate, m. p. 88°) was confirmed. In addition, two other *collidines* were isolated, one of b. p. 178—182°/756.7 mm. (*picrate*, orange rods, m. p. 143°; *chloroaurate*, m. p. 119—121°; *chloroplatinate*, m. p. 207° [decomp.]), and another of b. p. 185.5—186.5°/756.7 mm. (*picrate*, short, flattened, orange needles, m. p. 134°; *chloroaurate*, plates, m. p. 116—118°; *chloroplatinate*, orange crystals, m. p. 210° [decomp.]). These *collidines* do not appear to be identical with 4-methyl-2-ethylpyridine (preceding abstract) or with either 2:3:4- or 2:3:6-trimethylpyridine which might possibly have been produced; but it is thought that the compounds may not be pure.

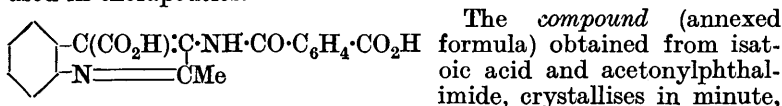
G. A. R. K.

**The Absorption Spectra of some Indole Derivatives.** F. W. WARD (*Biochem. J.*, 1923, **17**, 891—897).—Using the Hilger ultra-violet spectrum photometer, the absorption spectra of the following compounds have been charted: indole, indole-3-carboxylic acid, indole-3-aldehyde, indole-3-ethyl alcohol, indole-3-propionic acid, indole-3-alanine (tryptophane), 2:3-dihydroxyindole, 2-hydroxy-3-indole-aldehyde, isatin, and sodium indigotinsulphonate. The effect of substitution in the indole nucleus is discussed. J. P.

**Certain Quinoline-4-carboxylic Acids.** S. BERLINGOZZI and C. MARZELLA (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 403—406; cf. A., 1923, i, 482, 847).—The action of acetonyl- or phenacylphthalimide on isatoic acid gives rise, in the usual way, to compounds of the type:



When heated beyond their melting points, all these quinoline-4-carboxylic acids lose carbon dioxide, yielding the corresponding 3-amino- and 3-hydroxy-quinolines (*loc. cit.*). Those of the above acids which have a phenyl group in the 2-position may be regarded as derivatives of 2-phenylquinoline-4-carboxylic acid so largely used in therapeutics.



white needles, m. p. 267—268° (decomp.).

3-Amino-2-methylquinoline-4-carboxylic acid,  $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_2$ , obtained, together with phthalic acid, when the preceding compound is boiled with concentrated hydrochloric acid, forms lemon-yellow

prisms, m. p. 232—233° (decomp.), yields solutions which develop fluorescence on addition of a mineral acid, and gives 3-amino-2-methylquinoline when heated at 233—235°. Its *acetyl* derivative forms a white, microcrystalline powder, m. p. 272—273°.

*3-Hydroxy-2-methylquinoline-4-carboxylic acid*, prepared by the action of nitrous acid on the preceding amino-compound, forms minute, pale yellow crystals, m. p. 229—230° (decomp.), and is converted into 3-hydroxy-2-methylquinoline when fused; its alcoholic solutions are fluorescent and are coloured red by ferric chloride.

The compound formed by condensation of isatoic acid with phenacylphthalimide crystallises in lustrous, straw-yellow scales, m. p. 260° (decomp.).

*3-Amino-2-phenylquinoline-4-carboxylic acid* forms pale yellow needles and prismatic plates, m. p. 226° (decomp.), exhibits fluorescence in acid solution, and gives 3-amino-2-phenylquinoline when heated. Its *acetyl* derivative crystallises in lustrous, white scales, m. p. 257—258°.

*3-Hydroxy-2-phenylquinoline-4-carboxylic acid* is obtained as a lemon-yellow, microcrystalline powder, m. p. 206—207°, forms fluorescent alcoholic solutions which are reddened by ferric chloride, and gives 3-hydroxy-2-phenylquinoline when heated. T. H. P.

**The Absorption Spectra of Kynurenic Acid and some Related Quinoline Compounds.** F. W. WARD (*Biochem. J.*, 1923, **17**, 903—906).—The absorption spectra of quinoline, quinaldine, lepidine, quinaldinic acid, 2 : 6-dimethylquinoline, kynurenic acid, and of quinolylacetaldehyde have been mapped. The last-mentioned compound gives an abnormal spectrum and doubts are expressed as to its constitution. The effects of substituents in the quinoline nucleus are discussed. J. P.

**Some Heterocyclic Derivatives of Substituted o-Aminophenols.** A. KORCZYNSKI and ST. OBARSKI (*Bull. Soc. chim.*, 1923, **33**, [iv], 1823—1832).—4-Chloro-2-nitrophenol, on electrolytic reduction, gave 4-chloro-2-aminophenol (m. p. 185°; *diacetyl* derivative, m. p. 201°). The following were prepared in a similar manner: 4-chloro-6-bromo-2-aminophenol (*acetyl* derivative, m. p. 150°), 4-bromo-2-aminophenol, 4 : 6-dibromo-2-aminophenol, and 4 : 6-di-iodo-2-aminophenol.

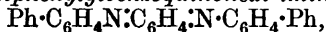
4-Chloro-2-aminophenol, on heating with acetamide (cf. Niementowski, A., 1898, i, 210) gave 4-chloro-1-methylbenzoxazole (m. p. 63°). The following compounds were obtained in a similar manner: 4-bromo-1-methylbenzoxazole (m. p. 70°), 4-chloro-6-bromo-1-methylbenzoxazole (m. p. 117°), and 5 : 6-dibromo-1-methylbenzoxazole (m. p. 127°). All the above oxazoles form yellow needles.

4-Chloro-2-aminophenol was converted (cf. Chetmicki, A., 1887, 477) by thiocarbonyl chloride, in presence of pyridine, into 4-chloro-1-thiolbenzoxazole (m. p. 283°), and the following compounds were prepared in a similar manner: 4-chloro-6-bromo-1-thiolbenzoxazole (m. p. 228°) and 4 : 6-dibromo-1-thiolbenzoxazole (m. p. 235°). All the above thiol derivatives form yellow needles, soluble in alkali.

4-Bromo-2-aminophenol (2 mols.) on boiling in alcoholic solution with chloroanil (1 mol.) affords 8-bromo-4-aminophenoxazone (giving a blue solution in concentrated sulphuric acid), the following compounds being similarly prepared: 8-chloro-2:10-dibromo-4-aminophenoxazone (reddish-violet solution in concentrated sulphuric acid), 2:8:10-tribromo-4-aminophenoxazone, and 2:8:10-tri-iodo-4-aminophenoxazone (blue solution in concentrated sulphuric acid). The above phenoxazones form red needles, not melting at 300°.

Chloroanil converts 4-nitro-2-aminophenol into a substance which forms orange-red needles. E. E. T.

**Diphenyl Phenylenediamines and the Colour of their Oxidation Products.** J. PICCARD and F. ABOUCHY (*Helv. Chim. Acta*, 1924, 7, 75—83).—To compare the auxochromic effect of the diphenyl group,  $\text{Ph}\cdot\text{C}_6\text{H}_4-$ , with those of phenyl and alkyl groups, the following derivatives of *p*-phenylenediamine were prepared, for oxidation into *meri*-quinonoid salts: *s*-di-*p*-diphenyl-*p*-phenylenediamine (I); *s*-diphenyldi-*p*-diphenyl-*p*-phenylenediamine (II), and tetra-*p*-diphenyl-*p*-phenylenediamine (III). To prepare the first compound, (I), *p*-dibromobenzene was condensed with *p*-acetamidodiphenyl, giving *s*-diacetyldi-*p*-diphenyl-*p*-phenylenediamine, colourless crystals, m. p. 245°. By alkaline hydrolysis this gave *s*-di-*p*-diphenyl-*p*-phenylenediamine, long, colourless spangles, m. p. 256°. The second base, (II), was prepared in two ways, (a) by condensing (I) with iodobenzene, and (b) by condensing *p*-iododiphenyl with *s*-diphenyl-*p*-phenylenediamine. *s*-Diphenyldi-*p*-diphenyl-*p*-phenylenediamine forms small crystals, m. p. 211°. The third base, (III), was also obtained in two ways, (a) by condensing (I) with *p*-iododiphenyl, and (b) by condensing *p*-di-iodobenzene with di-*p*-diphenylamine. The product, tetra-*p*-diphenyl-*p*-phenylenediamine, forms small, colourless crystals, m. p. 280°. Of these three bases, only the first can be oxidised to a quinonedi-imine. By oxidation with chromic acid, it gives *di*-*p*-diphenylbenzoquinonedi-imine,



a red, amorphous powder, m. p. 266°. It is less basic than diphenylbenzoquinonedi-imine, and the colours of its salts are deeper; its mono-acid salts are blue, di-acid salts violet, and *meri*-quinonoid salts green. *meri*Di-*p*-diphenylbenzoquinonedi-imonium picrate,  $[\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{NH}:\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{Ph}]^+$

$\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{Ph}][\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}]_2^-$ , forms a bluish-green powder, m. p. 208°. A picrate of the *meri*-quinonoid salt of the second base was also isolated; it forms a yellowish-green powder, m. p. 169°. The colours of the *meri*-quinonoid salts of the three bases in solution are respectively bluish-green, green, and yellowish-green. The colours of the *holo*-quinonoid salts are only developed in concentrated sulphuric acid solution, and are respectively violet, bluish-violet, and blue. It is noted that glacial acetic acid dissolves the quinonedi-imine compounds as bases, the colour of the salts being developed only on addition of water. The leuco-compounds are weaker bases

than the *holo*-quinonoid compounds, but the *meri*-quinonoid compounds are stronger bases than either of these. The auxochromic effect of the diphenyl group in *meri*-quinonoid salts in the phenylenediamine, benzidine, or fuchsine series is less than that of two phenyl groups, but considerably greater than that of one group. The phenylated salts in the benzidine series are deeper in colour than the diphenylated salts in the phenylenediamine series. The difference between the effect of the phenyl and diphenyl groups is more marked in the *holo*-quinonoid than in the *meri*-quinonoid salts. It may be stated as a general rule that the weight of a group has more effect in the active chromophore than in an auxochromic group.

E. H. R.

### The Reaction of Carbon Disulphide on *p*-Phenylenediamine.

C. E. BOLSER and E. B. HARTSHORN (*J. Amer. Chem. Soc.*, 1923, **45**, 2349—2355).—When *p*-phenylenediamine and carbon disulphide are boiled in alcoholic solution (Pawlewski, A., 1899, ii, 405), a small quantity of *pp'*-diaminodiphenylthiocarbamide is produced, together with an insoluble compound, which has been described as *p*-phenylenethiocarbamide,  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} > C:S$  (Lellmann, A., 1883, 185). This compound is now shown to be *di-p-phenylene-dithiocarbamide*,  $C_6H_4 \begin{smallmatrix} \text{NH} \cdot \text{CS} \cdot \text{NH} \\ \text{NH} \cdot \text{CS} \cdot \text{NH} \end{smallmatrix} > C_6H_4$ . In the first place, its formation may be almost entirely suppressed, the yield of diaminodiphenylthiocarbamide being correspondingly increased, by conducting the process in aqueous solution, by keeping the temperature of reaction low, and by decreasing the concentration of carbon disulphide. It is advisable frequently to remove, by filtration, the diaminodiphenylthiocarbamide, which is less soluble in warm alcohol than in hot, and still less soluble in water. This suggests that the simple thiocarbamide is an intermediate stage in the formation of the insoluble compound; that this is actually so is shown by the formation of the latter when carbon disulphide and *pp'*-diaminodiphenylthiocarbamide react in boiling alcoholic solution. The identity of the product with that formed directly from carbon disulphide and *p*-phenylenediamine is shown (although in neither reaction is an absolutely pure substance obtained) by the temperature of decomposition (285°), by the formation of *p*-phenylenediamine by the action of hot, concentrated acids, and by the formation of *p*-phenylenedithiocarbimide by the prolonged action of boiling acetic anhydride. The latter reaction proves that the compound has the above structure, since *p*-phenylenethiocarbamide could not give the dithiocarbimide, but should be converted into *p*-acetamidophenylthiocarbimide, white needles, m. p. 195—196°. The latter is produced by the action of boiling acetic anhydride on *di-p-acetamidophenylthiocarbamide*, a white solid, m. p. 235—237°, which is formed by the action of an excess of carbon disulphide on *p*-aminoacetanilide in boiling alcoholic solution. It was hoped that the hydrolysis of this derivative, which requires the use of hot, concentrated hydrochloric acid,



might give di-*p*-aminophenylthiocarbamide (thus avoiding the concurrent formation of the insoluble compound), but actually phenylenediamine hydrochloride is the sole product.

► The reduction, by means of stannous chloride and a mixture of glacial acetic acid and concentrated hydrochloric acid, of *azobenzene-p*-thiocarbimide,  $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NCS}$ , salmon-coloured needles, m. p. 94–95°, which is obtained by heating thiocarbonyl chloride and *p*-aminoazobenzene in carbon tetrachloride solution at 100°, gives diphenylenedithiocarbamide, but the latter does not appear until the solution is made alkaline. It is probable that the acid solution contains, in equilibrium with the dimeric compound, *p*-aminophenylthiocarbimide (hydrochloride). In fact, when the acetyl derivative (above) of the latter compound is boiled with glacial acetic acid, in the presence of this weaker acid diphenylenedithiocarbamide is precipitated, more of the same material being thrown down on dilution. It is evident that the tendency to the formation, by what is practically a tautomeric change, of this substance is so great, that free *p*-aminophenylthiocarbimide cannot exist, but, on liberation from its salts, immediately undergoes polymerisation.

W. S. N.

**New Methods of Splitting Pyrimidines. III. The Action of Iodine Solution on Pyrimidines.** L. W. BASS and O. BAUDISCH (*J. Amer. Chem. Soc.*, 1924, **46**, 181–183; cf. A., 1922, ii, 328).—Pyrimidines with unsubstituted nitrogen atoms and with a double bond between carbon atoms 4 and 5 absorb iodine from solution in the presence of sodium bicarbonate. On distillation of the reaction mixtures, after removal of excess iodine, carbamide is found in the residues as a scission product. No carbamide can be detected before the distillation. Substitution by an alkyl group in position 5 retards the rapidity of decolorisation of iodine solution. Hydrouracil decolorises iodine solution, but no carbamide is formed when the reaction mixture is distilled. 1:3-Dimethylthymine does not decolorise iodine solution. Thymine itself yields carbamide and acetol; no pyruvic acid is formed. When bromine is substituted for iodine, the pyrimidine ring is not split under the conditions of the experiments. F. A. M.

**New Methods of Splitting Pyrimidines. IV. A Study of the Mechanism of the Decomposition of Thymine.** O. BAUDISCH and L. W. BASS (*J. Amer. Chem. Soc.*, 1924, **46**, 184–189; cf. preceding abstract).—The action of various oxidising agents on thymine has been studied; the primary products of the reactions still contain the carbamide residue. The final products, carbamide, acetol, and pyruvic acid, are formed only when the primary products are heated in aqueous solution with sodium hydrogen carbonate. Acetol is formed as a direct hydrolytic product of thymine, whilst pyruvic acid is formed by the complete hydrolysis of an intermediate oxidation product. A mechanism is suggested to explain the decomposition of thymine under the conditions used.

F. A. M.

**New Methods of Splitting Pyrimidines. V. The Action of Oxygen plus Ferrous Salts on Thymine under the Influence of Light.** L. W. BASS (*J. Amer. Chem. Soc.*, 1924, **46**, 190—192; cf. preceding abstracts).—When in an atmosphere of oxygen aqueous solutions of thymine are illuminated using a quartz mercury arc, the pyrimidine is split to some extent into carbamide and pyruvic acid; no acetol is formed. The reaction is accelerated, but otherwise not affected, by ferrous sulphate or, to a smaller extent, by potassium ferrocyanide. No scission occurs in an atmosphere of nitrogen even in the presence of the above salts. F. A. M.

**Catalysis. III. Reduction of Uracil to Hydouracil.** E. B. BROWN and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1923, **45**, 2702—2708; cf. A., 1921, i, 806; 1922, i, 709).—Further experimental details are given, relating to the reduction of uracil to hydouracil by means of hydrogen, in the presence of colloidal platinum. Colloidal palladium may also be used. Sulphur compounds, even when present only as traces, completely inhibit the reaction, but the chlorides of sodium, potassium, calcium, and magnesium are quite without effect. W. S. N.

**Synthetic Researches on the Constitution of Bile-pigments. II.** H. FISCHER and J. MÜLLER (*Z. physiol. Chem.*, 1924, **132**, 73—103).—If dry ammonia is passed through a cold alcoholic solution of ethyl  $\alpha$ -acetyl- $\beta$ -methylsuccinate, crystals are obtained, m. p. 77° (decomp.), apparently of ethyl  $\beta$ -amino- $\Delta^{\beta}$ -pentene- $\gamma\delta$ -dicarboxylate, which on keeping or on warming in a vacuum at 40—50° completely change into ethyl 2-hydroxy-3:5-dimethylpyrrole-4-carboxylate, m. p. 127°, a compound which is also found in the mother-liquors from the crystals. This pyrrole derivative, when warmed in 50% sulphuric acid, yields  $\alpha$ -methyl-lævulic acid, and when treated with hydrazine hydrate, is converted into the *hydrazide* of 2-hydroxy-3:5-dimethylpyrrole-4-carboxylic acid, sharp-angled leaflets, decomposing at 212°. This compound may be converted by nitrous acid into the *azide* of 3:5-dimethyl-2-hydroxypyrrole-4-carboxylic acid, flat prisms, which decompose explosively at 114°, and this compound, in solution in boiling absolute ethyl alcohol, yields *ethyl 2-hydroxy-3:5-dimethylpyrrole-4-carbamate*, white needles, decomposing at 148°, whilst if methyl alcohol is used, the corresponding *methyl carbamate* is obtained as white, glistening needles, decomposing at 164°. From ethyl acetylsuccinate, the following corresponding series of compounds is obtained: *ethyl  $\beta$ -amino- $\Delta^{\beta}$ -butene- $\gamma\delta$ -dicarboxylate*, m. p. 122—124° (decomp.); *ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate*, m. p. 134°; (*hydrazide*, leaflets, decomposing at 232°; *azide*, needles, which decompose explosively at 135°; *methyl carbamate*, needles, m. p. 175°).

Ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate condenses with aldehydes in alcoholic solution in presence of hydrochloric acid, and the following compounds are described: *ethyl 2-keto-3-benzylidene-5-methyl-2:3-dihydropyrrole-4-carboxylate*, yellow leaflets,



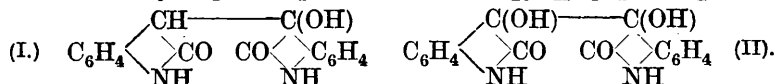
*pyrryl-3-ethanonoxalate*, fine, colourless, felted needles, m. p. 150.5°. The latter is readily decomposed by alkalis to yield 3-acetyl-2:4-dimethylpyrrole-5-carboxylate, and forms a *semicarbazone*, m. p. 201°, and a *ketazine-hydrazide*,  $C_{13}H_{17}O_3N_5$ , needles, m. p. 239° (decomp.). Ethyl 2:4-dimethylpyrryl-3-ethanonoxalate forms a *semicarbazone*, m. p. 198° (decomp.). Ethyl 2:4-dimethylpyrrole-3:5-dicarboxylate, when heated with hydrazine hydrate at 200° in a closed tube, yields 2:4-dimethylpyrrole. If 1'-*p*-toluoyl-4-carbethoxy-3-hydroxy-5-methylpyrrolidyl-3'-carbethoxy-2':5'-dimethylpyrrylmethene is treated with benzene-diazonium chloride, decomposition of that compound takes place simultaneously with coupling to give a mixture of 3-carbethoxy-2:5-dimethyl-1-*p*-toluylpyrrole-4-aldehyde and 2-benzeneazo-4-carbethoxy-3-hydroxy-5-methylpyrrole.

W. O. K.

**Oxidation-Reduction. IV. Electrode Potentials of Indigotinsulphonates.** M. X. SULLIVAN, B. COHEN, and W. M. CLARK (*U.S. Public Health Repts.*, 1923, **38**, 1669—1718).—A survey of the literature shows conflicting statements regarding the behaviour of indigotin and its sulphonates in vitro and in vivo, and a lack of satisfactory theories due to lack of quantitative data for the oxidation-reduction equilibrium. Indigotin-mono-, -di-, -tri-, and -tetra-sulphonates were prepared by Bloxam's method (A., 1906, ii, 819), and the electrode potentials at 30° were determined by elaboration of methods already described (A., 1923, ii, 726, etc.). The experimental results were in accord with the rational equation:  $E_h = E_o - [(RT/nF) \log_e (S_r/S_o)] + (RT/nF) \log_e [K_1(H^+) + (H^+)^2]$ , where  $E_h$  is the observed electrode potential referred to the hydrogen standard,  $S_r$  and  $S_o$  are the concentrations of total reductant and total oxidant,  $(H^+)$  is the hydrogen-ion concentration of the solution, and  $K_1$  the acid dissociation constant of one of the two hydrogen atoms of the hydrogenated leuco-compound (dissociation of the sulphonic acids not being considered). The number,  $n$ , of electrons in the reversible oxidation-reduction is 2. The second acidic hydrogen atom of the leuco-compound has a dissociation constant below  $10^{-12}$ . The values of  $E_o$  and  $K_1$  were as follows: indigotin-monosulphonate  $\rightleftharpoons$  leuco-compound, +0.262,  $1.6 \times 10^{-8}$ ; indigotin-disulphonate  $\rightleftharpoons$  leuco-compound, +0.291,  $4.9 \times 10^{-8}$ ; indigotin-trisulphonate  $\rightleftharpoons$  leuco-compound, +0.332,  $7.7 \times 10^{-8}$ ; indigotin-tetrasulphonate  $\rightleftharpoons$  leuco-compound, +0.365,  $11.2 \times 10^{-8}$ . Indigotin  $\rightleftharpoons$  indigo-white is not adapted to accurate experiments in aqueous solution. Approximate data indicate  $K_1 = 10^{-8}$  and  $E_o$  near that of the monosulphonate. Anomalies with borate buffers are shown, and evidence is given of a "salt effect" with other buffer systems, of the acidic nature of the leuco-compounds, and of the ionisation of only one hydrogen atom at moderate alkalinities. An electro-metric method of analysis of mixtures of the sulphonates is developed. The data cover all conditions for the reversible oxidation-reduction of an indigotinsulphonate and give their properties for use in colorimetric determinations of oxidation-reduction intensities of biological solutions.

CHEMICAL ABSTRACTS.

**Constitution of Isatan and Isatide.** A. WAHL and W. HANSEN (*Compt. rend.*, 1924, **178**, 393—396; cf. following abstract).—Isatan (I),  $C_{16}H_{12}O_3N_2$ , on heating in boiling naphthalene solution, affords indine (cf. Laurent, *Ann. Chim. Phys.*, 1840, [iii], **3**, 469); it results from the condensation of oxindole and isatin in presence of piperidine (cf. Stollé, A., 1914, i, 992), and is the product called isatide by Erdmann (*J. pr. Chem.*, 1840, [i], **24**, 1), who treated isatin with excess of ammonium hydrosulphide. Isatan was obtained by Laurent (*loc. cit.*) by reducing disulphoisatide with ammonium hydrogen sulphite. Isatide,  $C_{16}H_{12}O_4N_2$  (II), which



does not give indine on heating, is the product obtained by Laurent by treating isatin with a slight excess of ammonium hydrosulphide, and by Heller (A., 1904, i, 416) by reducing isatin with zinc and acetic acid. Isatide is formed rapidly when a mixture of dioxindole and isatin is treated, in alcoholic solution, with piperidine.

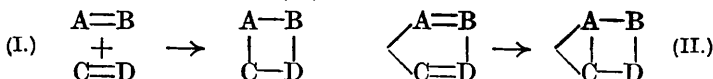
E. E. T.

**Transformation and Constitution of Disulphoisatide.** A. WAHL and W. HANSEN (*Compt. rend.*, 1924, **178**, 214—216).—The formula,  $C_{16}H_{12}O_2N_2S_2$ , given by Laurent (*Ann. Chim. Phys.*, 1840, [iii], **3**, 469) to disulphoisatide has been confirmed. The formation of indine by the action of alkali on disulphoisatide is shown to depend on the nature and concentration of the alkali used, and not to occur if air is excluded. The conversion is best effected by adding aqueous sodium carbonate to an aqueous-alcoholic solution of disulphoisatide. Isatin is produced simultaneously (55% of that obtainable on the basis of the equation:  $2C_{16}H_{12}O_2N_2S_2 + 2H_2O = C_{16}H_{10}O_2N_2 + 4H_2S + 2C_8H_5O_2N$ ). Sulphur is initially

formed, and reduces indine to leucoisindigotin, which is oxidised if air is present. The annexed formula (cf. Kohn and Ostersetzer, A., 1916, i, 607, and Lefèvre, *ibid.*, 430) is proposed for disulphoisatide, a disulphide formula being excluded, since on reduction it gives leucoisindigotin (A., 1923, i, 607).

E. E. T.

**The Additive Formation of Four-membered Rings. III. The Nomenclature of Four-membered Rings and the Formation and Properties of some Derivatives of Methylene-1:2:4-oxadi-imine.** C. K. INGOLD (*J. Chem. Soc.*, 1924, **125**, 87—102).—It has been found that the formation of a four-membered ring, by the additive union of double bonds (I) is of considerable generality, and this confirms the prediction (T., 1922, **121**, 2793) made from the analogy with the tautomeric change or internal addition reaction shown in (II):



A system of nomenclature is proposed for the new heterocyclic ring types that have been already produced. Part of the object of the work is to discover which of these types are the most stable. It has been shown earlier (*loc. cit.*, and T., 1923, 123, 2745) that certain types of azomethines and nitroso-compounds pass into stable cyclic bimerides. It is now shown that an azomethine and a nitroso compound of the particular type combine additively to give a stable 1:2:4-oxadi-imine (annexed formula). *Methylene-p-chloroaniline*,  $\text{CH}_2\text{:N}\cdot\text{C}_6\text{H}_4\text{Cl}$ , forms needles, m. p.  $142^\circ$ , the corresponding *p-bromo-derivative*, needles, having m. p.  $169^\circ$ . *p-Chloronitrosobenzene* has m. p.  $90^\circ$ , the corresponding *bromo-derivative* having m. p.  $94^\circ$ . The following compounds are also described: *2-phenyl-4-p-tolylmethylene-1:2:4-oxadi-imine* (needles, m. p.  $150^\circ$ ); the similar *4-p-chlorophenylmethylene* compound (needles, m. p.  $162^\circ$ ); the *4-p-bromophenyl* compound (needles, m. p.  $171^\circ$ ); *4-p-chlorophenyl-2-p-tolylmethylene-oxadi-imine* (needles, m. p.  $163^\circ$ ); the *4-p-bromophenyl* derivative (m. p.  $158^\circ$ ), the *2:4-dichloro-derivative* (m. p.  $171^\circ$ ), and the *2:4-dibromo-derivative* (m. p.  $175^\circ$ ). *p-Chlorophenylcarbylamine* forms needles (m. p.  $71^\circ$ ), the corresponding *bromocarbylamine* having m. p.  $99^\circ$ . Both have an odour somewhat less powerful than that of phenylcarbylamine itself, but the taste of the vapour is considerably stronger. *2-p-Chlorophenyl-4-p-bromophenylmethylene-1:2:4-oxadi-imine* forms needles, m. p.  $171^\circ$ .

*Phenyl-p-tolylcarbodi-imide*,  $\text{C}_6\text{H}_5\text{Me}\cdot\text{N}\cdot\text{C}\cdot\text{NPh}$  (b. p.  $170/12^\circ$  mm.) (converted by aqueous-alcoholic hydrochloric acid into phenyl-*p-tolyl*carbamide), *phenyl-p-chlorophenylcarbodi-imide* (b. p.  $175/11^\circ$  mm.), *p-bromodiphenylcarbodi-imide* (b. p.  $185/11^\circ$  mm.), *p-chlorophenyl-p-tolylcarbodi-imide* (b. p.  $175^\circ/10$  mm.), *p-bromophenyl-p-tolylcarbodi-imide* (b. p.  $188^\circ/10$  mm.), *pp'-dichlorodiphenylcarbodi-imide* (b. p.  $190^\circ/10$  mm.), *pp'-dibromodiphenylcarbodi-imide* (b. p.  $202^\circ/10$  mm.), and *p-chloro-p'-bromodiphenylcarbodi-imide* (b. p.  $198\text{--}200^\circ/11$  mm.) are, like the phenyl-*p-tolyl* derivative, viscous liquids, their constitutions being proved by conversion into the corresponding carbamides.

*p-Chlorophenyl-p-tolylcarbamide* (needles, m. p.  $297\text{--}299^\circ$  [decomp.]), *p-bromophenyl-p-tolylcarbamide* (needles, m. p.  $316\text{--}318^\circ$  [decomp.]), and *p-chloro-p'-bromodiphenylcarbamide* (needles, m. p. about  $300^\circ$  [decomp.]) were obtained (see *ante*) from the corresponding carbodi-imides.

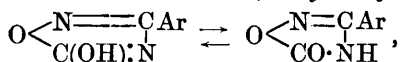
F. G. P.

**The Additive Formation of Four-membered Rings. IV. The Influence of Temperature on the Tendency towards Self-addition of the Nitroso-group.** C. K. INGOLD and H. A. PIGGOTT (*J. Chem. Soc.*, 1924, 125, 168—176).—Owing to the chromophoric character of the nitroso-group, the use of the colorimeter enables the reversible reaction  $2 \text{N}\cdot\text{O} \rightleftharpoons \begin{array}{c} \text{--N--O} \\ | \quad | \\ \text{O--N--} \end{array}$  to be

followed in greater detail than is the case with the reactions previously studied (see preceding abstract). The influence of temperature on the equilibrium is determined for the case of nitroso-

mesitylene in benzene solution. Using these results, the order of the reaction is calculated from certain equations, and shown to be in accordance with the chemical evidence. Nitrosomesitylene, the preparation of which (and of mesidine) from dimethylaniline is described, has m. p. 122—123° (cf. Pechmann and Nold, A., 1898, i, 310). The heat absorbed during the dissociation of 1 g.-mol. of dimeric nitrosomesitylene is calculated to be about 13,700 g.-cal. In 3% solution in benzene, dissociation occurs to the extent of about 18%; in a 2% solution, 21.6%. This corresponds with a molecular weight 245, agreeing fairly well with Bamberger's value 246 obtained (A., 1901, i, 141) cryoscopically in benzene solution. F. G. P.

**Dioximes. XVII.** G. PONZIO and B. ZANARDI-LAMBERTI (*Gazzetta*, 1923, 53, 818—824).—In some of their properties, 5-hydroxy-3-aryl-1 : 2 : 4-oxadiazoles (or hydroxyazoximes),



which are formed by withdrawal of two atoms of hydrogen from the  $\alpha$ -modifications of monoarylglyoximes, differ considerably from the 3 : 5-diaryl-1 : 2 : 4-oxadiazoles (or azoximes), which result on elimination of a molecule of water from a *s*-diarylglyoxime. Thus, the azoximes are either completely destroyed or slowly converted into nitriles by the action of reducing agents, whereas the hydroxyazoximes are very easily reduced to amidines,  $\text{NH}_2 \cdot \text{CR} \cdot \text{NH}$ , by means of hydriodic acid in presence of red phosphorus. Further, the hydroxyazoximes exhibit acid properties, the mean values of the ionisation constant at 25° being  $0.879 \times 10^{-5}$ ,  $0.022 \times 10^{-5}$ , and  $0.140 \times 10^{-5}$  for 5-hydroxy-3-phenyl-, *p*-tolyl-, and benzyl-1 : 2 : 4-oxadiazoles; thus, the *p*-tolyl compound is slightly weaker than carbonic acid, and the other two compounds are stronger.

Benzenylamidine, obtained by reduction of 5-hydroxy-3-phenyl-1 : 2 : 4-oxadiazole, gives a picrate, m. p. 235°; Dieckmann (A., 1892, 705) gave m. p. 228°. According to Pinner ("Die Imidoäther," 167), 2 : 4 : 6-triphenyl-1 : 3 : 5-triazine is formed when benzenylamidine hydrochloride is heated for six hours at 120—140° with benzoyl chloride. This reaction occurs at the ordinary temperature when benzenylamidine carbonate is treated with 20% sodium hydroxide solution and benzoyl chloride.

5-Hydroxy-3-*p*-tolyl-1 : 2 : 4-oxadiazole, prepared from *p*-tolenylamidoxime and ethyl chlorocarbonate (cf. Schubart, A., 1890, 47), is the product of the isomerisation of the oxide of *p*-tolyl cyanide oxime (cf. Avogadro, this vol., i, 294). By hydriodic acid and red phosphorus it is converted into *p*-tolenylamidine, which forms a *picrate*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{C}(\text{NH}) \cdot \text{NH}_2 \cdot \text{C}_5\text{H}_3\text{O} \cdot \text{N}_3$ , crystallising in yellow needles, m. p. 224—225° (decomp.), and a *carbonate*, crystallising in white laminæ, m. p. 127—128° (gas); the corresponding nitrate was described by Pinner (*loc. cit.*, 184). 5-Hydroxy-3-*p*-tolyl-1 : 2 : 4-oxadiazole forms the following derivatives: *sodium* salt, white powder; *silver* salt, white crystals, stable towards light; *methyl* ether, slender, white needles.

5-Hydroxy-3-benzyl-1 : 2 : 4-oxadiazole,  $\text{O} < \begin{array}{c} \text{N} \equiv \text{C} \cdot \text{CH}_2\text{Ph} \\ \text{C}(\text{OH}) \cdot \text{N} \end{array}$ , pre-

pared by the action of sodium hydroxide on the ethyl phenylethenylamidoximecarboxylate obtained by the interaction of ethyl chlorocarbonate and phenylethenylamidoxime,  $\text{CH}_2\text{Ph} \cdot \text{C}(\text{NOH}) \cdot \text{NH}_2$ , crystallises in large, lustrous laminæ, m. p.  $115^\circ$ . By hydriodic acid and red phosphorus it is converted into phenylethenylamidine,  $\text{CH}_2\text{Ph} \cdot \text{C}(\text{NH}) \cdot \text{NH}_2$ , the *picrate* of which forms yellow needles, m. p.  $224^\circ$  (decomp.). 5-Hydroxy-3-benzyl-1 : 2 : 4-oxadiazole forms a *sodium* salt, white powder; an insoluble *silver* salt, white, crystalline powder, stable towards light, and a *methyl ether*, crystallising in needles, m. p.  $112-113^\circ$ .

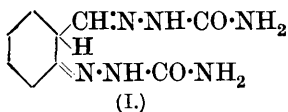
5-Hydroxy-3- $\alpha$ -naphthenyl-1 : 2 : 4-oxadiazole has m. p.  $196^\circ$ , and not  $189^\circ$  as stated by Richter (A., 1890, 62).  $\alpha$ -Naphthenylamidine,  $\text{C}_{10}\text{H}_7 \cdot \text{C}(\text{NH}) \cdot \text{NH}_2$ , crystallises in white laminæ, m. p.  $154^\circ$ , and its *picrate* in yellow needles, m. p.  $223^\circ$  (decomp.).

5-Hydroxy-3- $\beta$ -naphthenyl-1 : 2 : 4-oxadiazole, m. p.  $219-220^\circ$  (Richter, *loc. cit.*, gave  $216^\circ$ ), yields on reduction  $\beta$ -naphthenylamidine, the *picrate* of which forms reddish-yellow needles, m. p.  $240^\circ$  (decomp.).

T. H. P.

**Tetrahydroindazoles.** K. VON AUWERS, W. BUSCHMANN, and R. HEIDENREICH (*Annalen*, 1924, **435**, 277—321).—A study of the tetrahydroindazoles obtained by condensing hydrazine derivatives with hydroxymethylenecyclohexanone and 1-methyl-3-hydroxymethylenecyclohexan-2-one. In the preparation of the latter compound (cf. A., 1915, i, 818), acetone sodium (Freer, A., 1894, i, 65) and 1-methylcyclohexan-2-ol are formed as by-products. 1-Methyl-3-benzoxymethylenecyclohexan-2-one (needles, m. p.  $84-85^\circ$ ) is hydrolysed more readily by acids than by alkalis.

Semicarbazide reacts with hydroxymethylenecyclohexanone to give tetrahydroindazole-2-carbonamide (Wallach and Steindorff, A., 1904, i, 104), the constitution of which is now definitely established by its formation by the hydrolysis of the *semicarbazone* of benzoxymethylenecyclohexanone (needles, m. p.  $193^\circ$  if bath previously heated at  $190^\circ$ ). Excess of semicarbazide converts the hydroxymethylene ketone into the *disemicarbazone* (I), which in hot dilute



sulphuric acid solution affords the above carbonamide. The latter, as shown by Wallach (*loc. cit.*) occurs in two forms, although the latter author's m. p. observations are incorrect. The carbonamide, if obtained in the labile form (as in the first method given above), has m. p.  $158^\circ$ , but unless the m. p. bath is previously heated to within a few degrees of this temperature, the labile form passes, before its m. p. is reached, into the stable form (m. p.  $186-188^\circ$ ) (see *infra*). Wallach's second m. p. ( $220^\circ$ ) actually indicated the decomposition of the carbonamide to give cyanuric acid.

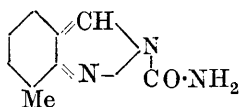
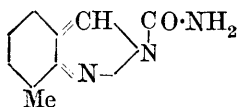
The above disemicarbazone (I) had m. p.  $193^\circ$  when first prepared, but after six months, m. p.  $203^\circ$ . The lower m. p. is that of the labile form, which was not subsequently obtained. The substance

*m*\*



becomes solid after melting at  $203^{\circ}$ , re-melting, with decomposition, at  $234\text{--}236^{\circ}$ .

Methyl-hydroxymethylenecyclohexanone affords (with semicarbazide in cold acetic acid solution) the normal *semicarbazone* (white needles, m. p.  $193^{\circ}$  or  $203^{\circ}$ , according to the rate of heating), the *benzoyl* derivative of the latter being identical with the *semicarbazone* (m. p.  $186^{\circ}$ ) of methyl-benzoxymethylenecyclohexanone. Excess of semicarbazide converts the methyl hydroxymethylene ketone into the *disemicarbazone* (prisms, m. p.  $215^{\circ}$  if heated suddenly, and  $237^{\circ}$  [decomp.]), together with a little 7-methyltetrahydroindazole-2-carbonamide, the latter also being formed in small quantities in the preparation of the monosemicarbazone. The carbonamide exists in two forms: *labile* form, monoclinic needles, m. p.  $138^{\circ}$  (if plunged suddenly into bath just below  $138^{\circ}$ ), then solidifying to give the *stable* form, tetragonal crystals, m. p.  $163^{\circ}$ . The *labile* form can be kept at the ordinary temperature, but passes into the *stable* form on heating in a toluene vapour-bath, or on boiling in alcoholic solution. The *labile* form results when the semicarbazone is treated in cold acetic acid solution with a little sulphuric acid, with subsequent addition of water, whereas if the solution is heated before addition of water, the latter precipitates the *stable* form. Again, when the parent ketone is treated with semicarbazide in presence of mineral acid, the carbonamide is formed, the production of the *labile* or of the *stable* form depending on the hydrogen-ion concentration. The carbonamide is converted by ammoniacal silver nitrate solution into the *silver* salt of 7-methyltetrahydroindazole, this salt, with carbamyl chloride, affording a mixture of the two forms of the carbonamide. The latter are shown to be



stereoisomerides (see annexed formulæ), and not structural isomerides. They are readily interconvertible; moreover,

under conditions when a 1-derivative might be expected to result (as when the parent ketone is treated with semicarbazide hydrochloride), the *labile* form, already proved to be a 2-derivative, is obtained. Polymorphism is also excluded as an explanation of the isomerism, on experimental grounds.

Tetrahydroindazole (m. p.  $84^{\circ}$ ), first obtained by Wallach (*loc. cit.*), is prepared by boiling tetrahydroindazole-2-carbonamide (or the parent semicarbazones) with mineral acids, and gives the following derivatives: *picrate*, m. p.  $155\text{--}156^{\circ}$ ; *silver* salt; 2-*acetyl* derivative, b. p.  $130^{\circ}/15$  mm.; and 2-*o-nitrobenzoyl* derivative, white needles, m. p.  $129\text{--}130^{\circ}$ .

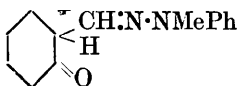
7-Methyltetrahydroindazole is a viscous oil, b. p.  $152.8^{\circ}/12$  mm., becoming solid at the temperature of mixtures of ether and solid carbon dioxide. The following derivatives are described: *hydrochloride*, white prisms; *picrate*, m. p.  $151\text{--}152^{\circ}$ ; *mercuric chloride* additive compound, white needles; *silver nitrate* additive compound,  $\text{Ag}(\text{C}_8\text{H}_{12}\text{N}_2)_2\text{NO}_3$ , white needles, m. p.  $132^{\circ}$ ; *silver* salt,  $\text{C}_8\text{H}_{11}\text{N}_2\text{Ag}$  (two forms, one soluble and one insoluble in ether); 2-*phenyl-*

carbonamide, white prisms, m. p.  $70^{\circ}$  (from the indazole and phenyl-carbimide); and 2-o-nitrobenzoyl derivative, leaflets, m.p.  $104-107^{\circ}$ . The parent indazole is obtained either by treating methyl-hydroxymethylenecyclohexanone semicarbazone with hot dilute sulphuric acid, or the ketone itself with hydrazine.

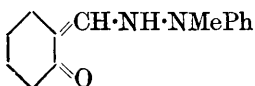
Hydroxymethylenecyclohexanone, when treated with phenylhydrazine, gives a mixture of 1- and 2-phenyltetrahydroindazoles, which are not interconvertible and are separable as the picrates. The constitution of the 2-phenyl derivative follows from its formation from the benzoylated ketone and phenylhydrazine. The intermediately formed *phenylhydrazone* of the benzoylated ketone has only a transitory existence (white needles, m. p. about  $80^{\circ}$ ), and rapidly passes into the above 2-phenylindazole derivative. 1-Phenyl-4:5:6:7-tetrahydroindazole forms leaflets, m. p.  $58-59^{\circ}$ , b. p.  $178^{\circ}/10$  mm. (*picrate*, m. p.  $125-126^{\circ}$ , and *perchlorate* are described). 2-Phenyltetrahydroindazole forms prisms, m. p.  $48.5-49.5^{\circ}$ , b. p.  $177^{\circ}/10$  mm. (*picrate*, m. p.  $126.5-127.5^{\circ}$ , and *perchlorate* are described).

In the interaction of hydroxymethylenecyclohexanone and phenylhydrazine, the higher the concentration of hydron, the smaller the proportion of 2-phenyl derivative formed, particularly if, at the same time, the temperature is kept low. Thus, when the ketone is treated at  $0^{\circ}$  with phenylhydrazine hydrochloride, only the 1-phenyl derivative is formed. This is explained as being due to the driving back, by hydron, of the dissociation of the hydroxymethylene group, with resulting increase in the proportion of the aldehydic form, from which the 1-compound would be formed (cf. Claisen, A., 1895, i, 62). In this connexion, the nature of the hydrazine derivative affects the proportion of 1- to 2-derivative obtained, this being, under comparable conditions, as follows: phenylhydrazine, 1:0, *as*-phenylmethylhydrazine, 2:1, benzylhydrazine, 3:4, methylhydrazine, 4:1, and semicarbazide, 0:1.

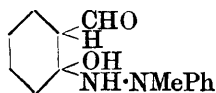
In order to throw light on the constitution of the intermediate compounds formed in the interaction of phenylhydrazine and hydroxymethylenecyclohexanone, the interaction of the latter with phenylmethylhydrazine has been studied. The main product (m. p.  $170-171^{\circ}$ ) is insoluble in alkali and may be either the *phenylmethylhydrazone* of 2-ketocyclohexylformaldehyde (II) or 1-methylphenylhydrazidomethenecyclohexan-2-one (III). A second product, soluble in alkali, is the *hydrate* (needles, m. p.  $123-124^{\circ}$ ) of the *acid* produced by the spontaneous oxidation of IV. There is also formed a third product (under slightly different conditions), viz., the *hydrate* of the *phenylmethylhydrazone* of 1-formylcyclohexan-2-one (needles, m. p.  $125-126^{\circ}$ ).



(II.)



(III.)



(IV.)

Methyl-hydroxymethylenecyclohexanone, with phenylhydrazine, affords a mixture of the 1- and 2-indazole derivatives, low temperatures and high concentrations favouring the production of the 1-derivative. The latter is a stronger base than the 2-derivative, and forms a stable *perchlorate* (m. p. 214—215°), which allows of its separation from its isomeride. The benzoyl derivative of the methylcyclohexanone affords a *phenylhydrazone* (m. p. 125°, with previous sintering), which rapidly passes, in solution, into 2-*phenyl-7-methyl-4 : 5 : 6 : 7-tetrahydroindazole* (a colourless oil, b. p. 181·4°/10 mm. The *methiodide*, m. p. 172°, gives 2-phenyltetrahydroindazole when heated). 1-*Phenyl-7-methyltetrahydroindazole* is a colourless oil, b. p. 175°/10 mm.; its *methiodide*, m. p. 154°, on heating, gives 1-phenyltetrahydroindazole.

The products of the alkylation of tetrahydroindazole depend on the nature of the alkyl group introduced and on the experimental conditions. Tetrahydroindazole, when heated in alcoholic solution with benzyl chloride in presence of alkali, or when heated alone with the chloride at water-bath temperatures, affords a mixture of the 1- and 2-benzyl derivatives, this mixture also being obtained by condensing benzylhydrazine with hydroxymethylenecyclohexanone. The benzoyl derivative of the latter ketone is converted by benzylhydrazine into 2-*benzylindazole* (colourless oil, b. p. 177°/10 mm.). 1-*Benzyltetrahydroindazole* is a colourless oil, b. p. 172°/10 mm. (*picrate*, m. p. 128—129°, and *perchlorate* are described).

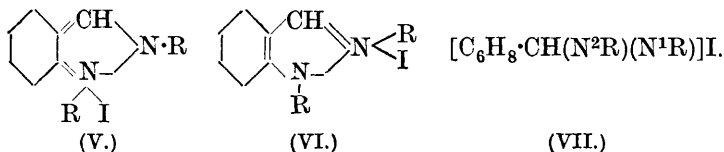
Tetrahydroindazole, when heated at 100° with ethyl bromide, gives 2-*ethyltetrahydroindazole* (a colourless oil, b. p. 118°/15 mm.; *picrate* has m. p. 150·5—151·5°), whilst when similarly heated in presence of alkali, it affords 1-*ethyltetrahydroindazole* (a colourless oil, b. p. 111°/14 mm.; *picrate* has m. p. 103—104°).

The methylation of tetrahydroindazole leads, in presence or in absence of alkali, to the formation of the 1- and 2-methyl derivatives, which cannot be separated. 2-*Methyltetrahydroindazole*, obtained from benzoxymethylenecyclohexanone, is a colourless oil, b. p. 93—94°/9 mm. or 103°/13 mm. (*picrate*, m. p. 166·5—167·5°).

7-Methyltetrahydroindazole on methylation, ethylation, or benzylation, in presence or in absence of alkali, always affords 2-derivatives, which may be obtained from the appropriate hydrazine and methyl-benzoxymethylenecyclohexanone. 2 : 7-*Dimethyl-4 : 5 : 6 : 7-tetrahydroindazole* is a colourless oil with a feeble blue fluorescence, has b. p. 111°/13 mm., and forms a *picrate*, m. p. 123—125°. 7-*Methyl-2-ethyltetrahydroindazole*, a colourless oil, b. p. 108·5°/10 mm., gives a *picrate*, m. p. 101—102°, and a *methiodide*, m. p. 102—103°, the latter affording 7-methyl-2-ethyltetrahydroindazole when heated. 7-*Methyl-2-benzyltetrahydroindazole*, a colourless oil, b. p. 181—183°/12 mm. or 152°/3 mm., forms a *methiodide* (leaflets, m. p. 175° [decomp.]), which is also obtained from 2 : 7-dimethyltetrahydroindazole and benzyl iodide, and, on heating, affords the two last-named substances. The fact that the 7-methyl group prevents alkylation in position 1 is to be ascribed to electrochemical (not

stereochemical) effects (cf. attempts to prepare 1 : 5-dialkylpyrazoles by Auwers and Broche, A., 1923, i, 151).

The formation of quaternary salts from the reduced indazoles is not altogether parallel to their formation in the ordinary series. The 2-methyl- and 2-ethyl-tetrahydroindazoles follow the general rule. Methyl iodide converts either 1- or 2-methyltetrahydroindazole into 1 : 2-dimethyl-4 : 5 : 6 : 7-tetrahydroindazolium iodide (m. p. 152—153°). Ethyl iodide converts either 1- or 2-ethyltetrahydroindazole into 1 : 2-diethyltetrahydroindazolium iodide (m. p. 98—99°). Since these quaternary salts afford mixtures of 1- and 2-alkyl derivatives when heated, they are given formulæ V or VI, or, better, VII :



2-Benzyltetrahydroindazole, when heated with ethyl iodide, affords the compound (m. p. 138—139°) obtained by heating 2-ethyltetrahydroindazole with benzyl iodide. The compound, on heating, affords pure 2-ethyltetrahydroindazole, and therefore is written as  $[C_6H_8 \cdot CH(N^2Et[Ph \cdot CH_2 \cdot])(N^1)]I$ , both alkyl groups being attached to the same nitrogen atom. Similarly, the compound,  $[C_6H_8 \cdot CH(N^2)(N^1Et[Ph \cdot CH_2 \cdot])]I$  (m. p. 127—128°), is formed from 1-benzyltetrahydroindazole and ethyl iodide or from the 1-ethyl derivative and benzyl iodide. The 1 : 1-quaternary salt, on heating, affords, not 1-ethyl-, but 2-ethyl-tetrahydroindazole.

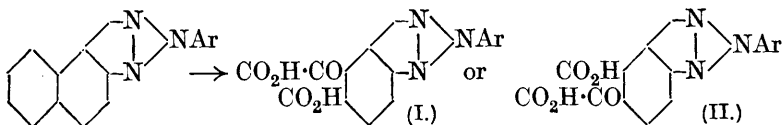
7-Methyltetrahydroindazole gives quaternary salts in which the two alkyl groups are attached to the same nitrogen atom (see *ante*). The *methiodides* of 1- and 2-phenyltetrahydroindazoles afford, when heated, the parent phenyl derivatives.

7-Methyltetrahydroindazole reacts with ethyl bromoacetate to give *ethyl 7-methyl-4 : 5 : 6 : 7-tetrahydroindazyl-2-acetate* (colourless oil, b. p. 166·5—167·5°/14 mm.; *picrate*, m. p. 127—130° [*indef.*]). The corresponding *acid* (also obtainable from the indazole and chloroacetic acid), obtained by hydrolysis, forms white needles, m. p. 168—169° (*silver salt* described), and has, unlike the indazole bases, a sweet taste.

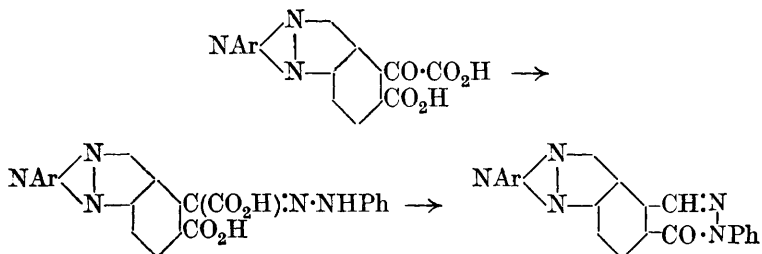
E. E. T.

**vic.-2 : N-Aryltriazolephthalonic Acids.** G. CHARRIER (*Gazzetta*, 1923, 53, 829—843).—It has been shown by Dimroth (A., 1902, i, 403) that, starting from the three isomeric *N*-phenyl derivatives of 1 : 2 : 3-triazolemonocarboxylic acid and eliminating the phenyl group by oxidation after nitrating and converting into the amino-derivative by reduction, one and the same acid is obtained; the desmotropy of the triazole ring is thus established. Oxidation of naphthalene by means of alkaline permanganate solution yields mainly phthalonic acid, and the author finds similarly that the 2-arylnaphthatriazoles give, under the same

conditions, principally the corresponding vicinal 2-aryltriazo-lephthalonic acids,



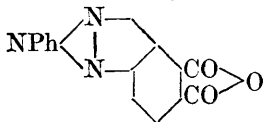
Since these acids are highly stable towards oxidising agents and are prone to form monometallic salts with the alkali metals, probably owing to the formation of an internal anhydride between the  $\cdot\text{CO} \cdot \text{CO}_2\text{H}$  group and the triazole ring, and further on account of the analogy existing between them and the product of the oxidation of naphthalic acid by permanganate in alkaline solution (cf. Graebe and Bossel, A., 1893, i, 593), formula (I) is regarded as preferable to formula (II). The constitution of these acids is shown also by their oxidation to the corresponding 2-aryltriazo-lephthalic acids (annexed formula), and by their ability to react as keto-acids, analogously to phthalonic acid, with phenylhydrazine hydrochloride to form phenylhydrazones. The latter are far more stable than those of phthalonic acid, since only by heating above their melting points are they transformed, like phenylhydrazones of a keto-acid, into derivatives of the corresponding ketotetrahydropyridazines (pyridazinones); a carboxyl group is eliminated at the same time, so that from a dibasic acid a neutral heterocyclic derivative is obtained :



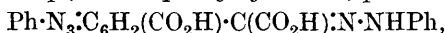
These acids behave as comparatively strong dibasic acids; they decompose carbonates, form well crystallised salts containing water of crystallisation, and readily yield normal and acid esters and amides. When subjected to prolonged energetic oxidation, they give the corresponding phthalic acids.

[With A. ODIFREDDI, A. MANFREDI, and E. MARS.]—vic.-2-Phenyltriazo-lephthalonic acid,  $\text{C}_{15}\text{H}_9\text{O}_5\text{N}_3$ , obtained by oxidising 2-phenylnaphthatriazole, crystallises in white or lustrous needles, m. p.  $242^\circ$ , and has an intense acid reaction towards litmus, methyl orange and phenolphthalein. It yields the following derivatives : monosodium salt,  $\text{C}_{15}\text{H}_8\text{O}_5\text{N}_3\text{Na} \cdot 4\text{H}_2\text{O}$ , m. p.  $324\text{--}325^\circ$ , gives aqueous solutions acid to litmus and phenolphthalein. The normal

barium salt crystallises with  $4\text{H}_2\text{O}$  and also with  $5\text{H}_2\text{O}$ , and when subjected to dry distillation in the anhydrous state yields *vic*.-2-phenyltriazolephthalic anhydride (annexed formula), which crystallises in slender, white needles, m. p.  $183\text{--}184^\circ$ , and, when treated with *m*-diethylamino-



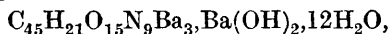
phenol and zinc chloride, gives a deep red, crystalline colouring matter; the hydrochloride of the latter dissolves in boiling alcohol to an intense reddish-violet, markedly fluorescent solution, and crystallises in slender, metallic green needles similar to the crystals of rhodamine base B hydrochloride. *Basic barium 2-phenyltriazolephthalonate*,  $\left[\text{PhN}_3\cdot\text{C}_6\text{H}_2\cdot\left\langle\begin{smallmatrix}\text{CO}\cdot\text{CO}_2 \\ \text{CO}_2\end{smallmatrix}\right\rangle\text{Ba}\right]_3\cdot\text{Ba}(\text{OH})_2\cdot 12\text{H}_2\text{O}$ , forms rosettes of slender, silky needles and decomposes before melting. The *strontium* salt,  $\text{C}_{15}\text{H}_{17}\text{O}_5\text{N}_3\text{Sr}\cdot 4\frac{1}{2}\text{H}_2\text{O}$ , forms lustrous, white needles and decomposes before melting. The *methyl* ester,  $\text{C}_{13}\text{H}_7\text{ON}_3(\text{CO}_2\text{Me})_2$ , forms minute, white prisms, m. p.  $87\text{--}88^\circ$ , and the *methyl hydrogen* ester,  $\text{C}_{16}\text{H}_{11}\text{O}_5\text{N}_3$ , colourless, prismatic crystals, m. p.  $201\text{--}202^\circ$ . The *ethyl* ester crystallises in colourless prisms, m. p.  $169\text{--}170^\circ$ . The *diamide*,  $\text{C}_{13}\text{H}_7\text{ON}_3(\text{CO}\cdot\text{NH}_2)_2$ , forms lustrous, colourless prisms, m. p.  $233\text{--}234^\circ$ , and, when boiled with 10% ammonia solution, yields the *ammonium* salt of the *monoamide*,  $\text{C}_{15}\text{H}_{13}\text{O}_4\text{N}_5$ , which crystallises in slender, white needles, m. p.  $250^\circ$  (decomp.). The *phenylhydrazine*, probably



crystallises in white, silky needles, m. p.  $206\text{--}207^\circ$  (decomp.), and acts as an energetic acid.

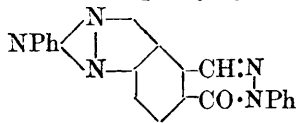
The monocarboxylic ketotetrahydropyridazinic acid, that is, the pyridazinone of *vic*.-2-phenyltriazolephthalonic acid, is not formed when the phenylhydrazine is boiled in acetic acid, but when heated at  $250^\circ$  the phenylhydrazine loses carbon dioxide and water, to give the decarboxylated *pyridazinone* (annexed formula), which crystallises in colourless prisms, m. p. about  $200^\circ$ .

When the phenylhydrazine is treated in boiling water with barium carbonate, phenylhydrazine separates and the pentahydrated normal *barium 2-phenyltriazolephthalonate*,  $\text{C}_{15}\text{H}_7\text{O}_5\text{N}_3\text{Ba}\cdot 5\text{H}_2\text{O}$ , and the *dodecahydrated basic barium* salt,

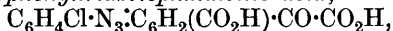


are formed.

The great resistance offered by *vic*.-2-phenyltriazolephthalonic acid to oxidising agents may be due to the existence of an anhydridic linking between the triazole nucleus and the  $\cdot\text{CO}\cdot\text{CO}_2\text{H}$  group, which is thus protected from the action of nascent oxygen. The acid is, however, attacked by chromic acid with formation of a compound which crystallises in aggregates of radiating leaflets, m. p.  $250^\circ$ , acts as an energetic acid, and has the nitrogen content of a *vic*.-2-phenyltriazolephthalic acid.



vic.-2-*p*-Chlorophenyltriazolephthalonic acid,




crystallises in slender, white needles, m. p. 264—265°; its monosodium salt (+2H<sub>2</sub>O) does not melt at 360°.

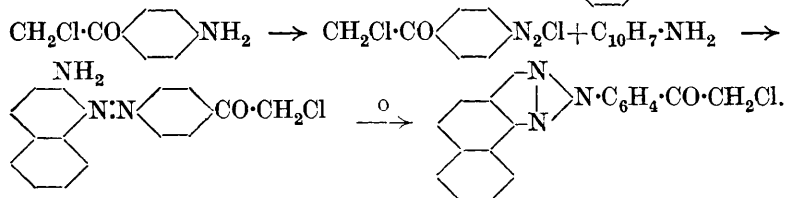
2-*p*-Bromophenyl-naphthatriazole, C<sub>10</sub>H<sub>6</sub>·N<sub>3</sub>·C<sub>6</sub>H<sub>4</sub>Br, prepared by oxidising *p*-bromophenylazo-β-naphthylamine by means of chromic acid in acetic acid solution, crystallises in white, silky needles, m. p. 200°.

vic.-2-*p*-Bromophenyltriazolephthalonic acid, obtained by the action of alkaline permanganate solution on the preceding compound, forms flat, white needles, m. p. 270°; its monosodium salt (+2H<sub>2</sub>O) does not melt at 320°.

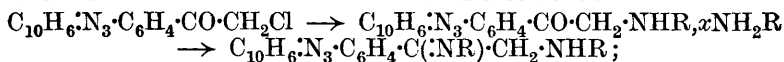
vic.-2-*p*-Carboxyphenyltriazolephthalonic acid, C<sub>16</sub>H<sub>9</sub>O<sub>7</sub>N<sub>3</sub>, crystallises in slender, white needles, m. p. 287—288° (decomp.), and is an energetic tribasic acid; its monosodium salt (+4½H<sub>2</sub>O) does not melt at 350°.

T. H. P.

**αβ-Naphthatriazoles.** G. CHARRIER and M. GALLOTTI (*Gazzetta*, 1923, **53**, 851—861).—The authors have prepared 2-*p*-chloroacetylphenyl-αβ-naphthatriazole by means of the following series of reactions: Ph·NHAc → CH<sub>2</sub>Cl·CO·NHAc →



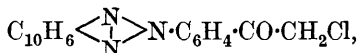
The mobile chlorine atom of the chloroacetyl group is readily replaced, giving the corresponding iodo- and cyano-derivatives. Hydrolysis of the latter gives the unstable ketonic acid, which loses carbon dioxide to form the corresponding ketone, 2-*p*-acetylphenyl-αβ-naphthatriazole. Treatment of the chloroacetyl compound with silver acetate yields the acetyl derivative of the corresponding ketocarinol, αβ-naphthatriazole-2-*p*-benzoylcarbinol, which may be obtained either by hydrolysis of the acetyl derivative or by the action of moist silver oxide on the chloroacetyl compound itself. The latter reacts normally with ammonia, yielding αβ-naphthatriazole-2-*p*-benzoylmethylamine, whilst with primary aliphatic amines both substitution and addition occur, the unstable compound thus formed losing water and alkylamine when treated with an acid or even with a solvent:



the resulting compound consists of the corresponding 2-*p*-β-alkyl-amino-α-alkyliminoethylphenyl-αβ-naphthatriazole. Aniline acts similarly to ammonia, the chlorine atom of the *p*-chloroacetyl group being replaced by the anilino residue.

[With R. SALA, Q. MINGOIA, and P. TORAZZI.]—*p*-Chloroacetylbenzeneazo- $\beta$ -naphthylamine,  $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$ , crystallises in thin, lustrous, garnet-red leaflets, m. p.  $172^\circ$ , and dissolves in concentrated sulphuric acid to a magenta-red solution. Its *phenylhydrazone* forms a red, crystalline powder with metallic green reflex, m. p.  $180^\circ$  (decomp.).

2-*p*-Chloroacetylphenyl- $\alpha\beta$ -naphthatriazole,

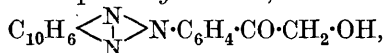


prepared by oxidising the preceding compound by means of chromic acid, forms thin, white leaflets, m. p.  $198^\circ$ , and dissolves in concentrated sulphuric acid to a yellow solution. Its *phenylhydrazone* crystallises in thin, pale yellow leaflets, m. p.  $156^\circ$ .

2-*p*-Iodoacetylphenyl- $\alpha\beta$ -naphthatriazole separates in lustrous, white needles, m. p.  $195^\circ$ .

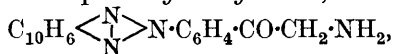
2-*p*-Cyanoacetylphenyl- $\alpha\beta$ -naphthatriazole,  $\text{C}_{19}\text{H}_{12}\text{ON}_4$ , crystallises in slender, yellow needles, m. p.  $185^\circ$ , with previous contraction, and, on protracted boiling with 50% sulphuric acid, gives 2-*p*-acetylphenyl- $\alpha\beta$ -naphthatriazole (cf. A., 1922, i, 771).

$\alpha\beta$ -Naphthatriazole-2-*p*-benzoylcarbinol,



crystallises in silvery leaves, m. p.  $191^\circ$ , and its *acetyl* derivative in slender, white needles, m. p.  $187^\circ$ .

$\alpha\beta$ -Naphthatriazole-2-*p*-benzoylmethylamine,



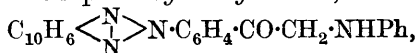
forms minute, almost colourless crystals, m. p.  $192^\circ$ , and gives a pale yellow *hydrochloride*, m. p.  $184^\circ$ .

2-*p*- $\beta$ -Methylamino- $\alpha$ -methyliminoethylphenyl- $\alpha\beta$ -naphthatriazole,

$\text{C}_{10}\text{H}_6 \left\langle \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix} \right\rangle \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NMe}) \cdot \text{CH}_2 \cdot \text{NHMe}$ , crystallises in yellow needles, m. p.  $160^\circ$ , and forms a yellowish-brown *hydrochloride*.

2-*p*- $\beta$ -Ethylamino- $\alpha$ -ethyliminoethylphenyl- $\alpha\beta$ -naphthatriazole,  $\text{C}_{22}\text{H}_{23}\text{N}_5$ , separates in slender, pale yellow needles, m. p. about  $150^\circ$  with previous contraction.

$\alpha\beta$ -Naphthatriazole-2-*p*-benzoylmethylaniline,



crystallises in lustrous, sulphur-yellow leaflets, m. p.  $277^\circ$ , and forms benzene solutions exhibiting pronounced greenish-yellow fluorescence; its *phenylhydrazone* separates in slender, lemon-yellow needles, m. p. about  $270^\circ$  (decomp.).

T. H. P.

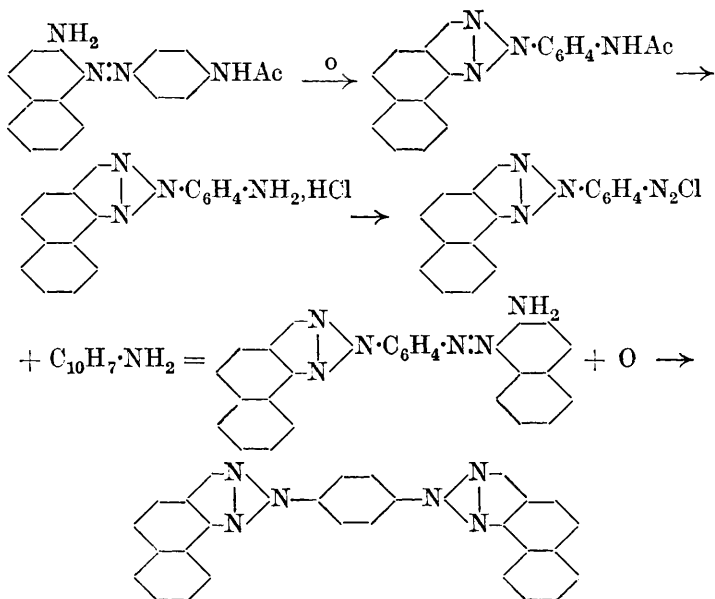
### Oxidation of Uric Acid by Iodine in Alkaline Solution.

J. MORE (*Compt. rend.*, 1924, 178, 498—501).—Oxidation of uric acid (1 mol.) by iodine (2 atoms), in potassium hydrogen carbonate solution, affords a substance (not isolated), which is converted by acetic acid into allantoin, and (cf. Biltz and Max, A., 1921, i, 893) is further oxidisable by iodine in acid solution. Oxidation



of uric acid by means of iodine in sodium hydroxide solution (cf. Kreidl, A., 1893, ii, 558) gives first a substance which affords a uroxanate on evaporation in alkaline solution, or allantoin on evaporating in acetic acid solution, and in presence of alkali may also pass into a less readily oxidised isomeride. The latter, however, yields the same products as above, on evaporation in alkaline or acid solution, and on oxidation with iodine gives *allantoxalic amide*. The latter, when treated with concentrated potassium hydroxide, affords potassium allantoxalate; the following salts are described:  $C_4H_3O_3N_4K, 1.5H_2O$ ;  $C_4H_3O_3N_4Na, 1.5H_2O$ , and  $C_4H_3O_3N_4(NH_4), H_2O$ . E. E. T.

**p-Phenylene-1:2-dinaphthaditriazole.** G. CHARRIER (*Gazzetta*, 1923, 53, 862—867).—This compound has been prepared by means of the following series of reactions:  $C_6H_5 \cdot NHAc \rightarrow NO_2 \cdot C_6H_4 \cdot NHAc \rightarrow NH_2 \cdot C_6H_4 \cdot NHAc \rightarrow N_2Cl \cdot C_6H_4 \cdot NHAc + C_{10}H_7 \cdot NH_2 \rightarrow$



It is a highly stable compound and, as is usual with  $\alpha\beta$ -naphthatriazoles, is oxidised by permanganate in alkaline solution, giving *vic.*-p-phenyleneditriazole-diphthalonic acid. Derivatives of the p-phenylene-1:2-dinaphthaditriazole have not previously been prepared (cf. Morgan and Chazan, A., 1922, i, 181). It is found possible to pass directly, by oxidation by means of alkaline permanganate solution, from 1:2-naphthatriazole-2-p-benzeneazo- $\beta$ -naphthylamine to the above diphthalonic acid, preparation of the corresponding naphthatriazole as an intermediate product being unnecessary. Similarly, *vic.*-2-phenyltriazolephthalonic acid may be prepared directly from 1-benzeneazo-2-naphthylamine.

[With G. BONOMI and T. BETTINAZZI].—*p*-Acetylaminobenzene-azo- $\beta$ -naphthylamine,  $C_{18}H_{16}ON_4$ , prepared by the interaction of *p*-acetylaminophenyldiazonium chloride and  $\beta$ -naphthylamine in alcoholic solution, crystallises in slender, orange-red needles, m. p.  $208^\circ$ .

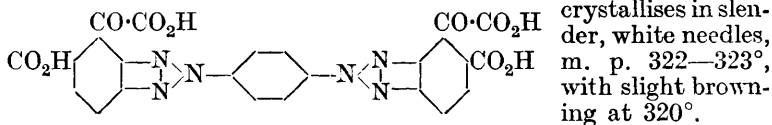
2-*p*-Acetylaminophenyl-1 : 2-naphthatriazole,  $C_{18}H_{14}ON_4$ , obtained by oxidising the preceding compound in acetic acid solution by means of chromic acid, forms slender, white needles, m. p.  $228^\circ$ , and exhibits marked blue fluorescence even in very dilute solutions.

2-*p*-Aminophenyl-1 : 2-naphthatriazole,  $C_{16}H_{12}N_4$ , crystallises in lustrous, silky, white needles, m. p.  $200^\circ$ .

1 : 2-Naphthatriazole-*p*-benzeneazo- $\beta$ -naphthylamine,  $C_{26}H_{18}N_6$ , separates in bright red needles, m. p.  $250^\circ$ .

*p*-Phenylene-1 : 2-dinaphthaditriazole,  $C_{26}H_{16}N_6$ , forms thin, pink laminæ, m. p.  $333^\circ$ .

vic.-*p*-Phenyleneditriazolediphthalonic acid (annexed formula),



2-Phenyltriazolephthalonic acid,

$Ph \cdot N_3 \cdot C_6H_2(CO_2H) \cdot CO \cdot CO_2H$  [ $N_3Ph : CO_2H : CO \cdot CO_2H = 12 : 4 : 3$ ], prepared by oxidising benzeneazo- $\beta$ -naphthylamine by means of alkaline permanganate solution, crystallises in lustrous, white needles, m. p.  $242^\circ$ .  
[T. H. P.]

**s-Trinitroarylazodiarylamines.** A. BERETTA (*Gazzetta*, 1923, **53**, 870—876).—By the action of picryl chloride on amino-azo-derivatives in alcoholic solution in presence of sodium acetate, the author has prepared the *s*-trinitrophenyl derivatives of various *o*-, *m*-, and *p*-aminoazo-compounds of the benzene and naphthalene series.

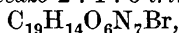
3'-Benzeneazo-2 : 4 : 6-trinitrodiphenylamine,  
 $(NO_2)_3C_6H_2 \cdot NH \cdot C_6H_4 \cdot N \cdot NPh$ ,

obtained from *m*-aminoazobenzene, crystallises in slender, yellow needles, m. p.  $212^\circ$ , and dissolves in concentrated sulphuric acid to a yellow solution. 4'-Benzeneazo-2 : 4 : 6-trinitrodiphenylamine (cf. Walther and Lehmann, A., 1904, i, 352) has m. p.  $178^\circ$ . 3'-Methyl-6'-*p*-tolueneazo-2 : 4 : 6-trinitrodiphenylamine,

$C_6H_4Me \cdot N \cdot N \cdot C_6H_3Me \cdot NH \cdot C_6H_2(NO_2)_3$ ,

prepared from *p*-tolueneazo-*p*-toluidine, forms slender, slightly orange, red crystals, m. p.  $201^\circ$ , and gives a red solution in concentrated sulphuric acid. 2'-Methyl-4'-*o*-tolueneazo-2 : 4 : 6-trinitrodiphenylamine crystallises in red needles, m. p.  $194^\circ$ , and dissolves in concentrated sulphuric acid to a red solution. 3'-Amino-4'-benzeneazo-2 : 4 : 6-trinitrodiphenylamine,  $C_{18}H_{13}O_6N_7$ , prepared from 2 : 4-diaminoazobenzene (chrysoidine), forms minute, red crystals, m. p.  $254^\circ$  (decomp.), and gives a red solution in concentrated sulphuric acid. 3'-Amino-6'-methyl-4'-benzeneazo-

2 : 4 : 6-trinitrodiphenylamine,  $C_{19}H_{15}O_6N_7$ , prepared from 2 : 4-diaminoazomethylbenzene (methylchrysoidine), forms slender, lustrous prisms with metallic reflexion, m. p.  $228^\circ$  (decomp.), and dissolves in concentrated sulphuric acid to a red solution. 3'-Acetylamino-6'-methyl-4'-benzeneazo-2 : 4 : 6-trinitrodiphenylamine crystallises in slender, orange-yellow prisms, m. p.  $215^\circ$  (decomp.). 3'-Amino-6'-methyl-4'-p-chlorobenzeneazo-2 : 4 : 6-trinitrodiphenylamine,  $C_{19}H_{14}O_6N_7Cl$ , prepared from 4'-chloro-2 : 4-diamino-5-methylazobenzene, crystallises in slender, metallic brown prisms, m. p.  $235^\circ$  (decomp.), and forms a red solution in concentrated sulphuric acid. The corresponding 3'-acetylamino-compound separates in slender, orange crystals, m. p.  $228^\circ$  (decomp.). 3'-Amino-6'-methyl-4'-p-bromobenzeneazo-2 : 4 : 6-trinitrodiphenylamine,



crystallises in slender, lustrous, brown needles, m. p.  $233^\circ$  (decomp.), and dissolves in concentrated sulphuric acid to a red solution. The corresponding acetylamino-derivative forms slender, orange needles, m. p.  $227^\circ$  (decomp.).

$\alpha$ -Benzeneazo- $\beta$ -naphthyl-2 : 4 : 6-trinitrophenylamine,



prepared from benzeneazo- $\beta$ -naphthylamine, crystallises in slender, reddish-brown needles, m. p.  $221^\circ$  (decomp.), and dissolves in concentrated sulphuric acid to a blue solution.  $\alpha_2$ -Benzeneazo- $\alpha_1$ -naphthyl-2 : 4 : 6-trinitrophenylamine forms slender, reddish-brown needles, m. p.  $193^\circ$  (decomp.), and yields a blue solution in concentrated sulphuric acid.

T. H. P.

**Studies in Dyes with Multiple Chromophores.** R. N. SEN and B. SETT (*J. Amer. Chem. Soc.*, 1924, **46**, 111—119).—Three types of azo-triphenylmethane dyes have been studied containing, respectively, one, two, and three azo-groups in the *p*-position to the central carbon atom. It has been found that the introduction of one azo-group deepens the colour (compare T., 1912, **101**, 1113), of two azo-groups lightens the colour, and of three makes it still lighter. The effect of the multiplication of chromophores has also been studied by introducing simultaneously an azo-methine group and an azo-group into chrysoidine, rosaniline, safranine, and Congo-red, and in each case the colour becomes lighter. The direct-dyeing property of Congo-red also disappears. The introduction of the azo-group has been found to deepen the colour in the case of an indamine dye as well as in the case of fluorescein.

The preparation and properties of the following dyes, which appear to be new substances, are described: phenetoleazosulphophenyltetramethyldiaminodiphenylcarbinol (from phenetoleazobenzaldehydesulphonic acid and dimethylaniline) dyes wool green; dimethylaminobenzeneazophenyltetramethyldiaminodiphenylcarbinol (from benzeneazodimethylaniline and tetramethyldiaminobenzhydrol) dyes wool blue; salicylazophenyldisalicylylcarbinol (from methylenedisalicylic acid and benzeneazosalicylic acid) dyes wool red; phenyldi(dimethylaminobenzeneazophenyl)carbinol (from benz-

aldehyde and benzeneazodimethylaniline) dyes wool violet; *phenetoleazosulphophenyldi(dimethylaminobenzeneazophenyl)carbinol* (from phenetoleazobenzaldehydesulphonic acid and benzeneazodimethylaniline) dyes wool yellow; *diphenetoleazosulphobenzylidenechrysoidine* (from chrysoidine hydrochloride and phenetoleazobenzaldehydesulphonic acid) dyes wool golden-yellow; *diphenetoleazosulphobenzylidene-rosaniline hydrochloride* (from rosaniline and phenetoleazobenzaldehydesulphonic acid) dyes wool bluish-red; *diphenetoleazosulphobenzylidene-safranine hydrochloride* (from safranine and phenetoleazobenzaldehydesulphonic acid) dyes wool red; *dimethylaminobenzeneazophenyldimethylquinoneimine hydrochloride* (from nitrosodimethylaniline hydrochloride and benzeneazodimethylaniline) dyes wool olive-green; *sulphobenzeneazofluorescein* (from diazotised sulphanilic acid and fluorescein) dyes wool orange.

F. A. M.

### Amine Oxidation. VIII. Oxidation of Aliphatic Amines.

S. GOLDSCHMIDT and V. VOETH (*Annalen*, 1924, **435**, 265—277).—Benzylamine is oxidised by potassium permanganate in aqueous or in acetone solution to give benzaldehyde, no intermediate compound being isolable even if oxidation be effected at  $-60^{\circ}$ . Since, however, benzaldehyde, under similar conditions, is rapidly oxidised to benzoic acid, it cannot be the primary product in the oxidation of benzylamine, which probably proceeds thus:  $\text{PhCH}_2\text{NH}_2 \rightarrow \text{PhCH}_2\text{N} \rightarrow \text{PhCH}:\text{O} + \text{NH}_3$ .

Dibenzylamine is oxidised by permanganate in acetone solution to give *benzoyltribenzylhydrazine* (white needles, m. p.  $181^{\circ}$ ), the constitution of which was established by synthesis (from tribenzoylhydrazine and benzoyl bromide); its formation is explained by the scheme:  $2(\text{PhCH}_2)_2\text{NH} \rightarrow 2(\text{PhCH}_2)_2\text{N} \rightarrow (\text{PhCH}_2)_2\text{N} \cdot \text{N}(\text{CH}_2\text{Ph})_2 \rightarrow (\text{PhCH}_2)_2\text{N} \cdot \text{NBz} \cdot \text{CH}_2\text{Ph}$ . Confirmation of this explanation was obtained: tetrabenzylhydrazine on oxidation with permanganate gives benzoyltribenzylhydrazine, which, on reduction with zinc dust and acetic acid, yields benzylbenzamide (and traces of benzaldehyde and dibenzylamine), and on treatment with mineral acids gives (per mol.) benzaldehyde (1 mol.) and *hydroxytribenzylhydrazine hydrochloride*. The latter (m. p.  $220$ — $240^{\circ}$  [indef.]) could not be obtained in a pure state and was found to contain dibenzylamine hydrochloride, whilst, on treating it with alkali, benzamide and tribenzylhydrazine were isolated.

The oxidation of di-*n*-propylamine by means of permanganate gives  $\alpha\beta$ -dipropionyl- $\alpha\beta$ -di-*n*-propylhydrazine,  
 $\text{COEt} \cdot \text{NPr}^{\alpha} \cdot \text{NPr}^{\alpha} \cdot \text{COEt}$ .

This substance, evidently formed by the oxidation of the first-formed tetrapropylhydrazine, was only obtained in a slightly impure state as a yellow oil possessing an odour like that of menthol, and beginning to decompose at  $40^{\circ}$  (more readily in presence of alkali) with formation of propaldehyde. The dipropionyl derivative, on being distilled, affords a mixture of propaldehyde, *n*-propylpropionamide,  $\text{NHPr}^{\alpha} \cdot \text{COEt}$  (pale yellow oil, b. p.  $64$ — $65^{\circ}$ /

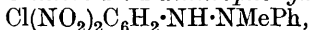
0.4 mm.), and *n*-propylidenepropionamide,  $\text{CHEt}\cdot\text{N}\cdot\text{COEt}$  (viscous, greenish-yellow oil, b. p.  $87^\circ/0.4$  mm.).

Aqueous permanganate with piperidine gave no isolable products, but in acetone solution oxidation proceeded much more rapidly than in the cases described already, to give *N*-piperidyl-*N*-2-piperidone as a yellowish-red oil, which, on distillation, was converted into a mixture of tetrahydropyridine and 2-piperidone (b. p.  $64$ — $65^\circ/0.4$  mm.). E. E. T.

**Certain Nitroarylhydrazines.** M. GIUA (*Gazzetta*, 1923, 53, 844—851).—The results obtained when various aromatic nitro-compounds are treated with semicarbazide show that the latter serves to replace by the residue  $\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , not only the nitro-group, but also labile halogen atoms. Thus, when heated on a water-bath in alcoholic solution containing sodium acetate, 1-chloro-2:4-dinitrobenzene and semicarbazide react in accordance with the equation:  $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2 + 2\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 = \text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 + \text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$ . In the case of nitro-compounds containing a labile nitro-group, the formation of nitrous acid renders the reaction somewhat complicated, and, although the yields of nitrophenylsemicarbazides are good, various secondary products are also formed. With  $\beta$ - and  $\gamma$ -trinitrotoluenes the first phase of the reaction is probably expressed by the equation:  $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_3 + 2\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 = \text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 + \text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}_3 + 2\text{H}_2\text{O}$ ; the azide of carbamic acid has not been observed among the secondary products, but small proportions of cyanuric acid, which is one of the many transformation products of this azide, have been detected (cf. Curtius and Schmidt, A., 1923, i, 1080).

4:6-Dinitro-*m*-tolylsemicarbazide, obtained by the action of semicarbazide on  $\gamma$ -trinitrotoluene, forms crystals, m. p.  $237$ — $238^\circ$  (decomp.). 2:4-Dinitro-*m*-tolylsemicarbazide, similarly obtained from  $\beta$ -trinitrotoluene, forms crystals, m. p.  $185^\circ$  (decomp.), and in alcoholic solution yields a reddish-brown coloration with alkalis. 5-Chloro-2:4-dinitrophenylsemicarbazide, prepared from 1-chloro-2:4:5-trinitrobenzene, forms yellow crystals, m. p.  $217$ — $218^\circ$  (decomp.). 2:4-Dinitrophenylsemicarbazide,  $\text{C}_7\text{H}_7\text{O}_5\text{N}_5$ , prepared from 1-chloro-2:4-dinitrobenzene, forms pale yellow crystals, m. p.  $205$ — $207^\circ$  (decomp.).

$\alpha$ -Methyl- $\alpha$ -phenyl-5-chloro-2:4-dinitrophenylhydrazine,



obtained by the interaction of *as*-methylphenylhydrazine and 1-chloro-3:4:6-trinitrobenzene, crystallises in orange-yellow lamellæ, m. p.  $120$ — $121^\circ$ , and dissolves in concentrated sulphuric acid to a reddish-brown solution.

Acetone 4:6-dinitro-*m*-tolylhydrazone,  $\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_4$ , crystallises in yellow needles, m. p.  $144$ — $145^\circ$ , and in alcoholic solution gives a dark red coloration with an alkali. Other 4:6-dinitro-*m*-tolylhydrazones are those of: acetophenone,  $\text{C}_{15}\text{H}_{14}\text{O}_4\text{N}_4$ , crystallising in orange-yellow needles, m. p.  $215$ — $216^\circ$ ; ethyl phenyl ketone,  $\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}_4$ , forming a red, crystalline powder, m. p.  $183$ — $184^\circ$ ;

*benzaldehyde*,  $C_{14}H_{12}O_4N_4$ , crystallising in reddish-yellow needles, m. p. 224—225°; *anisaldehyde*, separating in garnet-red prisms, m. p. 238—239° (decomp.); *p-tolualdehyde*,  $C_{15}H_{14}O_4N_4$ , forming lustrous, deep red needles, m. p. 237—238°; *cinnamaldehyde*,  $C_{16}H_{14}O_4N_4$ , forming bright red needles, m. p. 263—264° (decomp.).  
T. H. P.

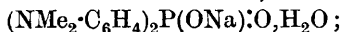
### Additive Reactions of the Phosphorus Halides. VIII. Kinetic Evidence in Regard to the Mechanism of the Reaction.

J. B. CONANT and V. H. WALLINGFORD (*J. Amer. Chem. Soc.*, 1924, 46, 192—202; cf. A., 1923, i, 498).—The reaction between benzaldehyde and phosphorus trichloride proceeds to a definite equilibrium both in the absence of a solvent and in benzene solution. The composition of the equilibrium mixture accords with the law of mass action. An earlier explanation of the mechanism of the reaction between carbonyl compounds, phosphorus trichloride, and acetic acid or anhydride assumed that this addition reaction was an intermediate step; this explanation is now abandoned. The gradual addition of small amounts of water to a mixture of benzaldehyde and the trichloride causes an irreversible reaction to take place. The product appears to be an open-chain phosphorus compound which readily loses hydrogen chloride to form a phostonic acid derivative (cf. Conant and Macdonald, A., 1921, i, 69). The reaction between a trichloride, an aldehyde, and acetic acid must be either a direct interaction of three molecules or a reaction in which some open-chain additive product of an unstable nature is an intermediate; the authors favour the latter alternative. F. A. M.

**Action of Halogen Derivatives of Phosphorus on some Phenolic Bases.** M. BOURNEUF (*Bull. Soc. chim.*, 1923, 33, [iv], 1808—1823).—When dimethylaniline (2 mols.) is heated at 70° with phosphorus trichloride (1 mol.), *p*-dimethylaminophenyldichlorophosphine,  $NMe_2 \cdot C_6H_4 \cdot PCl_2$ , is primarily formed, since sodium carbonate converts the product into a mixture (with dimethylaniline) of *tetramethyldiaminodiphenylphosphine oxide*,  $(NMe_2 \cdot C_6H_4)_2PHO$ , m. p. 169° (insoluble), and *dimethylaminophenylphosphinic acid* (soluble, and stable towards boiling water; cf. Michaelis and Schenk, A., 1888, 834). The above oxide, in presence of water and air, gives *tetramethyldiaminodiphenylphosphinic acid* (m. p. 249—250° on Maquenne block, or 199° [decomp.] in capillary tube), the latter being formed, together with *hexamethyltriaminotriphenylphosphine dihydroxide*,  $(NMe_2 \cdot C_6H_4)_3P(OH)_2$ , (m. p. 321° on Maquenne block) in the original condensation.

Diethylaniline and phosphorus trichloride give non-crystalline products.

Dimethylaniline (4 mols.), when heated with 1 mol. of phosphorus oxychloride at 130°, the product then being treated with sodium hydroxide, gives a mixture of (1) *tetramethyldiaminodiphenylphosphinic acid*, affording dimethylaniline when heated with calcium carbonate or with mineral acids; *sodium salt*,



(2) tetramethyldiaminodiphenylmethane, and (3) *hexamethyltri-aminotriphenylphosphine oxide*, m. p.  $262^{\circ}$ , and the corresponding hydroxide (cf. *supra*).

Diethylaniline is converted by phosphorus oxychloride into *tetraethyldiaminodiphenylphosphinic acid* (m. p.  $195^{\circ}$  [decomp.] or  $253\text{--}254^{\circ}$  on Maquenne block), which is decomposed on heating with calcium carbonate or with mineral acids to give diethylaniline; it forms a *dihydrochloride* (hygroscopic, m. p.  $185^{\circ}$  on Maquenne block), a *sodium salt* (crystallising with 6 or  $7\text{H}_2\text{O}$ ), and a *barium salt*.

Orthophosphoric acid and aniline give only aniline pyrophosphate.  
E. E. T.

**Studies Concerning the Direct Preparation of Organo-beryllium Halides.** H. GILMAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2693—2695).—Metallic beryllium, even when freshly cleaned by treatment with very dilute pure nitric acid, does not react with methyl iodide, ethyl iodide, benzyl bromide, bromobenzene, chlorobenzene, or  $\alpha$ -bromonaphthalene, using as solvents anhydrous ether, anisole, benzene, or  $\beta$ -ethoxynaphthalene, and as catalysts iodine, bromine, dimethylaniline, ethyl acetate, or freshly prepared Grignard reagent. Experiments in which freshly sublimed beryllium iodide was used, and one in which the reaction mixture was exposed to X-rays, were also unsuccessful.  
W. S. N.

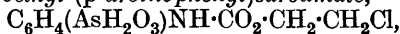
**Action of Polyhalogenated Derivatives of Methane and Ethane on Magnesyl [Magnesium Alkyl] Compounds. III.** R. BINAGHI (*Gazzetta*, 1923, **53**, 879—887; cf. A., 1922, i, 313, 1002).—Towards magnesium ethyl bromide, tetrachloromethane behaves similarly to chloroform, giving only ethylene and methane. With magnesium phenyl bromide, however, it yields, not tetraphenylmethane, but hexaphenylethane, triphenylmethyl peroxide, and triphenylcarbinol. This reaction exhibits marked analogy to the formation of hexaphenylethane by the action of zinc on triphenylchloromethane (cf. Gomberg, A., 1901, i, 77, 638; 1913, i, 259), which is yielded by the first phase of the reaction  $3\text{MgPhBr} + \text{CCl}_4 = \text{CPh}_3\text{Cl} + 3\text{MgBrCl}$ . The latter compound then reacts with another molecule of magnesium phenyl bromide, giving hexaphenylethane and bromobenzene, which also occurs among the products of the reaction  $2\text{CPh}_3\text{Cl} + \text{MgPhBr} = \text{MgCl}_2 + \text{PhBr} + \text{CPh}_3\text{CPh}_3$ . That the reaction proceeds thus is confirmed by the simultaneous formation of triphenylcarbinol, which, under the experimental conditions employed, could not arise except by the hydrolysis of the triphenylchloromethane either by the water added to precipitate the basic magnesium salt or by the current of steam used to remove the bromobenzene and diphenyl. Atmospheric oxidation of hexaphenylethane explains the formation of triphenylmethyl peroxide, which is not obtained when an atmosphere of hydrogen is employed.

In the reaction between magnesium ethyl bromide and tetrachloromethane, the first phase consists of the addition of four molecules of the magnesium alkyl compound to one molecule of the methane derivative, evolution of gases occurring only when

the product of the reaction is either left for some time or heated:  $\text{CCl}_4 + 4\text{MgEtBr} = 4\text{MgClBr} + 4\text{C}_2\text{H}_4 + \text{CH}_4$ .

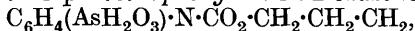
*Triphenylmethyl peroxide*,  $\text{O}:\text{O}(\text{CPh}_3)_2$ , forms a lustrous, white, microcrystalline powder, m. p.  $186^\circ$ , and yields rather low values for the molecular weight in freezing naphthalene. By dissolution in cold, concentrated sulphuric acid and subsequent addition of the solution to ice, triphenylcarbinol is obtained. Its *hexanitro*-derivative,  $\text{O}:\text{O}[\text{C}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_3]_2$ , has m. p.  $208\text{--}210^\circ$ . T. H. P.

**Arsino-aryl-amino-alcohols.** C. W. RODEWALD and R. ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 3102—3105).—Amino-arylsinic acids on condensation with  $\beta$ -chloroethyl and  $\gamma$ -chloropropyl chloroformates yield  $\omega$ -chloroalkyl-(arsino-aryl)carbamates. On treatment with two molecular equivalents of aqueous alkali, the  $\beta$ -chloroethyl compounds are converted into arsino-aryl oxazolidones and the  $\gamma$ -chloropropyl compounds into 3-arsino-aryl-tetrahydro-1 : 3 : 2-oxazones. Excess of alkali hydrolyses the oxazolidones to  $\beta$ -arsino-aryl amino-ethanols and the oxazones to  $\gamma$ -arsino-aryl-aminopropanols.  $\beta$ -Chloroethyl (p-arsinophenyl)carbamate,



has m. p. above  $250^\circ$ , the corresponding (o-arsinophenyl)carbamate having m. p.  $156\text{--}157^\circ$ .  $\beta$ -Chloroethyl (2-methyl-5-arsinophenyl)carbamate has m. p.  $193\text{--}195^\circ$ . The  $\gamma$ -chloropropyl (p-arsinophenyl)carbamate,  $\text{C}_6\text{H}_4(\text{AsH}_2\text{O}_3)\text{NH}\cdot\text{CO}_2\cdot[\text{CH}_2]_3\cdot\text{Cl}$ , and the corresponding o-arsinophenylcarbamate melt at  $245\text{--}246^\circ$  and  $130\text{--}132^\circ$ , respectively.  $\gamma$ -Chloropropyl (2-methyl-5-arsinophenyl)carbamate has m. p.  $160\text{--}162^\circ$ . 3-p-Arsinophenyl-2-oxazolidone,  $\text{C}_6\text{H}_4(\text{AsH}_2\text{O}_3)\cdot\text{N}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2$ , forms colourless plates, m. p. above  $280^\circ$ .

3-o-Arsinophenyl-2-oxazolidone crystallises in colourless plates, m. p.  $212\text{--}213^\circ$ . 3-p-Arsinophenyl-1 : 3 : 2-oxazone,



crystallises in white plates, m. p.  $245\text{--}247^\circ$ .  $\beta$ -(p-Arsinophenyl)-aminoethanol,  $\text{C}_6\text{H}_4(\text{AsH}_2\text{O}_3)\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$ , has m. p.  $173\text{--}174^\circ$ ; the corresponding o-arsinophenyl derivative has m. p.  $144\text{--}146^\circ$ .  $\beta$ -(2-Methyl-5-arsinophenyl)aminoethanol has m. p.  $144\text{--}146^\circ$ .  $\gamma$ -(p-Arsinophenyl)aminopropanol has m. p.  $167\text{--}168^\circ$ ; the similar o-arsinophenyl compound has m. p.  $84\text{--}85^\circ$ .  $\gamma$ -(2-Methyl-5-arsinophenyl)aminopropanol melts at  $142\text{--}143^\circ$ . p-Arsinophenyl- $\beta$ -hydroxyethyl nitrosoamine,  $\text{C}_6\text{H}_4(\text{AsH}_2\text{O}_3)\text{N}(\text{NO})\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$ , is obtained from the corresponding aminoethanol and nitrous acid. It crystallises in bright yellow needles, m. p.  $236^\circ$ . p-Arsinophenyl- $\gamma$ -hydroxypropyl nitrosoamine,  $\text{C}_6\text{H}_4(\text{AsH}_2\text{O}_3)\text{N}(\text{NO})\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$ , is prepared similarly. It forms yellow crystals, m. p.  $142\text{--}143^\circ$ . The arsino-aryl-amino-alcohols are much less toxic than the corresponding arsanilic acids. F. G. P.

**The Protein Matter of Bile.** J. F. LOGAN (*J. Biol. Chem.*, 1923, **58**, 17—32).—Attempts have been made by various methods to isolate a pure protein from ox bile, and elementary analyses have been made of several of the preparations obtained. The



results, however, indicate that, in each case, the product was probably a mixture of glucoprotein with a small amount of nucleoprotein. Direct acid hydrolysis did not liberate a reducing carbohydrate, but when this followed preliminary treatment with alkali the product had slight reducing properties. E. S.

**Proteins of Wheat Bran. I. Isolation and Elementary Analyses of a Globulin, Albumin, and Prolamine.** D. B. JONES and C. E. F. GERSDORFF (*J. Biol. Chem.*, 1923, **58**, 117—131).—Wheat bran, as free as possible from other portions of the wheat kernel, has been found to contain 17.25% of protein ( $N \times 6.25$ ). By extracting the bran successively with water, 4% sodium chloride, 70% alcohol, and 0.5% sodium hydroxide, 86.61% of the total protein has been removed and an albumin, a globulin, and an alcohol-soluble protein (prolamine) have been isolated from the first three extracts. Elementary analyses gave the following results: albumin, C=53.21, H=6.71, N=15.42, S=1.35%; globulin, C=53.43, H=7.40, N=17.76, S=0.91%; prolamine, C=54.25, H=6.75, N=15.35, S=1.35%. E. S.

**Theory of Vegetable Tanning. II. Dehydration of the Gelatin Sol by Tannic Acid, Crystalline Tannins, and Simpler Phenols.** H. G. B. DE JONG (*Rec. trav. chim.*, 1924, **43**, 35—67; cf. A., 1923, i, 821).—The stability of a gelatin sol is governed by two factors, electric charge and hydration. At the isoelectric point,  $p_H = 4.7$ , the gelatin sol is uncharged, but retains its stability above the gelation temperature (about 40°) on account of its hydration. Increase of the hydrogen-ion concentration causes the particles to assume a positive charge, up to a maximum, beyond which the charge decreases. In the same way, decrease of the hydrogen-ion concentration imparts a negative charge to the particles up to a point, beyond which discharge takes place. Isoelectric or discharged sols can be coagulated by addition of dehydrating substances such as alcohol. Hydration changes in a sol can be followed by viscosity measurements, although the charge can also influence the viscosity (the quasi-viscous effect). This view of gelatin sols, it is claimed, expresses their behaviour better than the view which regards them as ion disperse systems.

It is shown by viscosimetric measurements that gelatin sols at 40° obey Poiseuille's law, and that the viscosity minimum is situated, at 40°, at the isoelectric point. The effect of tannic acid and phenols on gelatin sols was studied viscosimetrically at this temperature at different hydrogen-ion concentrations. At a small concentration of hydrochloric acid (0.003*N*), tannic acid has a marked dehydrating action, indicated by a lowering of the viscosity, but no precipitation occurs. At the isoelectric point tannic acid has both a dehydrating and a positive charging action on account of its own slight acidity. Consequently the viscosity minimum of a gelatin sol containing tannic acid lies at a small nominal concentration of alkali, which serves to restore the medium to the  $p_H$  of the isoelectric point. Further addition of alkali causes a powerful

rehydration. The dehydration is relatively greatest at the isoelectric point, and, if pushed far enough, causes coagulation. The primary action of tannic acid on gelatin sols is therefore the same as on agar sols (*loc. cit.*). Phenol, pyrocatechol, resorcinol, quinol, pyrogallol, phloroglucinol, and ethyl gallate all have a similar dehydrating action on gelatin sols, the dehydrating action increasing rapidly with the number of phenolic groups. In the case of the two crystalline tannins, *d*-catechin and hamameli tannin, the dehydration is more powerful than with the simpler phenolic compounds. In the case of digalloylglucose, however, the positively charging influence of the tannin, tending to increase the viscosity, exceeds the dehydrating action, tending to lower the viscosity, at the isoelectric point, so that the viscosity is actually raised. However, a little sodium hydroxide in this case causes complete coagulation. Picric acid added to an isoelectric gelatin sol exerts at first a positively charging action, but with greater concentrations dehydration becomes very powerful, the positively charging action decreases, and finally precipitation occurs. Sodium picrate has no dehydrating action.

E. H. R.

**Gradual Decomposition of Proteins. Partial Hydrolysis of Keratin (Hog Bristles).** E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1924, **132**, 1—11).—Hog bristles (400 g.) were heated with 1% hydrochloric acid (2 litres) in an autoclave at 120° for five hours, the product was neutralised with ammonia and then evaporated to dryness, mixed with sand and extracted with ethyl acetate. From the extract there were obtained *d*-alanylglycine anhydride, m. p. 250° (decomp.); prolyl-leucine anhydride, m. p. 158°,  $[\alpha]_D^{20} -46.3^\circ$  (in alcohol) (apparently partly racemised); *l*-prolyl-*d*-valine anhydride, m. p. 250—252°, and a compound,  $C_{14}H_{23}O_3N_3$ , m. p. 180—182°, which yields, on hydrolysis, proline, leucine, and alanine, and is formed from these by the loss of 3 mols. of water. From the product of the hydrolysis of hog bristles, using 70% sulphuric acid for seven days, the only pure compound isolated was *l*-leucylserine,  $[\alpha]_D^{21} -44.3^\circ$  (in water), and from the product of the hydrolysis by 70% sulphuric acid for fourteen days, a *valylvaline*, m. p. 255—260°,  $[\alpha]_D^{20} +3.5^\circ$  (in water), was obtained. In both cases, however, other scission products were shown to be present.

V. O. K.

### Biochemistry.

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**Iron Content of the Blood and Spleen in Infectious Equine Anæmia.** L. H. WRIGHT (*J. Agric. Res.*, 1923, **26**, 239—242).—Analyses of the blood and spleens of a number of normal and anæmic animals are given. It would appear that the average total of the solids—iron, hæmoglobin, and erythrocytes—is considerably greater in the case of normal horses. Anæmia is indicated

more by a lack of iron, and therefore of hæmoglobin, than by the number of erythrocytes. The increased iron content of the spleens of young horses is not considered to be entirely due to the larger amount of blood in the organ. A. G. P.

**Relation between the Phosphate in Blood and Urine.** V. B. WIGGLESWORTH and C. E. WOODROW (*Proc. Roy. Soc.*, 1924, B, 95, 558—570).—After the ingestion of acid or of alkaline sodium phosphate containing 1.5—2 g. of phosphorus, there is a 50—60% increase in the phosphate content of the blood, and simultaneously a large increase in the urinary phosphate. The urinary excretion of phosphorus is roughly proportional to the excess of phosphate above a certain value in the blood. Little change in the rate of excretion of phosphorus is caused by large variations in the amount of water excreted. The plasma and corpuscles normally contain equal amounts of inorganic phosphate, but when the phosphate in the whole blood is increased, that in the plasma exceeds that in the corpuscles. The organic fraction of the acid-soluble phosphorus does not increase after phosphate ingestion, or after ingestion of glucose with or without phosphate. W. O. K.

**Some Experiments and Remarks on the Possible Transformation of *d*-Glucose in the Intestine and on the Nature of the Blood-sugar.** S. VAN CREVELD (*Biochem. J.*, 1923, 17, 860—871).—In agreement with Stiven and Reid (*A.*, 1923, i, 1153), the observations of Hewitt and Pryde (*A.*, 1920, i, 648) have not been confirmed. Using the aqueous humour of the eye and the blood-serum ultra-filtrate, it is shown that, although the former fluid when freshly collected decolorises potassium permanganate, neither fluid shows any mutarotation, and the copper-reducing value and the rotatory power are in close correspondence. In general, from the author's observations, no experimental support is forthcoming for the view that "reactive" sugars are intermediate metabolites, but the view that such may possibly occur is not abandoned. J. P.

**The Absence of Effect of Insulin on the Heat Production in Isolated Frog's Muscle.** R. AZUMA and W. HARTREE (*Biochem. J.*, 1923, 17, 875—877).—Insulin has no effect either on the initial or on the recovery heat production of the isolated sartorius muscle of the frog. Injection of insulin into the intact frog produces convulsions which are relieved by glucose administration. J. P.

**Studies on Carbohydrate Metabolism. II. On the Preparation of an Anti-diabetic Hormone from Yeast.** I. H. B. HUTCHINSON, W. SMITH, and L. B. WINTER (*Biochem. J.*, 1923, 17, 683—692).—A glucokinetic substance with physiological reactions closely resembling those of insulin may be extracted from yeast by methods similar to those used for preparing the pancreatic hormone. The lowering of blood-sugar may be followed by con-

vulsions which are relieved by glucose injections. Various yeasts give very variable results, and only in the case of active yeasts does the activity increase on culturing. J. P.

**Studies on Carbohydrate Metabolism. III. On the Formation of an Anti-diabetic Hormone by the Action of a Bacillus. (Preliminary Communication.)** H. B. HUTCHINSON, W. SMITH, and L. B. WINTER (*Biochem. J.*, 1923, **17**, 764—767).—Injection into rabbits of an extract of the medium in which cultures of a coliform bacillus from yeast had been grown, produced hypoglycaemia and convulsions which were relieved by glucose administration. J. P.

**The Transformation of Creatine into Creatinine.** A. HAHN and L. SCHÄFER (*Z. Biol.*, 1924, **80**, 195—210).—A series of experiments on rabbits and on human beings shows that neither oral administration nor subcutaneous injection of creatine causes an increased output of creatinine. Of the creatine administered, a variable proportion appears in the urine; the fate of the remainder is unknown. The transformation of creatine into creatinine is a function of the muscles, and depends on the physico-chemical conditions there obtaining (probably the most important being the hydrogen-ion concentration), and not on the action of an enzyme. C. R. H.

**The Fate of Indolepropionic Acid in the Animal Organism.** F. W. WARD (*Biochem. J.*, 1923, **17**, 907—915).—Indolepropionic acid was prepared by the anaërobic action of a mixed culture of *Bacillus coli*, *B. chauvei*, *B. sporogenes*, and *B. oedemaciens* on tryptophan (cf. Hopkins and Cole, A., 1903, i, 590). Intravenous injection of indolepropionic acid gives rise to a keto or enol form of a 2-hydroxyindole compound. Indole-ethyl alcohol is oxidised to indole-acetic acid, whilst indolecarboxylic acid is excreted unchanged as a conjugated compound, and is therefore not an intermediate step in the oxidation of indolepropionic acid. J. P.

**Experiments with Two Methods for the Study of Vitamin-B.** H. C. SHERMAN and HARRIET EDGEWORTH (*J. Amer. Chem. Soc.*, 1923, **45**, 2712—2718).—The importance of vitamin-B as a factor in food values makes it desirable that quantitative methods of known precision be applied in all studies of the vitamin contents of different foods. The gravimetric yeast-growth method was employed, using the Williams medium, and dried skimmed milk was used as the source of the vitamin. The growth was continued for thirty hours at 18°, being then arrested by the addition of formaldehyde. Consistent results were obtained, the probable errors being of the order of 1% of the observed numerical values. The method is open to the objection that the increased growth measured may be due to the introduction of other substances favourable to yeast-growth. The rat-growth method was also used and gave quantitative results, the probable error being in this case 2—4% of the numerical values. F. G. P.

**A Critical Investigation and an Application of the Rat-growth Method for the Study of Vitamin-B.** H. C. SHERMAN and ADELAIDE SPOHN (*J. Amer. Chem. Soc.*, 1923, **45**, 2719—2728).—The rats used were fed on basal diets designed to be devoid of vitamin-B, and to contain all the other essential food factors in as nearly as possible the optimum proportions. Variations in the basal diets were made, fixed amounts of milk being used as sources of vitamin. It appears to be established from the results obtained that all increases of growth resulting from the addition of the milk to the basal diets used may be attributed to the vitamin-B thus furnished. There is no evidence of any measurable diminution of vitamin-B in milk powder heated dry at 100°, with free access of air. Probably about one-fourth of the vitamin is destroyed when the milk is heated in the fluid state for six hours at 100°.

F. G. P.

**A Quantitative Study of the Destruction of Vitamin-B by Heat.** H. C. SHERMAN and M. R. GROSE (*J. Amer. Chem. Soc.*, 1923, **45**, 2728—2738).—The juice of canned tomatoes was used as a source of vitamin-B in this investigation, and the effect of heating at 10° intervals over the range of 100—130° has been examined, using the rat-growth method (see preceding abstract) as a measure of the vitamin content. At 100°, in a slightly acid medium, there is an appreciable destruction of the vitamin, and the results obtained at different temperatures show that the temperature coefficient of the destructive process is distinctly lower than that of most chemical reactions, resembling, in this respect, that of vitamin-C. It is therefore improbable that the vitamin is an unstable protein, and inappropriate to group it with enzymes, since typical enzymes have shown rates of destruction by heat with high temperature coefficients up to the point at which the enzymic activity was entirely destroyed.

F. G. P.

**A Preliminary Note on the Destruction of Vitamin-B by Age.** G. M. FINDLAY (*Biochem. J.*, 1923, **17**, 887—890).—Indian lentils and peas which had been kept for thirty-eight years and had lost their power of germination showed, when fed to rats, a slight loss of vitamin-B in comparison with recent samples of these seeds.

J. P.

**The Alleged Specific Colour Reaction for the Antiscorbutic Factor.** H. D. KAY and S. S. ZILVA (*Biochem. J.*, 1923, **17**, 872—874).—The blue colour given by the Bezssonoff reagent (*Bull. Soc. Chim. biol.*, 1922, **4**, 83) with certain preparations of the antiscorbutic vitamin is not specific. The constituent responsible for the coloration is, like the vitamin, destroyed by oxidation.

J. P.

**Contributions towards the Study of the Lipoids of the Human Brain.** F. POPESCU (*Bul. Soc. Chim. România*, 1923, **5**, 83—92).—The author describes in detail the isolation of the lipoids present in the human brain, and extends the general methods for the determination of lipoids in blood (Grimbert and Laudet, A., 1913,

ii, 164) to this case. A new method for the desiccation of the brain by means of freezing is described. After complete freezing, the brain is maintained at 40° for half an hour and the soft paste so obtained dried rapidly and completely in a vacuum. Extraction of the dried powder with acetone removes cholesterol, fats, and the phosphatides. The cholesterol separates from the hot extract on cooling, and is removed by filtration. The whole of the cholesterol present in the brain is found to exist in the free state and not combined with oleic acid. From the residue, a new *lipoid*, of the phosphatide group, having the composition C = 67.02%, H = 9.93%, N = 2.50%, P = 0.534%, was isolated. This is soluble in alcohol and acetone, insoluble in cold ether, is precipitated by cadmium chloride, and gives no reaction with nitric or sulphuric acid. The solution of the lipoids remaining is precipitated with lead acetate, and yields mainly lecithin and a small quantity of kephalin. The residue from the acetone extraction is extracted with light petroleum; addition of alcohol to the concentrated extract precipitates kephalin (7—8%), and the alcoholic solution contains lecithin (5.5%).

The residue insoluble in acetone and light petroleum is finally extracted with alcohol, and this extract yields the substances contained in the grey matter (protagon), sphingomyelin (containing phosphorus) and phrenosin, and kersin (phosphorus-free).

The determination of the lipoids present in a tubercular brain shows that the quantity of cholesterol is larger, and the quantity of other lipoids smaller, than in the normal brain.

For details of the separation and determination, the original paper must be consulted.

J. W. B.

**Gradual Decomposition of Proteins. Partial Hydrolysis of Keratin (Hog Bristles).** E. ABDERHALDEN and E. KOMM.—(See p. 343.)

**Auto-histo-radiographic Method for the Detection in Organs of Injected Polonium.** A. LACASSAGNE and (MME.) J. S. LATTÈS (*Compt. rend.*, 1924, 178, 488—490).—The authors have made use of the  $\alpha$ -ray emission of polonium, and its relatively long period of disintegration of 140 days, to obtain auto-radiograms of organs capable of retaining it. A rabbit was injected with polonium salts and killed after six days. Thin sections of the principal organs were made and placed on the sensitive surface of a photographic plate. After several days' exposure, records were obtained of the distribution of polonium. Retention by the various organs was very unequal, being greatest in the organs of elimination.

A. B. H.

**Researches on Cellular Disintegration.** A. NODON (*Compt. rend.*, 1924, 178, 486—487).—It is shown that living organisms, vegetable and animal, exhibit radioactivity, which appears to be a function of the degree of vitality of the organism. The radioactivity varied with the nature of the organism, and was increased by sunlight. The conclusion is drawn that both the disintegration

of radium and that of the living cell have their origin in exterior ultra-radiations, also that the atoms constituting the living material must acquire special properties, which allow them to disintegrate in a manner similar to those of the radioactive elements.

A. B. H.

[Cellular Disintegration.] D. BERTHELOT (*Compt. rend.*, 1924, 178, 487).—The author observed in 1909 and 1910 phenomena similar to those observed by Nodon (preceding abstract). These he found to be due solely to changes of humidity.

A. B. H.

**The Extraction of the Concretion Gland and Nephridium of *Cyclostoma elegans*.** P. QUAST (*Z. Biol.*, 1924, 80, 211—222).—A qualitative analysis of the concretion gland indicated the presence of silicates among the inorganic constituents and of uric acid, xanthine, hypoxanthine, and adenine among the organic ones. In the nephridium were found creatinine and allantoin.

C. R. H.

**On the Participation of a Peroxidase in the Appearance of the Pigment in *Drosophila melanogaster*, Loew.** DE LUNA (*Compt. rend.*, 1924, 178, 525—527).—It is shown that a peroxidase takes part in the pigmentation of *Drosophila*. The peroxidase has the same distribution as the pigment. The appearance of the pigment is a function of temperature if the quantities of oxygen and peroxidase are constant; anaesthetics retard pigmentation.

A. B. H.

**The Extractives of *Eledone moschata*.** D. ACKERMANN, F. HOLTZ, and F. KUTSCHER (*Z. Biol.*, 1924, 80, 155—162).—From this organism the authors have isolated betaine, taurine, lactic acid, and in addition two new bases which are designated *eledonine* ( $C_{14}H_{30}O_3N_2$ ) and *homoeledonine* ( $C_{15}H_{32}O_3N_2$ ). They both give chloraurates melting indefinitely at 225—235°. The formula previously given to crangonine (A., 1908, ii, 53) is revised and now becomes  $C_{13}H_{28}O_3N_2$ , so that these three bases would appear to be members of an homologous series.

C. R. H.

**The Extractives of *Holothuria tubulosa*.** D. ACKERMANN, F. HOLTZ, and H. REINWEIN (*Z. Biol.*, 1924, 80, 163—170).—In addition to betaine, adenine, and lactic acid, there was obtained from the lysine fraction a *chloraurate* (m. p. 134°) of a base isomeric with homoeledonine (see preceding abstract). This substance on hydrolysis with hydrochloric acid gives betaine, and has therefore been named betainogen.

C. R. H.

**The Extractives of *Mytilus edulis*.** D. ACKERMANN (*Z. Biol.*, 1924, 80, 193—194).—Adenine was obtained in the purine fraction, and in the filtrate from the phosphotungstic acid precipitation was found the cyclose mytilitol (A., 1921, i, 764).

C. R. H.

**Proteins of Milk-serum. Their Separation by the Acetone Method.** M. PIETTRE (*Compt. rend.*, 1924, 178, 333—335).—The milk is coagulated rapidly by shaking at 35° and adding rennet,



drop by drop, until casein begins to separate in a flocculent condition, after which the serum is filtered off by suction. It is rendered feebly acid with hydrochloric acid, extracted with ether, and the residual liquid precipitated by means of acetone and filtered. The precipitate is digested with water, and *N*/10-hydrochloric acid added in sufficient quantity to precipitate the lactoglobulin, which is then collected (using a centrifuge) and found to have  $[\alpha]_D -31^\circ 12'$  in aqueous sodium hydroxide solution. The clear filtrate on precipitating, *e.g.*, with alcohol, affords the pure lactalbumin, with  $[\alpha]_D -41.23^\circ$ . Milk contains, on the average, 2.3 g. of globulin and 3.2 g. of albumin per l. E. E. T.

**Observations on certain Reducing and Oxidising Reactions of Milk.** P. HAAS and T. G. HILL (*Biochem. J.*, 1923, 17, 671—682).—There is present in milk an oxygen acceptor capable of reducing sodium nitrate to nitrite, to which the name “*atite*” is provisionally given, and also an oxygen donator bringing about the reverse conversion of nitrite to nitrate (*cf.* Bach, A., 1911, i, 759) which has been called “*itate*.” *Atite* is precipitated with the milk proteins, and, although thermolabile, is not regarded as being an enzyme. Unlike *atite*, which is most active in the absence of oxygen, *itate* is active only in its presence, but in its thermolability and precipitation reactions it resembles the former. Both substances require an accelerator, aldehydes, notably acetaldehyde, being most active. Acetaldehyde in the presence of oxygen destroys both *atite* and *itate*. The diminution in the peroxydase reaction of milk is parallel to the rate of destruction of *itate*, and the possible identity of the last with peroxydase is considered. *Atite* is distinct from Schardinger’s reductase. J. P.

**The Protein Matter of Bile.** J. F. LOGAN.—(See p. 341.)

**The Occurrence of Amines in Urine.** P. N. VAN ECK (*Pharm. Weekblad*, 1924, 61, 65—73).—In testing samples of urine for blood, it was occasionally observed that a beautiful orange-red colour developed on addition of benzidine and glacial acetic acid, and before the addition of hydrogen peroxide. Out of 61 samples of urine, 25 gave positive results. Investigation failed to show that this was due to any specific malady or remedy. Negative tests were obtained with some twenty substances likely to be present in urine, and with the extracts obtained by shaking urine with the ordinary organic solvents. It was found, however, that the distillates from many urines gave the reaction, and contained alkylamines; the lower alkylamines were then examined, and all gave the reaction. By testing urine from healthy persons it was found that a positive result always followed a meal of pickled herrings, in which amines were identified, and that amines could be identified in the distillates from these urines, by the *isonitrile* and nitroprusside reactions.

A collection of observations on the occurrence of alkylamines in animal and vegetable matter from various sources is given.

S. I. L.

**Camphorylcarbamates and their Physiological Action.** H. E. FIERZ-DAVID and W. MÜLLER.—(See i, 301.)

**The Physiological Effect of Gossypol.** P. MENAUL (*J. Agric. Res.*, 1923, **26**, 233—237).—The toxic effect of gossypol on rabbits was slow to appear if the substance was given with the food, but when it was injected directly into the blood-stream, the effects were apparent almost at once. It was found that gossypol prevents the normal oxygen-interchange in the blood, and also has a hæmolytic effect. Death is caused by a reduced oxygen-carrying power of the blood, which considerably increases the work of the respiratory and circulatory organs. This explained the condition of dead animals, viz., a passive hyperæmia and œdema of the lungs and some hydrothorax, which is directly due to the effect of gossypol and does not result from bacterial action. A. G. P.

**Hypnotic Properties of Hydrobenzoin and of its Alkylated Homologues (Symmetrical Diarylglycols). Relations between Physiological Activity and Molecular Weight.** M. TIFFENEAU and C. TORRES (*Compt. rend.*, 1924, **178**, 237—239).—The hypnotic effect, on the stickleback, of hydrobenzoin, and of its methyl, ethyl, isopropyl, butyl, isobutyl, and isoamyl derivatives has been measured (cf. A., 1923, i, 676). It is concluded that the hypnotic effect and molecular weight increase together. When, in a series (e.g., in the present one, at the isoamyl member) the solubility limit is reached, the hypnotic effect then decreases as the molecular weight increases, unless biliary substances are added to promote absorption by the organism. E. E. T.

**Constitution and Mode of Action of Biochemical Catalysts or Enzymes. Effects of Electrolysis on Enzymes of Pancreatic Juice and on the Amylase of Germinated Barley.** F. MAIGNON (*Compt. rend.*, 1924, **178**, 420—423).—Preparations of the enzymes from the pancreatic juice of the cow, and of amylase from barley have been found to contain calcium, iron, and chlorine. On being electrolysed in aqueous solution, coagulation sets in near the anode, but not near the cathode. Finally, coagulation ceases, and the enzyme is found to be inactive, owing to removal of the inorganic constituents by electrolysis. The author concludes that the chlorine-ion is attached to the proteinic micellæ, the kations (Fe and Ca) being free in the liquid medium. In the case of hydriion, the latter is adsorbed on the external surface of the micellæ, this explaining (on ordinary adsorption theories) the great catalytic activity of that hydriion. E. E. T.

**The Azine and Azonium Compounds of the Proteolytic Enzymes.** I. H. R. MARSTON (*Biochem. J.*, 1923, **17**, 851—859).—Dyes of the azine group (eurhodines, safranines, indulines), but not their leuco-bases, quantitatively precipitate the proteolytic enzymes pepsin, trypsin, erepsin, and papain from their solutions. The enzyme is regarded as attaching itself to the azine nitrogen atom or atoms. Pepsin may be recovered in solution from the pepsin-azine precipitate by treatment with 0.5% hydrochloric acid and removal of the dye by extraction with amyl alcohol. It is

suggested that the proteolytic enzymes may become attached to proteins, preliminary to hydrolysing them, through the nitrogen atoms of diketopiperazine groupings, and the results are interpreted in favour of the view that such groupings are present in the protein molecule. J. P.

**Further Studies on the Enzymic Degradation of Polypeptides Composed of Amino-acids not yet found among the Degradation Products of the Proteins.** E. ABDERHALDEN and A. MOSCHINI (*Fermentforschung*, 1923, 7, 176—178).—Yeast maceration juice degrades *d*-*n*-valyl-*l*-tyrosine but not *l*-*n*-valyl-*l*-tyrosine. In the former case, the formation of tyrosine and *d*- $\alpha$ -amino-*n*-valeric acid was demonstrated. The dipeptides were synthesised by combining *l*-tyrosine or its ester with *d*- or *l*- $\alpha$ -bromo-*n*-valeryl chloride. S. S. Z.

**The Action of Enzyme Solutions on 3:5-Di-iodo-*l*-tyrosine and Glycyl-3:5-di-iodo-*l*-tyrosine.** E. ABDERHALDEN and W. STIX (*Fermentforschung*, 1923, 7, 179—182).—Yeast maceration juice effects a cleavage in glycyl-3:5-di-iodo-*l*-tyrosine. Extract of pancreas and of the mucous membrane of the stomach do the same, but more slowly. Thyroid extract and thyroid press-juice have no action on the compound. S. S. Z.

**The Action of the Enzymes of the Gastro-intestinal Tract on Diketopiperazine.** E. ABDERHALDEN and K. GOTO (*Fermentforschung*, 1923, 7, 169—175).—It is concluded that neither trypsin nor pepsin has an appreciable hydrolytic action on *d*-alanylglycine anhydride, and that the hydrolysis which is effected by alkaline or acid solutions of these enzymes is due to that alkalinity or acidity. The anhydride was obtained by hydrolysing silk residues. S. S. Z.

**Urease. II. The Mechanism of the Zymolysis of Urea.** W. R. FEARON (*Biochem. J.*, 1923, 17, 800—812).—Using the method described by the author (A., 1923, i, 497), it is shown that cyanic acid and ammonia, but not carbamic acid, are intermediate products of the zymolysis of urea (cf. Mack and Villars, A., 1923, i, 405). Soja urease, which carries a negative electric charge, adsorbs urea from alcoholic solution and ammonia from aqueous solution. It is concluded that urease adsorbs its substrate, and that the adsorbed urea is then decomposed into ammonia and cyanic acid. The former is readsorbed as such by the enzyme and the latter is hydrolysed by the solvent water. The enzyme is again liberated by combination of the adsorbed ammonia with ammonium hydrogen carbonate and is free to adsorb more urea. The cyclic process continues until arrested by accumulation of ammonium carbonate or by exhaustion of the substrate. J. P.

**Studies on Enzyme Action. The Relationship between the Chemical Structure of certain Compounds and their Effect upon the Activity of Urease.** E. W. ROCKWOOD and W. J. HUSA (*J. Amer. Chem. Soc.*, 1923, 45, 2678—2689).—The effect of various compounds on the activity of urease obtained from jack-bean meal has been studied, and the following results have been obtained.

Certain compounds exert a promoter effect on the catalytic activity of the urease, others have an inhibitory action. These effects are independent of changes in hydrogen-ion concentration. The promoter effect is related to the presence of both amino and carboxyl groups. Compounds containing only one of these groups were not promoters. The promoter action seems to be a function of the distance between the groups, all the  $\alpha$ -amino-acids used being marked promoters,  $\beta$ -amino-acids having a slight effect, and  $\gamma$ -amino-acids none. With the aminobenzoic acids, the order of decreasing effect is ortho, meta, para. A second amino or carboxyl group in an  $\alpha$ -amino-acid increases the promoter action.  $\alpha$ -Amino-acids of the heterocyclic nitrogen compounds have a slightly greater effect than simple  $\alpha$ -amino-acids. Ammonium chloride, guanidine sulphate, creatine, and creatinine have no promoter effect. Enzymes appear to be of a protein nature or to occur associated with protein, and when the protein is removed from the enzyme solution, the activity is lost. The experiments which show the promoter action of  $\alpha$ -amino-acids and peptones indicate that the protein part of enzyme preparations is an important factor in the action of the enzyme. The results obtained also tend to disprove the hypothesis that the promoter effect is due chiefly to prevention of decomposition of the enzyme.

F. G. P.

#### Experiments Demonstrating the Existence of Specific Cytolysins for the Various Organs of the Animal Organism.

A. ZERKOWITZ (*Fermentforschung*, 1923, 7, 223—228).—It is claimed that some of the experiments carried out with the blood sera of normal and castrated rabbits, and the testicles and other organs of these animals, confirm the author's hypothesis of the existence of specific cytolysins.

S. S. Z.

**Carbohydrate and Fat Metabolism in Yeast.** I. S. MACLEAN and D. HOFFERT (*Biochem. J.*, 1923, 17, 720—741).—Yeast incubated in oxygenated water shows a diminished carbohydrate content and an increase in fat. Propyl, butyl, and *iso*amyl alcohols inhibit this conversion, whilst the sodium salts of formic, propionic, and butyric acids, glycol, glycerol, and acetone, in 0.1 *M*-solution, behave like water. Incubation in 0.5% solutions of ethyl alcohol, or of the sodium salts of acetic, lactic, and pyruvic acids gives the same results as 0.5% solutions of dextrose; in the first two cases increase of the total carbohydrate of the yeast-cell is observed. In the presence of dextrose, lævulose, and sucrose the yeast-cell stores both carbohydrate and fat. Maltose is exceptional in producing a greater carbohydrate and lesser fat storage than the other sugars investigated. It is suggested that maltose is assimilated as such by the yeast-cell. Continuous oxygenation during incubation greatly increases the amount of fat produced, but has little or no effect on the carbohydrate. In oxygenated solutions, added phosphate reduces the amount of carbohydrate stored and increases the fat formation. Phosphate is taken up by the cell in proportion to the sugar concentration of the solution; more phosphate is taken up from oxygenated than from non-oxygenated solutions. It is

suggested that the formation of hexose phosphate is the first stage in the conversion of carbohydrate into fat. J. P.

**Irregularities of the Lactic Fermentation in Presence of certain Antiseptics.** A. LUMIÈRE (*Compt. rend.*, 1924, **178**, 258—260).—It is shown that the supposed irregularity observed by Richet (*ibid.*, 1923, **177**, 1262) in connexion with the antiseptic action of mercuric chloride is due to the use, by this author, of inocula from non-uniform bacterial suspensions. If the latter are well shaken, in order to break up large aggregates, perfectly uniform results are obtained with antiseptics. E. E. T.

**Production of  $\beta$ -Hydroxybutyric Acid by Microbial Processes.** M. LEMOIGNE (*Compt. rend.*, 1924, **178**, 253—256; cf. A., 1923, i, 881).—The alcoholic extract of fresh cultures of *Bacillus M.* gives, on evaporation and distillation of the residue,  $\alpha$ -crotonic acid.  $\beta$ -Hydroxybutyric acid is therefore a normal physiological product of the bacillus, and is formed from intracellular reserve material. E. E. T.

**Variations in Hydrogen-ion Concentration under the Influence of the Assimilation of Nitrates by *Aspergillus repens*, De Bary.** BACH (*Compt. rend.*, 1924, **178**, 520—522).—When *Aspergillus repens*, De Bary, is allowed to grow in a suitable medium containing nitrates and for which  $p_H$  has an initial value between 3.6 and 8.4, the hydrogen-ion concentration after ten days approximates to the value  $p_H = 6$ . The addition of potassium phosphate reduces the rate of the change, but does not alter its sense. A. B. H.

**The Accumulation and Formation of Urea in Mushrooms.** N. N. IVANOV (*Biochem. Z.*, 1923, **143**, 62—74).—The urea content and nitrogen distribution in mushrooms, artificially cultivated in manure, has been estimated at various stages of growth. The dried fungi may contain up to 13% of urea. The amount of urea increases during the ripening process until spore formation begins, autolysis of the proteins and chitin leading to an increase in the amino compounds, which are then converted to urea. By treatment with chloroform, the formation of urea may be inhibited. The high urea content is ascribed to the artificial culture in the nitrogen-rich medium. A close analogy is drawn between the formation of urea and asparagine (cf. also A., 1923, i, 428, 520). J. P.

**The Migration of Inulin in the Grafts of Composites.** H. COLIN and R. FRANQUET (*Compt. rend.*, 1924, **178**, 518—520).—It is shown that when a branch of a plant containing inulin is grafted on a subject which does not normally contain this substance, the latter migrates into the subject, but undergoes hydrolysis to lævulose. It is sometimes possible, however, to detect the inulin in the immediate vicinity of the graft. The optical rotations of the sugars above and below the graft are frequently in opposite direction. A. B. H.

**The Acidity of Maize and its Relation to Vegetative Vigour.** A. M. HURD (*J. Agric. Res.*, 1923, **25**, 457—468).—Measurements

of the hydrogen-ion concentration and titratable acidity of the expressed juice of maize plants, showed these two factors to vary inversely as the vigour of the plant. Alterations in sap density did not account for variations in acidity, with the exception of a few cases where particularly high values were obtained. The concentration of titratable acid in the leaf-juice was always greater than in the stalk, whatever the state of vigour of the plant. In vigorous plants, the  $p_H$  values of the leaf juices were greater than those of the stalk juices. This relationship was reversed in the case of weakly, stunted plants. The density of the juice of the leaves was greater than that of the stalks, whether the plant was vigorous or otherwise. Variations in the acidity of plants of the same strain but in a different environment were considerably greater than those of different varieties under similar conditions of growth and vigour.

A. G. P.

**On the Significance of the Ash Content of certain Marine Algæ.** P. HAAS and B. RUSSELL-WELLS (*Biochem. J.*, 1923, **17**, 696—706).—From a comparison of the sulphate content of the hydrolysed aqueous extracts of certain marine algæ (*Rhodophyceæ* and *Phæophyceæ*) with the sulphate content observed after incineration, it is found that the former is greater than the latter and frequently in the ratio 2 : 1. This is ascribed to the presence of a complex calcium organic sulphate of the type  $R\langle\begin{smallmatrix} O\cdot SO_2\cdot O \\ O\cdot SO_2\cdot O \end{smallmatrix}\rangle Ca$ , in which the calcium, but not the sulphate, is freely ionised. These colloidal complexes have a measurable conductivity and osmotic properties to which considerable importance is attached (cf. Harwood, T., 1923, **123**, 2254).

J. P.

**On the Determinable Iodine of *Laminaria flexicaulis*.** P. FREUNDLER (*Compt. rend.*, 1924, **178**, 515—517).—The iodine content of perfectly fresh *Laminaria flexicaulis* has been determined by three methods. The author concludes that the alga contains, in addition to its normal iodide content, a fairly constant quantity of a substance of unknown composition which is transformed into iodide on the death of the organism.

A. B. H.

**Quantitative Diurnal Variation of Starch in Green Plant Leaves.** P. P. STANESCU (*Compt. rend.*, 1924, **178**, 117—119).—The starch-content of green leaves has been determined hourly or half-hourly, successive strips being cut from the same leaf at these intervals, and extracted with boiling water and alcohol. At the end of the day, the leaf is reassembled, and developed by immersion in iodine-iodide solution. The variation of starch-content throughout the day is then clearly seen. With most leaves (particularly from March to July) a single daily starch maximum is observed (*Robinia pseudacacia*, etc.). In August and September, two maxima are often observed. Several maxima are rarely found (*Rhus typhina* showing five). With *Chelidonium majus* and *Atriplex patula*, maxima and minima succeed each other rhythmically, whilst with *Urtica dioica* starch suddenly appears and as suddenly disappears again.

E. E. T.

**Galuteolin, a New Glucoside from *Galega officinalis*.** G. BARGER and F. D. WHITE (*Biochem. J.*, 1923, **17**, 836—838).—From the seeds of *Galega officinalis* a glucoside,  $C_{21}H_{20}O_{11} \cdot 3H_2O$ , to which the name *galuteolin* is given, has been isolated. It contains no methoxyl groups. On hydrolysis, it yields dextrose and an insoluble yellow colouring matter decomposing at 290—300°, of the composition  $C_{15}H_{10}O_6$ , identified as luteolin, which, when boiled with acetic anhydride containing a trace of sulphuric acid or pyridine, forms a tetra-acetyl compound,  $C_{15}H_6O_6(C_2H_3O)_4$ , long, colourless needles, m. p. 221—223°. Luteolin occurs as such in the seeds of *Galega officinalis*. The temperatures at which hydroxyflavones such as luteolin sublime in a high vacuum are characteristic. J. P.

**Localisation of the Cyanogenetic Glucosides in *Prunus occidentalis* and *P. myrtifolia*.** E. MAMELI-CALVINO (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 423—430).—By means of Treub's Prussian blue reaction the author has established the localisation of a cyanogenetic glucoside in the bark and leaves of *Prunus occidentalis* and *P. myrtifolia*. Peche's mercurous nitrate method is unsuitable for this purpose, since the reagent may be reduced by the action of cellular constituents which yield no hydrocyanic acid. Microchemical investigation fails to reveal the presence of alkaloids in the bark or leaves of these two species. T. H. P.

**A Labile Form of Protein and its Relation to Living Protoplasm. II.** O. LOEW (*Biochem. Z.*, 1923, **143**, 156—160).—The occurrence is described, in various vegetable cells, of rounded, highly refractive protein droplets resembling the "caffeine proteosomes" previously discovered by the author (A., 1915, i, 1079). These are coagulated by the vapour of ether and chloroform, and combine with bases to form insoluble stable complexes. They also combine readily with water and are made insoluble by neutral salt solutions and by hydrocyanic acid. The reactivity of these droplets is discussed in relation to protoplasmic activity. J. P.

**Proteins of Wheat Bran. I. Isolation and Elementary Analyses of a Globulin, Albumin, and Prolamine.** D. B. JONES and C. E. F. GERSDORFF.—(See this vol., i, 342.)

**Detection and Distribution of Phytosterols in Latex.** G. KLEIN and K. PIRSCHLE (*Biochem. Z.*, 1923, **143**, 457—472).—An improvement is effected in the method available for the extraction of phytosterols from dried plant residues, by shaking the extract dissolved in light petroleum with 50% aqueous sodium hydroxide, whereby the impurities, which render recrystallisation difficult, are hydrolysed and may be subsequently washed out with aqueous sodium carbonate and distilled water. Crystallisation of the phytosterols then proceeds readily. Euphorbone has been obtained in this way, not only from the *Euphorbiaceæ*, but also from many other latex-forming plants, and its nature as a phytosterol has been established by the digitonin test (cf. Windaus, A., 1910, ii, 462).

The presence of 0.1 to 2.0% of phytosterol in latex is regarded as characteristic. A *bromo-* (m. p. 83°) and a *nitro-*derivative of euphorbone are described; a benzoyl derivative was not obtained (cf. Emmerling, A., 1908, i, 438). The physiological significance of phytosterols is discussed. J. P.

**A Crystalline Metabolic Product from *Sparassis ramosa*.** R. FALCK (*Ber.*, 1923, 56, [B], 2555—2556).—Remarkable growth of crystals is observed in pure cultures of *Sparassis ramosa* both in the substrate and on the surface. On the latter they are formed as long needles, in the former as small, rounded crystalline aggregates. The substance possesses the power of protecting the cultures from impurities in a remarkable manner. It can be isolated almost quantitatively by distillation of the substrate with steam. Its constitution has been elucidated by Wedekind and Fleischer (this vol., i, 174), by whom it has been designated "sparassol."

H. W.

**The Effect of Physiologically Acid and Alkaline Nitrogenous Fertilisers.** F. MÜNTER (*Z. Pflanz. Düng.*, 1923, A, 2, 497—516).—The results of pot trials of the effect of various fertilisers on the yield of wheat and linseed are reported. They confirm the conclusions of earlier experiments. Physiologically acid nitrogenous fertilisers such as ammonium sulphate increase the availability of phosphorus in sandy soils so long as the soil reaction remains alkaline. Where a soil contains very small quantities of calcium carbonate, ammonium sulphate may depress the yield. The production of "alkali" in the soil as a result of heavy dressings of sodium nitrate depresses the availability of phosphorus and crop yield. Flax is more sensitive to alkalinity than is wheat.

G. W. R.

**Physiological Function of Iodine in the Sugar-beet.** J. STOKLASA (*Compt. rend.*, 1924, 178, 120—122).—Iodine (present as potassium iodide), although inimical to many plants, is absorbed by the leaves and roots of the sugar-beet, the weight of the whole plant and the percentage sucrose content increasing as a result. The moderate use (about 2 lb. per acre) of potassium iodide as a practical fertiliser in sugar-beet growing is therefore to be recommended, this applying even in the second year. A too free use (*e.g.*, 4 lb. per acre) of iodide, however, diminishes the growth and sucrose content, some arabinose appearing in the roots. E. E. T.

**Lysimetric Studies. Soil and Subsoil in Calcium-Magnesium Interchange.** W. H. MACINTIRE, W. M. SHAW, and J. B. YOUNG (*Soil Sci.*, 1923, 16, 321—341; cf. A., 1923, i, 1168).—Further data are given in connexion with lysimetric studies on soils treated with different compounds of calcium and magnesium. It is shown that the general effect of calcium dressings is to depress the outgo of magnesium from the soil and to increase the outgo from the subsoil. Magnesium dressings have a similar effect on the outgo of calcium from soil and subsoil.

G. W. R.



## Organic Chemistry.

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**Physical Properties of the Paraffin Hydrocarbons.** R. E. WILSON and W. H. BAHLKE (*Ind. Eng. Chem.*, 1924, **16**, 115—122).—Curves are presented between the following physical properties: vapour pressure and temperature, heat of vaporisation and vapour pressure, liquid density and temperature, and specific heat and temperature for the paraffin hydrocarbons from butane to tetracosane. These are compiled from published data and corrected and extended as follows: the vapour-pressure curve by Hildebrand's generalisation that the slope of the curve for any liquid is a constant if the vapour concentration is constant, with application of a correction based on Young's data for the lower members of the series; the heat of vaporisation on Hildebrand's similar rule that the molal entropy of vaporisation for all normal liquids is the same at equal vapour concentrations; the liquid density curve by the theorem of corresponding states. The critical data are calculated from Young's results and from the vapour-pressure curve. Only scanty specific heat data are available. [Cf. *B.*, 1924, 243.] C. I.

**Characteristics of the Hydrocarbons in [American] Mid-continent Kerosene.** C. R. WAGNER (*Ind. Eng. Chem.*, 1924, **16**, 135—136).—The distillate from Oklahoma crude petroleum contains paraffins only in the most volatile fractions. When treated with half its volume of liquid sulphur dioxide at  $-10^{\circ}$ , a fraction soluble in the latter is separated of similar boiling point but higher specific gravity, the proportion of this fraction to the whole rising with the boiling point. In the case of a kerosene, b. p. 198—244°, the  $\text{SO}_2$ -soluble fraction amounted to 5.4%. This fraction was subjected to repeated fractional distillation under reduced pressure, yielding four main fractions, the freezing points, indices of refraction, elementary analyses, and molecular weights of which were determined. The suggested formulæ are  $\text{C}_{12}\text{H}_{18}$ ,  $\text{C}_{14}\text{H}_{20}$ ,  $\text{C}_{13}\text{H}_{18}$ , and  $\text{C}_{14}\text{H}_{18}$ ; it appears probable that these compounds are partly hydrogenated substituted naphthalenes. Their characteristic property, which is common to all  $\text{SO}_2$ -soluble fractions of this petroleum, is that they are readily nitrated even by dilute nitric acid. The  $\text{SO}_2$ -insoluble oil was similarly fractionated and examined. This fraction is unaffected by sulphuric acid ( $d = 1.68$ ) and consists essentially of members of the cyclohexane series. C. I.

**Velocity of Oxidation of Paraffin Wax. I—IV.** F. FRANCIS [with W. F. MILLARD, C. H. RUTT, C. M. WATKINS, R. W. WALLINGTON, and C. P. GARNER] (*J. Chem. Soc.*, 1924, **125**, 381—393).—Paraffin wax, obtained from shale oil and fusing at 55—56°, is oxidised exothermally by a stream of air or oxygen at 100—135°. Commencement of reaction is preceded by a latent period, after which the oxygen content rises to 11—16% in 70—1800 hours. The

latent period may be reduced by heating the wax, previous to oxidation, in a sealed vacuum (a treatment which does not alter the physical constants of the material, but slightly increases its solubility in chloroform and acetone), by the use of catalysts, and by previous treatment with sulphuric acid at  $100^{\circ}$ , which causes a loss in weight of about 5% of the material. Wax which, after being heated in a vacuum, was recrystallised from acetone had the same latent period as the untreated material. The latent period may therefore be ascribed to (a) the formation of a positive catalyst, (b) the destruction of a negative catalyst present in the original wax, or (c) isomeric change brought about by the action of heat, particularly the formation of unsaturated substances (cf. T., 1922, 121, 498, 1534). Commencement of the oxidation is marked by the formation of carbon dioxide, and formic acid is always produced in the later stages of the reaction. The oxidation in presence of catalysts appears to take place in stages.

Wax treated at  $100^{\circ}$  with a stream of oxygen required 1060 hours to attain an oxygen content of 7%; with air at  $100^{\circ}$  the latent period was too long to determine, but at  $120^{\circ}$  an oxygen content of 7% was reached after 285 hours. Untreated wax in the presence of 5% of turpentine reached an oxygen content of 7% in 800 hours with air and in 320 hours with oxygen at  $100^{\circ}$ , in 285 hours with air at  $120^{\circ}$ , and in 46 hours with oxygen at  $135^{\circ}$ .

The temperature coefficient of the oxidation with oxygen is 1.6, whilst that of the latent period is 2.9. These values suggest that the rate of oxidation is governed by a physical process, but that the latent period is accompanied by a chemical change. Wax from lignite, having m. p.  $46-47^{\circ}$ , and containing 0.7% of oxygen, commenced to oxidise with oxygen at  $135^{\circ}$  after 10 hours, and contained 7% of oxygen after 24 hours.

F. G. W.

**Action of Iodine on Hydrocarbons.** F. J. NELLENSTEYN (*Chem. Weekblad*, 1924, 21, 102—106).—Iodine acts on all hydrocarbons, sometimes in the cold, but generally at high temperatures, forming hydrogen iodide, with separation of carbon and formation of colloidal carbon solutions. Treatment of paraffin oil at  $160^{\circ}$  gave a coal-like product, some 70% of the iodine added being driven off, mostly as hydrogen iodide, partly as free iodine. Reaction occurred at the ordinary temperature with a distillate from a Borneo asphaltic oil,  $d\ 0.886$ , b. p.  $192-300^{\circ}$ ; at  $160^{\circ}$ , the iodine was converted nearly quantitatively into hydrogen iodide, carbon being formed both as a precipitate and in the colloidal condition. The results are interpreted as indicating reaction of the iodine with dissociation products of the hydrocarbons, containing only one carbon atom, e.g.  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$ . A highly unsaturated "cracked" gas-oil distillate,  $d\ 0.866$ , b. p.  $58-150^{\circ}$ , reacted with iodine very strongly at the ordinary temperature; the carbon which separated contained 30—37% of adsorbed iodine, not removable by thiosulphate or sodium hydroxide, but partly removed by alcohol. A high adsorbing power is to be expected, since the carbon is formed at low temperatures. The action of iodine is therefore analogous to that

of oxygen, in that hydrogen is removed from dissociation products containing only one atom of carbon, with separation of the latter in the colloidal condition, thus forming asphalt. S. I. L.

**Acceleration of the Reaction between Ethylene and Sulphuric Acid.** W. GLUUD and G. SCHNEIDER (*Ber.*, 1924, 57, [B], 254—255).—The absorption of ethylene by sulphuric acid is catalytically accelerated by the presence of lead sulphate, calcium sulphate, ferric sulphate, anhydrous copper sulphate, or, particularly, ferric ammonium alum. The most suitable catalyst, however, is silver sulphate added to the extent of 0.5—1% of the weight of sulphuric acid; in contrast to the other catalysts, this material retains its activity over long periods, so that higher concentrations of ethyl hydrogen sulphate can be attained. It is readily recovered by electrolysis. H. W.

**Contact Condensation of Acetylene.** N. ZELINSKY (*Ber.*, 1924, 57, [B], 264—276).—The pyrogenic condensation of acetylene in the presence of activated birch or lime charcoal has been studied; the adsorbent properties of the material give, in effect, the action of very greatly increased pressure without involving the dangers incurred in working with compressed acetylene. The method has the advantage that the temperature can be raised without danger to 600—650°, at which the process proceeds most advantageously, and that, in consequence of the presence of charcoal, the condensation occurs quietly and without explosion of the acetylene, which need not therefore be diluted with an indifferent gas. The deposition of carbonised matter on the contact material takes place to only a very minor extent, and the formation of solid hydrocarbons (cuprene) is not observed. Further hydrogenation of the aromatic hydrocarbons which are produced is scarcely observable. The main product of the change is benzene.

The most favourable conditions for the condensation of acetylene are secured when the gas is passed at the rate of 20 litres per hour through a hard glass tube, about 1 metre long and 1.5—2.4 cm. internal diameter, heated at 650°. The escaping gases consist mainly of acetylene containing some ethylene; the yield of tar exceeds 70% of that theoretically possible.

The tar is reddish-brown in colour and aromatic in odour. Colour and transparency depend considerably on the temperature and freshness of the contact agent. Its density varies according to the temperature of the experiment from 0.911 (600°) to 0.995 (660°), but never exceeds 1. It is separated by distillation into the following fractions: light oil, b. p. below 170°, 49.0% (45% below 150°); middle oil, b. p. 170—230°, 11.7%; heavy oil, b. p. 230—270°, 9.5%; anthracene oil, 21.2%; pitch, 6.8% (loss 1.8%). The preliminary fraction contains small amounts of diacetylene,  $\text{CH}_3\text{C}\equiv\text{C}:\text{CH}$ . The light oil consists mainly of benzene (35% of the tar) accompanied by small amounts of toluene and *p*-xylene (cf. A., 1923, i, 1169). The presence of styrene in the fraction, b. p. 140—150°, and of indene in the fraction, b. p. 150—180°,

is established. The middle oil solidifies at the atmospheric temperature to a yellow, crystalline mass, impregnated with liquid; it contains chiefly naphthalene. The green heavy oil contains large quantities of crystals of fluorene. The red anthracene oil deposits the hydrocarbon freely at the atmospheric temperature.

Reduction of the portion of the light oil boiling below  $150^{\circ}$  in the presence of nickel gives a mixture of cyclic hydrocarbons in which cyclohexane predominates; it has b. p.  $70-110^{\circ}$ ,  $d_4^{20}$  0.7805,  $n_D^{21}$  1.4238.

Acetylene is rapidly converted at  $650^{\circ}$  in the presence of active platinised asbestos into a pale yellow, transparent, aromatic tar, the yield being 45–50%; a portion of the acetylene, however, suffers decomposition in such a manner that the catalyst becomes coated with soot which ultimately inhibits the reaction; the tar is characterised by its very low content (5%) in pitch. Palladised asbestos is unsuitable for the condensation of acetylene. In the presence of pure, ignited asbestos, condensation of acetylene takes place at  $650^{\circ}$  with the production of a viscous, black, aromatic tar,  $d_4^{19}$  1.000; the yield is about 40%. The action proceeds quietly without explosion, but cannot be continued over long periods on account of the deposition of soot. H. W.

**Derivatives of  $\Delta^{\alpha}$ -Butylene.** M. DE MONTMOLLIN and P. MATILE (*Helv. Chim. Acta*, 1924, 7, 106–111).—By the action of cold aqueous hypochlorous acid on  $\Delta^{\alpha}$ -butylene, *butylene- $\alpha$ -chlorohydrin*,  $\text{CH}_2\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ , is obtained as a colourless liquid, b. p.  $141^{\circ}$ . When oxidised with chromic acid, it gives chloromethyl ethyl ketone, a liquid with a pungent odour, b. p.  $135-137^{\circ}$ ; this is also formed as a by-product with the butylenechlorohydrin, together with  $\alpha\beta$ -dichlorobutane and some higher chlorinated products, including (?)  $\alpha\beta\gamma$ -trichloro-*n*-butane, b. p.  $165-168^{\circ}/725$  mm. *Butylene  $\alpha$ -bromohydrin*, prepared from  $\alpha$ -butylene and hypobromous acid, is a colourless liquid, b. p.  $56-58^{\circ}/11$  mm. By oxidation it gives bromomethyl ethyl ketone, b. p.  $145^{\circ}/725$  mm. This ketone is also formed as a by-product with the bromohydrin, together with some  $\alpha\beta$ -dibromobutane and a *bromobutylene bromohydrin*, b. p.  $79-80^{\circ}$ . The above chloromethyl ethyl ketone gives with phenylhydrazine a compound, yellow crystals, m. p.  $210-215^{\circ}$  (decomp.), whilst bromomethyl ethyl ketone gives a compound, greenish-yellow crystals, m. p.  $200-205^{\circ}$  (decomp.). Both appear to contain two phenylhydrazine residues, and should be the same phenylhydrazido-phenylhydrazone; the difference cannot yet be explained.

*$\alpha$ -Butylene diacetate* is obtained by heating  $\alpha\beta$ -dibromobutane with fused potassium acetate and glacial acetic acid; it is a colourless liquid with an agreeable odour, b. p.  $196-199^{\circ}$ . When this liquid is saturated with gaseous hydrogen bromide,  *$\alpha$ -bromo-sec.-butyl acetate*,  $\text{CH}_2\text{Me}\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\text{Br}$ , a pale yellow liquid, b. p.  $76^{\circ}/15$  mm., is formed.  *$\alpha$ -Butylene oxide*,  $\text{CH}_2\text{Me}\cdot\text{CH}\begin{smallmatrix} \diagup \text{CH}_2 \\ \diagdown \text{O} \end{smallmatrix}$ , is formed by the action

of potassium hydroxide solution on the chloro- or bromo-hydrin; it is a colourless liquid, b. p. 58.5—59.0°. It is converted by 25% ammonia solution into  $\alpha$ -amino-sec.-butyl alcohol, b. p. 168—170°.

E. H. R.

**Alkaline Reduction of the Carbon Tetrahalides and of Potassium *aci*-Nitroform.** R. O. GRIFFITH and L. HUNTER (*J. Chem. Soc.*, 1924, 125, 463—464).—The carbon tetrahalides are effectively reduced by phenylhydrazine, arsenious oxide, or sulphites in alkaline solution. The action of acetone, hydrazine, antimonious oxide, and stannites is less certain. In the reduction of trichlorobromomethane to chloroform by means of aqueous sodium arsenite, dichlorobromomethane was not formed. Bromoform is reduced to methylene bromide by alkaline reagents, with the production of much formate, and chloroform is hydrolysed to formate without the production of methylene chloride. The action of alkaline reducing agents on potassium *ac*initroform does not produce potassium dinitromethane, the salt being completely decomposed with the formation of ammonia. Hydrazine or phenylhydrazine reacts with evolution of nitrogen, a result which may explain the abnormally large production of nitrogen in the reaction between these compounds and tetranitromethane (T., 1923, 123, 2305; and 1920, 117, 880).

F. G. W.

**Preparation and Reactions of the Dihalogenodinitromethanes.** R. A. GOTTS and L. HUNTER (*J. Chem. Soc.*, 1924, 125, 442—450).—The action of potassium hydroxide, iodide, cyanide, and nitrite, and of sodium thiosulphate, on the dihalogenodinitromethanes was investigated to test the hypothesis of Macbeth (T., 1922, 121, 1118), that the activity of halogen atoms in similarly constituted molecules is the result of an induced positive polarity. In general, the stability of the compounds investigated conforms to the order  $\text{Cl} > \text{Br} > \text{I}$ , although in the case of the mixed dihalogenodinitromethanes exclusive removal of the more positive atom does not take place.

Potassium hydroxide reacts with dichloro- and dibromo-dinitromethanes according to the equation,  $\text{CCl}_2(\text{NO}_2)_2 + 2\text{KOH} = \text{CKCl}(\text{NO}_2)_2 + \text{KClO} + \text{H}_2\text{O}$ . In the case of chlorobromodinitromethane, the product is a mixture of the potassium salts of chloro- and bromo-dinitromethane. Chloriododinitromethane behaves similarly to the chlorobromo-compound, losing more iodine than chlorine.

Potassium iodide reacts with the dihalogenodinitromethanes according to the equation,  $\text{CX}_2(\text{NO}_2)_2 + 2\text{KI} = \text{CKX}(\text{NO}_2)_2 + \text{KX} + \text{I}_2$ , both halogens being removed in part, but chlorobromodinitromethane gives also a small proportion of the iodo-salt.

Potassium cyanide behaves more energetically than the iodide, and both halogen atoms can be removed according to the equations,  $\text{CX}_2(\text{NO}_2)_2 + \text{KCN} = \text{CKX}(\text{NO}_2)_2 + \text{CNX}$  and  $2\text{CKX}(\text{NO}_2)_2 + 2\text{KCN} + \text{H}_2\text{O} = 2\text{CKH}(\text{NO}_2)_2 + \text{KX} + \text{CNX} + \text{KCNO}$ ; potassium chloro-

dinitromethane, however, remains unaffected on prolonged treatment with potassium cyanide.

Potassium nitrite acts as a reducing agent only in the case of chloriododinitromethane, according to the equation,  $\text{CClI}(\text{NO}_2)_2 + 2\text{KNO}_2 = \text{CKCl}(\text{NO}_2)_2 + \text{KNO}_3 + \text{NO} + \text{I}$ . The action of potassium nitrite in presence of carbonate on dibromodinitromethane is represented by the equations,  $\text{CBr}_2(\text{NO}_2)_2 + \text{KNO}_2 + \text{K}_2\text{CO}_3 = \text{CK}(\text{NO}_2)_3 + \text{KBr} + \text{KBrO} + \text{CO}_2$ , and  $\text{CBr}_2(\text{NO}_2)_2 + \text{KNO}_2 + \text{K}_2\text{CO}_3 = \text{CKBr}(\text{NO}_2)_2 + \text{KBr} + \text{KNO}_3 + \text{CO}_2$ . Chlorobromodinitromethane yields the nitroform salt in much smaller proportion, and none is obtained from the dichloro-compound.

Sodium thiosulphate reduces potassium bromo- and iodo-dinitromethanes to potassium dinitromethane; the chloro salt is reduced much more slowly.

The action of acids on potassium bromodinitromethane is represented by the equation,  $2\text{CKBr}(\text{NO}_2)_2 + \text{H}_2\text{SO}_4 = \text{CBr}_2(\text{NO}_2)_2 + \text{K}_2\text{SO}_4 + \text{N} + \text{NO} + \text{CO}_2 + \text{H}_2\text{O}$ . Potassium chlorodinitromethane behaves analogously. For the purposes of preparation, the direct action of halogens gives better yields than that of acids. Copper, lead, and ferrous salts have a similar action to that of mineral acids, but the silver monohalogenodinitromethanes can be obtained as stable, crystalline substances.

Dichloronitromethane is best prepared by the action of strong nitric acid on 2:4-dichloroacetanilide, and purified by conversion into the potassium salt, from which it is regenerated by the action of aqueous chlorine; it is a colourless oil,  $d_4^{25}$  1.6616, not solidifying above  $-10^\circ$ . Dibromodinitromethane, similarly purified, is a colourless, pungent oil,  $d_4^{25}$  2.3946, m. p.  $7.4^\circ$ . *Potassium chlorodinitromethane*, light yellow prisms exploding at  $83-85^\circ$ , decomposes on keeping. *Silver chlorodinitromethane*, long, yellow needles, explodes at  $80-81^\circ$ . Chlorobromodinitromethane is best prepared in presence of sodium acetate, and forms a colourless, pungent liquid,  $d_4^{25}$  2.0472. *Potassium iododinitromethane*, obtained by the action of iodine on potassium dinitromethane in aqueous solution, forms orange-yellow plates, exploding at  $154^\circ$ . It does not darken on exposure when pure. The *silver* salt forms insoluble, pale yellow, glistening leaflets, exploding at  $109-110^\circ$ . F. G. W.

**Aliphatic Nitro-alcohols. II.** R. WILKENDORF and M. TRÉNEL (*Ber.*, 1924, 57, [B], 306-309).—An extension of previous work (A., 1923, i, 288).

$\beta$ -Chloro- $\beta$ -nitroethyl alcohol condenses with acetaldehyde in aqueous solution, in the presence of a little potassium carbonate, to form  $\beta$ -chloro- $\beta$ -nitrobutane- $\alpha$ -*γ*-diol,  $\text{OH}\cdot\text{CH}_2\cdot\text{CCl}(\text{NO}_2)\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$ , long needles, m. p.  $104^\circ$ ; with propaldehyde, it gives  $\beta$ -chloro- $\beta$ -nitropentane- $\alpha$ -*γ*-diol, colourless needles, m. p.  $107^\circ$  (decomp.). It does not appear to react with higher aldehydes.

The sodium derivative of  $\beta$ -chloro- $\beta$ -nitroethyl alcohol is converted by methyl iodide in methyl-alcoholic solution into  $\beta$ -chloro- $\beta$ -nitropropyl alcohol, m. p.  $114^\circ$ .

$\beta$ -Chloro- $\beta$ -nitroethyl alcohol is transformed by cautious treat-

ment with a mixture of nitric acid (*d* 1.4) and concentrated sulphuric acid into  $\beta$ -chloro- $\beta$ -nitroethyl nitrate, a colourless liquid, *d*<sup>18</sup> 1.568, which, when cautiously heated, decomposes into nitric acid and  $\alpha$ -chloro- $\alpha$ -nitroethylene, a liquid, b. p. 54—55°/14 mm., which violently attacks the eyes; the latter substance can also be prepared by the action of phosphoric oxide on  $\beta$ -chloro- $\beta$ -nitroethyl alcohol; in the presence of sodium hydrogen carbonate, it passes readily into a polymeride, m. p. 126—130° (decomp.), according to the manner of heating. H. W.

**Preparation of Ethyl Ether by Williamson's Method.** W. B. S. BISHOP (*J. Soc. Chem. Ind.*, 1924, 43, 23—24r).—Pure ethyl ether is obtained readily by Williamson's method, using ethyl iodide and sodium ethoxide. The yield is 80% of the theoretical (calculated on the ethyl iodide used). The oxidised copper gauze test for halogens is capable of detecting as little as 0.00004 g. of iodine present as ethyl iodide in 1 c.c. of ether. W. P. S.

**Catalytic Dehydration of Ethyl Alcohol and Ether by Alumina.** R. N. PEASE and C. C. YUNG (*J. Amer. Chem. Soc.*, 1924, 46, 390—403).—The dehydrations were carried out in an electrically heated glass bulb of 35 c.c. capacity containing the alumina. The alcohol was run in from a burette at a uniform rate, and, when equilibrium conditions had been obtained, a test was made. It is found that appreciable quantities of ether as well as ethylene are formed from alcohol and that at 275° and 300° the amount of alcohol decomposed attains a maximum corresponding with about 65% conversion, whereas at 350° the reaction proceeds to complete dehydration with the production of ethylene. The maximum yield of ether was 60% at 250°. Ether decomposes readily at temperatures above 275°. The results are explicable on the theory that the dehydration of alcohol to ether is a reversible equilibrium corresponding with about 65% conversion, and that decomposition of the alcohol occurs in steps. Whilst the direct dehydration to yield ethylene is a possible mechanism, it is not necessary to assume it in order to account for the results. Water vapour and ethylene diminish somewhat the efficiency of the catalyst towards dehydration of alcohol. Alumina which has been used in the dehydration of ether appears to be peculiarly activated with respect to alcohol, and the yield of ethylene is nearly doubled. A. B. S.

**Autoxidation of Ethers.** A. M. CLOVER (*J. Amer. Chem. Soc.*, 1924, 46, 419—430).—The oxidising properties acquired by ethyl ether when exposed to the air (A., 1922, i, 619) have been observed with several other ethers. In three cases, the ether peroxides have been obtained, whereas in the other cases, owing to the high boiling point of the ether, the peroxides could not be isolated. Aldehydes, esters, acids, and hydrogen peroxide were also formed. The hydrolysis of the peroxides, which yields acids, hydrogen peroxide, and aldehydes, is considered to occur in accordance

with the schemes:  $\text{OR}\cdot\text{CHR}'\cdot\text{O}\cdot\text{OH} + \text{H}_2\text{O} \rightarrow \text{R}'\text{CHO} + \text{ROH} + \text{H}_2\text{O}_2$  or  $\text{OR}\cdot\text{CHR}'\cdot\text{O}\cdot\text{OH} \rightarrow \text{R}'\text{CO}_2\text{H} + \text{ROH}$  or  $\text{R}'\text{CO}_2\text{R} + \text{H}_2\text{O}$ . The ethers experimented with were: propyl ether; isopropyl ether; *n*-butyl ether; isoamyl ether, b. p. 168—171°; methylenediethyl ether, b. p. 86—89°; benzylmethyl ether, benzylethyl ether, b. p. 183—185°; dibenzyl ether. In the case of propyl, *n*-butyl, and methylenediethyl ethers, the *peroxides* were isolated and analysed.

A. B. S.

**Sulphochromic Oxidation and  $\beta$ -Oxidation.** M. POLONOVSKI (*Compt. rend.*, 1924, **178**, 576—578).—A study of the oxidation of aliphatic acids by means of dilute sulphuric acid-dichromate solutions at 100°. Acetic acid is unaffected. Propionic acid is oxidised slowly and incompletely, through pyruvic and acetic acids ( $\alpha$ -oxidation). Butyric acid is oxidised rapidly, through acetoacetic acid ( $\beta$ -oxidation;  $\alpha$ -oxidation is shown not to occur from a consideration of the oxidation-time curves). Valeric acid undergoes  $\beta$ -oxidation, which in this case produces propionic acid, oxidation decelerating as a result.

E. E. T.

**Electrolysis of Potassium Oleate.** G. W. F. HOLROYD and J. E. W. RHODES (*J. Chem. Soc.*, 1924, **125**, 438—442).—The apparent transport number of the oleic-ion in 0.2*N*-potassium oleate solution was found to be 0.725, in agreement with that obtained by McBain and Bowden (*T.*, 1923, **123**, 2417) under different experimental conditions. Oleic acid is the chief product at the anode; neither oxygen nor oxidation products in amount demanded by the equation,  $2\text{R}\cdot\text{CO}_2 + \text{H}_2\text{O} = 2\text{R}\cdot\text{CO}_2\text{H} + \text{O}$ , were found. The apparatus used was a modification of Ostwald's, arranged to allow collection of gases evolved.

F. G. W.

**Bromine Derivatives of  $\alpha$ -Elæostearic Acid.** M. ISHIO (*J. Pharm. Soc. Japan*, 1923, No. 501, 789—796; cf. *T.*, 1903, **83**, 1042; 1912, **101**, 2082; Nicolet, *A.*, 1921, i, 390).—Dibromo- $\alpha$ -elæostearic acid (73 g.), colourless plates, m. p. 91°, is prepared by adding bromine to a solution of  $\alpha$ -elæostearic acid (150 g.) in ether or light petroleum cooled below -15°; if chloroform is used as solvent, a tetrabromide (35 g.), m. p. 115°, is produced from the acid (100 g.) or from the dibromide. The dibromide is changed by alcoholic potassium hydroxide solution into a viscous oil free from the halogen, the reduction of which with hydrogen in the presence of platinum black yields stearic acid. When the tetrabromide is treated with alcoholic potassium hydroxide, a dibromide,  $\text{C}_{18}\text{H}_{30}\text{O}_2\text{Br}_2$  or  $\text{C}_{18}\text{H}_{32}\text{O}_2\text{Br}_2$ , lustrous crystals, m. p. 40—40.5°, is produced.

K. K.

**Perilla Oil. III. Bromides of the Linolenic Acids of Perilla Oil.** K. H. BAUER (*Chem. Umschau*, 1924, **31**, 83—86; cf. *A.*, 1923, i, 180).—Considerable quantities of linolenic acid hexabromides, prepared from perilla oil, were debrominated with zinc and alcohol and the linolenic acid obtained was brominated



again. The precipitated bromides were separated. The soluble bromides were then debrominated and the separated fatty acids submitted to oxidation by Hazura's method. The solid oxidation products were mixed with sand and extracted in succession with boiling ether, light petroleum, and alcohol. From the alcoholic extract a small quantity of an acid, m. p. 143—147°, was obtained. The aqueous solution of the soluble oxidation products yielded a small quantity of a yellowish-brown oil and linusic acid, m. p. 203°. *iso*Linusic acid was not found. The hexabromides obtained from perilla oil were satisfactorily recrystallised from boiling xylene, whereby hexabromostearic acid, m. p. 179—181°, was isolated. All attempts to separate the product into components by fractional crystallisation of large quantities were without effect, so that the substance is presumably homogeneous. Owing to the uncertainty surrounding the oxidation of and formation of additive compounds from these highly unsaturated substances, it is not considered safe to assume that, because linusic acid is the only hydroxy acid obtained from the soluble brominated linolenic acids, the oxidation of  $\beta$ -linolenic acid yields this acid only. Attempts to prepare hexahydroxystearic acids from hexabromostearic acids by treating them with silver oxide were unsuccessful. The effect of allowing perilla oil to remain for a long time in the dark in contact with a small quantity of iodine (conditions favourable to the transformation of  $\alpha$ - into  $\beta$ -elæostearic acid in the case of tung oil) was studied; steric rearrangement did not occur under the conditions chosen.

H. C. R.

**Glycerides of Lard. II. Synthetical.** C. AMBERGER and A. WIESEHAHN [and, in part, J. BAUCH] (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 291—299).— $\alpha$ -Oleo- $\beta\gamma$ -distearin [glyceryl  $\alpha$ -oleate  $\beta\gamma$ -distearate], m. p. 42°, was synthesised by Fischer and Pfähler's method (A., 1920, i, 807) from  $\alpha$ -mono-olein and stearyl chloride.  $\alpha$ -Palmito- $\alpha\beta$ -diolein, synthesised in a similar manner from  $\alpha$ -monopalmitin and oleyl chloride, is a dark yellow oil which solidifies at 0°. Attempts to synthesise oleopalmitostearin were unsuccessful. A comparison of the properties of the mixed glycerides isolated from lard with those synthesised (cf. A., 1922, i, 804) and those obtained by their hydrogenation, leads to the conclusion that the following are present:  $\beta$ -palmito- $\alpha\gamma$ -distearin,  $\beta$ -stearo- $\alpha\gamma$ -dipalmitin,  $\alpha$ -oleo- $\alpha\beta$ -distearin,  $\alpha$ -palmito- $\alpha\beta$ -diolein, and probably  $\beta$ -oleo- $\alpha$ -palmito- $\gamma$ -stearin.

H. C. R.

**Crystalline Bromides of Linseed Oil.** H. TOMS (*Analyst*, 1924, **49**, 77—81).—A substance, m. p. 153° (corr.), is obtained by successive treatment of the crude bromide from linseed oil with ethyl acetate, alcohol, and ether. Its analysis agrees closely with the formula,  $C_{57}H_{94}O_6Br_{16}$ , from which it is concluded that it is a linolic-dilinenic bromoglyceride. Its solubility in ethyl acetate at 15—20° is 0.15—0.20 g. per 100 c.c. The residue obtained from the ethyl acetate mother-liquor yields a small amount of material, m. p. 117° (corr.). The analysis of this substance corresponds

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approximately with the formula,  $C_{57}H_{98}O_6Br_{12}$ , and it may be trilinolic bromoglyceride or an oleic-linolic-linolenic bromoglyceride. Attempts were made to determine the bromide which was insoluble in ethyl acetate, and there were indications that the amount of the most unsaturated glyceride in linseed oil is a constant proportion of the total unsaturated substances present. H. C. R.

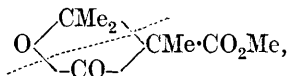
**Uncommon Animal Fats.** W. N. RAE (*Analyst*, 1924, 49, 83—84).—The analytical characters of the fats of the following wild animals of Ceylon are given: leopard (*Felis pardus*), sambhur (*Cervus unicolor*), spotted deer (*C. axis*), peafowl (*Pavo cristatus*), and wild boar (*Sus cristatus*). The values for leopard's fat agree closely with those given by Lewkowitsch for tiger's fat, and the values for the two members of the deer tribe agree with those of the chamois. European wild boar fat, however, differs considerably from that of the Ceylon wild boar. [Cf. *B.*, 1924, 264.] H. C. R.

**$\beta$ -Lactones of  $\beta$ -Hydroxybutyric Acid and its Alkyl Derivatives and the Influence of Constitution on the Decomposition of  $\beta$ -Lactones.** H. SALKOWSKI, jun. (*J. pr. Chem.*, 1923, 106, 253—265).—When  $\alpha$ -dialkylated  $\beta$ -hydroxybutyric acids are distilled they decompose into acetaldehyde and a dialkylacetic acid. A somewhat similar reaction to this is the thermal decomposition of methyl  $\beta$ -hydroxy- $\alpha$ -methylisopropylmalonolactone,  $O \begin{smallmatrix} \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CMe} \cdot \text{CO}_2\text{Me}$ , into acetone, dimethylketen, and carbon dioxide. To determine whether the decomposition of the  $\beta$ -hydroxybutyric acid may be preceded by the intermediary formation of a  $\beta$ -lactone which then decomposes into aldehyde and keten, the latter subsequently taking up the elements of water,  $\beta$ -lactones of  $\beta$ -hydroxybutyric acid,  $\beta$ -hydroxy- $\alpha$ -ethyl- and  $\beta$ -hydroxy- $\alpha\alpha$ -dimethylbutyric acids, were prepared and their thermal decomposition was studied.

The required hydroxybutyric acid derivatives were prepared by reduction of the corresponding derivatives of ethyl acetoacetate with sodium amalgam.  $\beta$ -Hydroxy- $\alpha$ -ethylbutyric acid is a viscous liquid, b. p.  $123^\circ/0.8$  mm.  $\beta$ -Hydroxy- $\alpha\alpha$ -dimethylbutyric acid forms a viscous liquid, b. p.  $108$ — $110^\circ/0.02$  mm., which slowly crystallises to bunches of needles, m. p.  $34^\circ$ . Part of the acid is converted into an anhydride,  $\text{OH} \cdot \text{CHMe} \cdot \text{CMe}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{CHMe} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ , b. p.  $200$ — $203^\circ/15$  mm., a very viscous liquid. The  $\beta$ -hydroxy-acids were converted into  $\beta$ -bromo-acids. For this purpose  $\beta$ -hydroxybutyric acid and  $\beta$ -hydroxy- $\alpha$ -ethylbutyric acid had first to be converted by distillation into the corresponding crotonic acid and the product treated with liquid hydrogen bromide.  $\beta$ -Bromo- $\alpha$ -ethylbutyric acid is a yellow, viscous liquid, b. p.  $140$ — $143^\circ/15$ — $16$  mm.;  $\beta$ -bromo- $\alpha\alpha$ -dimethylbutyric acid forms brown needles, m. p.  $42^\circ$ , b. p.  $115^\circ/0.2$  mm. The lactones were obtained by treating the acids with sodium carbonate solution and extracting with ether.  $\alpha$ -Ethyl- $\beta$ -butyrolactone has b. p.  $75^\circ/13$  mm. (cf. Johansson and Hagman, A., 1922, i, 426) and  $\alpha\alpha$ -dimethyl- $\beta$ -butyrolactone has b. p.  $63$ — $65^\circ/14$  mm. The thermal decomposition of the lactones in each

case gave carbon dioxide and an olefine,  $\beta$ -butyrolactone giving propylene,  $\alpha$ -ethyl- $\beta$ -butyrolactone giving amylene, and  $\alpha\alpha$ -dimethyl- $\beta$ -butyrolactone giving  $\alpha$ -methylbutylene. The decomposition is therefore different from that of the  $\alpha\alpha$ -dialkyl- $\beta$ -hydroxybutyric acids.

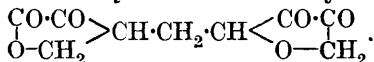
The type of  $\beta$ -lactone decomposition occurring in the case of methyl  $\beta$ -hydroxy- $\alpha$ -methylisopropylmalonolactone,



the so-called ketone-splitting, can probably only take place when the  $\beta$ -carbon atom is tertiary. E. H. R.

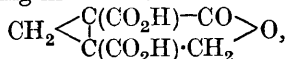
### Condensation between Pyruvic Acid and Formaldehyde.

Y. ASAHINA and S. TERADA (*J. Pharm. Soc. Japan*, 1923, No. 502, 855—878).—The action of pyruvic acid on formaldehyde gives a compound,  $\text{C}_9\text{H}_8\text{O}_6$ , colourless plates, m. p. 239—240° (decomp.), which is shown to be methylenebis- $\alpha$ -ketobutyrolactone,



It gives the following derivatives: *ammonium* salt,  $\text{C}_9\text{H}_7\text{O}_6 \cdot \text{NH}_4$ , white, silky crystals; *potassium* and *sodium* salts; unstable *silver* salt,  $\text{C}_9\text{H}_6\text{O}_6\text{Ag}_2$ , white scales; *ethyl* ester, m. p. 124—125°; *monoacetyl* derivative, scales, m. p. 135°; *dibenzoyl* compound, m. p. 122°; *phenylhydrazine* salt,  $\text{C}_9\text{H}_8\text{O}_6 \cdot (\text{Ph} \cdot \text{NH} \cdot \text{NH}_2)_2$ , white crystals, m. p. 195—196°; *phenylhydrazone*,  $\text{C}_9\text{H}_8\text{O}_4(\text{N} \cdot \text{NH} \cdot \text{Ph})_2$ , m. p. 225—227° (decomp.); *semicarbazide* compounds, m. p. 196—197° (decomp.), and m. p. 182—183° (decomp.), respectively; *chloro*-compounds, m. p. 151—152°, and m. p. 183—184°. When heated at 145° with concentrated sulphuric acid, it yields an anhydride,  $\text{C}_9\text{H}_6\text{O}_5$ , white crystals, which do not melt below 300°.

Methylenebis- $\alpha$ -ketobutyrolactone is oxidised by silver oxide to the substance,  $\text{CH}_2 < \begin{array}{c} \text{C}(\text{CH}_2\text{OH}) \cdot \text{CO} \\ | \\ \text{C}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \end{array} > \text{O}$ , colourless, hexagonal crystals, m. p. 185—185.5°. It is not coloured by ferric chloride, but gives the pine-shaving reaction and contains one carboxy group, one lactone ring, and one hydroxy group. It yields a *methyl* ester, silky crystals, m. p. 105—105.5°, a *monoacetyl* derivative, m. p. 130°, and *monobenzoyl* compound, m. p. 130—131°. When heated with hydriodic acid and red phosphorus, it gives two *iodine compounds*,  $\text{C}_7\text{H}_{10}\text{O}_4\text{I}_2$ , m. p. 168—169° and 143—144°, respectively. When reduced with sodium amalgam, the former iodine compound gives *cis*- $\alpha\gamma$ -dimethylglutaric acid and the other the *trans*-isomeride. It is oxidised by fuming nitric acid to the *dicarboxylic acid*,



white crystals, m. p. 219—220°, which gives the pine-shaving reaction and contains two carboxyl groups and one lactone ring. Its *dimethyl* ester, prisms, melts at 77.5—78.5°. By heating with hydriodic acid and red phosphorus, it gives an *iodine compound*,

$C_6H_8O_4I_2$ , m. p. 167—168°, the reduction of which with sodium amalgam produces  $\alpha\alpha$ -dimethylsuccinic acid. The similarity between the relation of  $\beta$ -tetronic acid to methylenebis- $\beta$ -tetronic acid and that of  $\alpha$ -tetronic acid to methylenebis- $\alpha$ -ketobutyrolactone was observed spectrographically. K. K.

**Influence of Strong Acids on the Solubility of Oxalic Acid.**

W. HERZ and E. NEUKIRCH (*Z. anorg. Chem.*, 1923, **131**, 303—309).—The solubility of oxalic acid is depressed by the addition of a strong acid (hydrochloric, sulphuric, nitric) up to a certain concentration of the latter, after which it is increased. No action could be detected between oxalic and sulphuric acids up to a 3.5-molar concentration of the latter. Nitric acid exerts an oxidising effect, apparently due to impurities, and the figures obtained with this acid are not accurate. The results obtained are compared with those calculated on the solubility-product principle, the agreement being fair except in the case of nitric acid. [Cf. *B.*, 1924, 277.]

S. K. T.

**Photochemical Sensitisation of the Maleic Ester Transformation by means of Bromine.** J. EGGERT [with W. BORINSKI] (*Physikal. Z.*, 1924, **25**, 19—21).—A study of the transformation of maleic ester in carbon tetrachloride solution, in presence of bromine, into fumaric ether, under the influence of energy of wave-lengths 557, 436, and 365  $\mu\mu$ , gave the following results:—(1) The photochemical efficiency at 18° with blue light (436  $\mu\mu$ ) is 565, much greater than the figure calculated from the equivalent law. (2) The transformation is proportional to the number of absorbed quanta, but independent of the concentrations of bromine and solvent within wide limits; it is proportional to the quantum dimension at uniform temperatures, and increases for the same radiated energy exponentially with the temperature. These results appear contradictory, and seem to indicate that the activated molecule can survive several collisions. S. I. L.

**Correlation of Additive Reactions with Tautomeric Change.**

**II. Reversibility in Relation to the Stability of Carbon Chains.** E. H. INGOLD (USHERWOOD) (*J. Chem. Soc.*, 1924, **125**, 435—438).—Failure to obtain a homologue by the method which leads to the formation of the parent substance may be due to the structure of the homologue admitting of some retrograde additive reaction by which it can break down. The influence of homology on the reversibility of such addition reactions thus becomes the determining factor in the ability to exist of various types of carbon structure.

The influence of homology on the reversibility of the aldol addition process is very marked. Thus in the cases of acetaldehyde, isobutaldehyde, and  $\alpha$ -methylbutaldehyde, the percentages of aldol present in the equilibrium mixtures at 25° and 62° are, respectively, 100, 92 and 39, and 41 and 9. The failure of Neustädter (*A.*, 1907, i, 14) to obtain  $\alpha$ -methylbutaldehyde must be ascribed to the experimental limitations imposed on the aldol reaction by the

influence of temperature and structure on its reversibility. In the case of acetaldehyde, reversibility could not be detected at the ordinary temperature, and experiments at  $60^{\circ}$  were rendered impossible by the formation of crotonaldehyde.

The position of the equilibrium, in the case of  $\alpha$ -methylbutaldehyde, was determined by keeping the aldehyde or aldol, mixed with an equal volume of saturated aqueous potassium carbonate, in a closed vessel at a known temperature for a definite time, and working up as previously described (T., 1923, **123**, 1723), except that the distillation was finished at  $125^{\circ}$  in an atmosphere of carbon dioxide.  $\alpha$ -Methylbutaldol forms a rather viscous, colourless liquid, b. p.  $103\text{--}104^{\circ}/6$  mm., with a characteristic earthy odour.

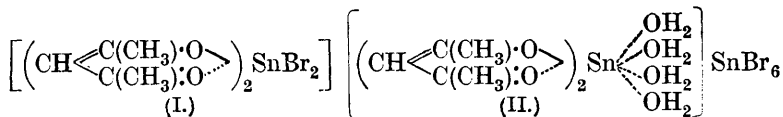
F. G. W.

**Dichloroacetaldoxime.** O. ROUTALA and W. NEUVIUS (*Ber.*, 1924, **57**, [B], 252—254).—*Dichloroacetaldoxime*,  $\text{CHCl}_2\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ , a colourless liquid with a penetrating odour, b. p.  $67\text{--}69^{\circ}/17$  mm.,  $40\text{--}44^{\circ}/2\text{--}3$  mm. (partial decomp.), is prepared by the action of hydroxylamine hydrochloride on crude dichloroacetaldehyde obtained from trichlorolactic acid. It is converted by hydroxylamine at the atmospheric temperature into glyoxime. With phenylcarbimide, it yields the compound,  $\text{C}_9\text{H}_8\text{O}_2\text{N}_2\text{Cl}_2\cdot\text{C}_6\text{H}_6$ , which darkens at  $155^{\circ}$  but has not a definite m. p. Attempts to transform it into the monoxime of glyoxal were not successful. H. W.

**Condensation Products of Diethyl Ketone.** J. B. EKELEY and M. S. CARPENTER (*J. Amer. Chem. Soc.*, 1924, **46**, 446—450; cf. Ekeley and Howe, A., 1923, i, 997).—The protracted action of an excess of diethyl ketone on sodium ethoxide at  $10^{\circ}$  leads to the production of a mixture of *homomesityl oxide* [ $\gamma$ -ethyl- $\delta$ -methyl- $\Delta^7$ -heptene- $\epsilon$ -one],  $\text{CET}_2\cdot\text{CMe}\cdot\text{COEt}$ , and *homoisophorone*,  $\text{C}_{15}\text{H}_{28}\text{O}$ . The former substance is a colourless liquid with a strong, mint-like odour and taste, b. p.  $98\text{--}102^{\circ}/20$  mm.,  $d_4^{20}$  0.8535,  $n_D^{20}$  1.4501. Homoisophorone is a pale yellow, slightly viscous liquid, b. p.  $137\text{--}140^{\circ}/8$  mm.,  $d_4^{20}$  0.91456,  $n_D^{20}$  1.4831. A. B. S.

**Residual Affinity and Co-ordination. XVII. Stannic Derivatives of  $\beta$ -Diketones.** G. T. MORGAN and H. D. K. DREW (*J. Chem. Soc.*, 1924, **125**, 372—381).—The product of the reaction between molecular proportions of stannic chloride and acetylacetone in chloroform solution is a white, crystalline precipitate, m. p.  $150^{\circ}$  (decomp.), which deliquesces rapidly in air with formation of a crystalline substance, m. p.  $98^{\circ}$ . If instead of isolating this product, the reaction mixture is boiled with a second molecular proportion of acetylacetone, stannic bisacetylacetone dichloride, m. p.  $202\text{--}203^{\circ}$ , is obtained. This substance, contrary to Diltthey's statement (A., 1906, i, 342), is soluble in hot benzene, and its molecular weight in that solvent corresponds with the monomeric formula,  $\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2\text{Cl}_2$ . The corresponding dibromide, obtained by the interaction of stannic bromide and copper acetylacetone in chloroform solution, does not react with stannic bromide when the two substances are dissolved together in anhydrous solvents, but

the introduction of water leads to the formation of tetra-aquostannic bisacetylacetone stannibromide,  $[(\text{H}_2\text{O})_4\text{Sn}(\text{C}_5\text{H}_7\text{O}_2)_2]\text{SnBr}_6$ . Stannic bisacetylacetone dibromide (I) and the tetra-aquo compound (II) exhibit co-ordination numbers of six and eight, respectively.



The formation of stannic bis- $\beta$ -diketone dibromides is a general reaction between stannic bromide and the copper salts of the  $\beta$ -diketones in chloroform, and proceeds according to the following equations:  $3\text{SnBr}_4 + 3\text{CuAc}_2 = 3\text{SnAc}_2\text{Br}_2 + 3\text{CuBr}_2$ ;  $3\text{CuBr}_2 + \text{CuAc}_2 = 2\text{Cu}_2\text{Br}_2 + 2\text{AcBr}$ , where  $\text{Ac}$  is the univalent  $\beta$ -ketonic chelate group and  $\text{AcBr}$  the corresponding bromo- $\beta$ -diketone. The *cis-trans* (octahedral) isomerism theoretically possible has not yet been detected among these co-ordination compounds.

*Stannic bisacetylacetone dibromide*, transparent, colourless, lustrous, six-sided prisms, or aggregates of flaky crystals, m. p.  $187^\circ$ , separates from benzene as the double compound  $[\text{SnBr}_2(\text{C}_5\text{H}_7\text{O}_2)_2]_2 \cdot \text{C}_6\text{H}_6$ , which loses the solvent at  $70$ – $110^\circ$ . *Tetra-aquostannic bisacetylacetone stannibromide*, obtained as described above or by the interaction of stannic bromide and stannic bisacetylacetone dibromide in presence of moisture, forms large, transparent, colourless prisms, m. p.  $105$ – $107^\circ$ . When boiled with benzene, it loses water and dissociates into stannic bromide and the bisacetylacetone dibromide. *Stannic bisbenzoylacetone dibromide* is a white, microcrystalline powder, m. p.  $213$ – $214^\circ$ , soluble in hot acetylacetone, with which it reacts to form benzoylacetone and the bisacetylacetone dibromide. *3-Bromobenzoylacetone* was isolated as colourless prisms with an aromatic lachrymatory odour, m. p.  $43$ – $45^\circ$ . *Stannic bisdibenzoylmethane dibromide*, shining, sulphur-yellow crystals, m. p.  $276$ – $278^\circ$ , is only slowly hydrolysed by aqueous potassium hydroxide (40%) with formation of acetophenone. *Stannic bis-3-ethylacetylacetone dibromide*, transparent, colourless, six-sided prisms, m. p.  $164$ – $166^\circ$  after softening at  $162^\circ$ , and *3-bromo-3-ethylacetylacetone*, a pale yellow, lachrymatory liquid, b. p. about  $195^\circ$ , are described. F. G. W.

**The  $\alpha$ - and  $\beta$ -Forms of certain Monosaccharides.** O. SVANBERG and K. O. JOSEPHSON (*Ber.*, 1924, **57**, [B], 297–299).—It is proposed to discriminate between the  $\alpha$ - and  $\beta$ -forms of monosaccharides by observation of their differing affinity towards invertase. In the cases of dextrose and xylose, a distinct difference is observed in the behaviour of the two forms of the sugar; the  $\alpha$ -variety of one sugar resembles exactly the  $\beta$ -variety of the other.

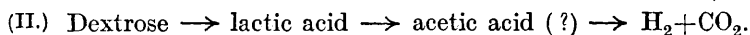
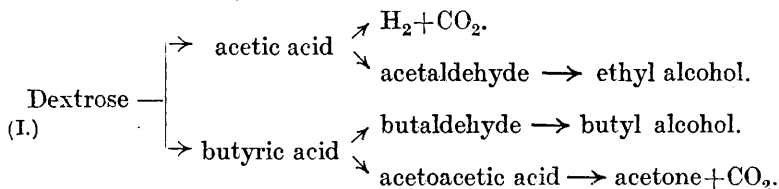
Amongst the monosaccharides, certain instances are encountered in which the more strongly dextro-rotatory variety (the  $\alpha$ -form according to Hudson) can only be converted slowly, if at all, into the corresponding acetone-sugar, whereas in others (pentoses) the

$\alpha$ -variety readily undergoes this change. When the  $\alpha$ -sugar is very inert, the  $\beta$ -sugar is highly active.

The conclusions based on the two methods are identical in the cases of dextrose and xylose, but the available experimental data are insufficient to permit an extended proposal for the designation of  $\alpha$ - and  $\beta$ -forms.

H. W.

**Molecular Configuration in the Sugars and Acid Production by *Bacillus Granulobacter Pectinovorum*.** H. B. SPEAKMAN (*J. Biol. Chem.*, 1923, **58**, 395—413).—The non-volatile acid produced during the fermentation of starch by *Bacillus granulobacter pectinovorum* (cf. Reilly, Hickinbottom, Henley, and Thaysen, A., 1920, i, 465) has been identified as lactic acid, and the rates of formation of this acid, as well as those of acetic and butyric acids, during the fermentation of starch, arabinose, xylose, dextrose, galactose, and mannitol have been studied. From the results obtained, the fermentation of dextrose is provisionally regarded as taking place in two ways, according to the following schemes (cf. also A., 1920, i, 797) :



The author also tentatively advances the theory that the rupture of the sugar molecule takes place preferentially and most rapidly between those carbon atoms the hydroxyl groups of which are adjacent to one another. On this basis, mannose, which contains two pairs of adjacent hydroxyl groups, would be expected to be fermented more rapidly than dextrose or galactose, which only contain one such pair. Further, whereas the fermentation of dextrose should proceed mainly according to scheme (I), that of galactose should proceed mainly according to scheme (II). These deductions appear to be confirmed by experiment. Similar deductions from the configurations of the pentoses are also in accord with fact, but the theory appears to fail with respect to dulcitol, which, unlike mannitol, is not fermented by the bacillus (cf. also Robinson, A., 1922, i, 971).

E. S.

**Relations between Rotatory Power and Structure in the Sugar Group. I. The Halogenoacyl and Nitroacyl Derivatives of the Aldose Sugars.** C. S. HUDSON (*J. Amer. Chem. Soc.*, 1924, **46**, 462—477).—Investigations have been carried out with a view to determine the probable structure and physical constants of the as yet undiscovered  $\alpha$ -halogenoacetylglucoses and related sugars as a help to their syntheses.

The application of van't Hoff's hypothesis of additive optical

superposition to the two forms of dextrose penta-acetate permits the calculation of the rotation of the acetylated basal chain which is common to both varieties. If this value is subtracted from the known rotation of acetylbromoglucose, the numerical value for the halogenated carbon atom can be deduced. An extension of this method of calculation to a series of halogenoacetyl- and nitroacetyl-glucoses shows that the rotation of the terminal asymmetric carbon atom in these compounds is approximately a constant quantity for the various aldoses. A comparison of the calculated and observed values for a series of halogenoacetyl sugars, such as bromo- and chloro-acetyldextrose, indicates that they are to be classified as  $\alpha$ -forms instead of, as previously,  $\beta$ -varieties.

Van't Hoff's theory is applicable also to the glucosamines and to derivatives of deoxyglucose. Bromoglucodesose tribenzoate (Bergmann, Schotte, and Leschinsky, A., 1923, i, 653), is an  $\alpha$ -derivative whereas deoxymethylglucoside tribenzoate prepared from it is a  $\beta$ -form. Toluene-*p*-sulphonyltriacytylbromoglucose (Freudenberg and Ivers, A., 1922, i, 524) is also an  $\alpha$ -variety, whereas the corresponding tetra-acetate and the methylglucoside belong to the  $\beta$ -series.

A. B. S.

**Relations between Rotatory Power and Structure in the Sugar Group. II. The Halogenoacetyl Derivatives of a Ketose Sugar [*d*-Fructose].** C. S. HUDSON (*J. Amer. Chem. Soc.*, 1924, 46, 477—483; cf. preceding abstract).—The theory of optical superposition may be applied to ketoses, the effect of the halogenated terminal carbon atom being of the same magnitude as for the aldoses.

In the case of the two isomeric lævulose penta-acetates, the calculated values for  $[\alpha]_D$  are  $-5^\circ$  and  $-103^\circ$  in chloroform, whereas the observed rotations of the two known isomerides are  $[\alpha]_D^{20} +34.7^\circ$  and  $-121^\circ$  in the same solvent. It seems very unlikely that the dextrorotatory form is the expected  $\alpha$ -derivative; possibly it has a different ring structure from the compounds hitherto examined. The other isomeride,  $[\alpha]_D^{20} -121^\circ$ , may be the  $\beta$ -form, although a difference of  $18^\circ$  causes doubt; the fact that normal  $\beta$ -bromo- and fluoro-acetyl-lævuloses can be prepared from it are evidence in favour of the  $\beta$ -modification.

A. B. S.

**Relations between Rotatory Power and Structure in the Sugar Group. III. The Biose of Amygdalin [*Gentiobiose*] and its Configuration.** C. S. HUDSON (*J. Amer. Chem. Soc.*, 1924, 46, 483—489).—The identity of the biose of amygdalin with gentiobiose is established by the observation that the rotation of the biose chain of amygdalin, as calculated from the rotations of two of its derivatives, isoamygdalin and prulaurasin, has the same value as the rotation of the chain of gentiobiose. The line of evidence is entirely independent of that of Haworth and Leitch (T., 1922, 121, 1921) or Kuhn (A., 1923, i, 589). The combined results prove the configuration of gentiobiose to be that of 1 : 6- $\beta$ -glucosidoglucose. Maltose and gentiobiose are the  $\alpha$ - and  $\beta$ -glucos-



idic forms respectively of 1:6-glucosidoglucose; they constitute the first  $\alpha\beta$  pair of compound sugars to be definitely allocated.

A. B. S.

**Polysaccharides. XXII. Lichenase and Reserve Cellulose [Lichenin]. XXIII. The Separation of Lichenase into Constituent Enzymes.** P. KARRER and others.—(See i, 471.)

**Polysaccharides. XXIV. The Occurrence of Lichenin (Reserve Cellulose) in Lichens and other Plants.** P. KARRER, M. STAUB, and J. STAUB (*Helv. Chim. Acta*, 1924, 7, 159—162).—The preparation of lichenin is described from the lichens *Evernia vulpina*, *Usnea barbata*, L., and *Parmelia furfuracea*, Ach.; it is shown to be identical with that from Iceland moss, *Cetraria Islandica*. It also occurs in many other plants, such as barley, oats, maize, spinach, beans, hyacinth bulbs and others. [Cf. i, 471.]

E. H. R.

**Starch Iodide.** A. LOTTERMOSER (*Z. angew. Chem.*, 1924, 37, 84—85; cf. this vol., i, 269).—The partition of iodine between starch, aqueous potassium iodide, and carbon tetrachloride was determined, using the partition coefficient of iodine between carbon tetrachloride and *N*/10-potassium iodide ( $=1.16$  at  $25^\circ$ ). The partition of iodine between carbon tetrachloride, aqueous potassium iodide, and soluble starch was also examined by the potentiometer method (cf. A., 1922, i, 10). The results agreed with those obtained by ultrafiltration of the starch iodide solution and analytical determination of the individual components before filtration and in the ultrafiltrate. Starch iodide is thus shown to be an adsorption product. The  $I_3$ -ion is most strongly adsorbed, the adsorption curve being normal. At the same time, the  $I$ -ion and undissociated  $KI$  and  $KI_3$  are also adsorbed, whilst the expulsion of free iodine from the surface generally increases with increasing concentration. The determination of the partition of iodine between benzene, water, and starch (cf. von Euler and Myrbäck, A., 1922, i, 527, 1120) gave unsatisfactory results owing to the uncertainty of the partition coefficient of iodine between benzene and water. Analogous experiments using carbon tetrachloride in place of benzene give results in agreement with those quoted above, so that there is no evidence of chemical combination between the iodine and starch. Adsorbed iodine is given up again very incompletely by starch, so that the curves obtained by adjusting the equilibrium from "above" and "below" do not coincide. The actual adsorption equilibrium is, however, rapidly attained, but the starch continues to adsorb iodine owing, apparently, to a very gradual diffusion of the latter into it.

W. T. K. B.

**Starch-Iodine Reaction.** N. R. DHAR.—(See ii, 242.)

**Topochemical Reactions. Esterification and Mercerisation of Cellulose.** R. O. HERZOG and G. LONDBERG (*Ber.*, 1924, 57, [B], 329—332).—Röntgen examination shows that the esterification of ramie fibre and a number of varieties of artificial silk is a normal, heterogeneous process which proceeds from exterior

to interior accompanied by solution of the cellulose esters. The progress of the reaction does not depend on the degree of arrangement of the crystallites, but on the previous chemical and physical treatment of the material. The nitration of cellulose, on the other hand, is a typical topochemical reaction occurring in the swollen fibre as in a homogeneous chemical system; denitration of cellulose nitrate under mild conditions takes place similarly.

Röntgen photographs of ramie or hemp fibres which have been mercerised without tension by sodium hydroxide solution (about 17%) and subsequently washed until free from alkali, exhibit Debye-Scherrer rings in place of the original point diagrams, showing that the crystallites have taken all possible positions. When the fibre is mercerised under such tension that the length remains unchanged, however, a point diagram is subsequently obtained, showing that the crystals lie, as originally, with the same axis in the direction of the fibre, that the crystals of mercerised cellulose have the same axial ratio and angles as the crystals of the original cellulose, and that the molecule of mercerised cellulose differs but little from that of the original cellulose, possibly to such an extent as is involved by the displacement of an oxygen linking.

H. W.

**Quantitative Determination of the Fluorescent Powers (the Spectro-fluorescometry) of Cellulose and its Derivatives.**

S. J. LEWIS (*J. Soc. Dyers and Col.*, 1924, **40**, 29—40).—The work previously described (*A.*, 1923, ii, 334) has been extended and the methods have been improved so that the investigation of the fluorescent powers of cellulosic substances is now claimed to be easily carried out and even capable of application to industrial problems. Particularly, the spark source of ultra-violet light has been replaced by a cooled rotating tungsten arc, whereby the original feebleness of the spectrum between  $\lambda$  2750—3300 and  $\lambda$  2640—2730 is avoided, the necessary time for exposure has been shortened, and the method is about one thousand times more efficient, the accuracy being within 1%.

The fluorescent powers of various classes of cellulosic substances such as pure papers, pure cellulose, hydrocellulose, oxycellulose, and cellulose acetate have been determined in reference to a new standard (a specially purified paper) and the type of fluorescent curve for each class has also been determined. The previous conclusion that the fluorescent power of a cellulosic substance is independent of its physical condition has been confirmed. For instance, the fluorescent curves of cellulose acetate powder, paper, and transparent film are very similar, and the fluorescent power of oxycellulose is almost independent of its method of preparation.

Numerous curves representing the fluorescent powers of cellulose and related substances are given and discussed.

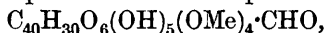
A. J. H.

**The Viscose Reaction.** B. RASSOW and M. WADEWITZ (*J. pr. Chem.*, 1923, **106**, 266—332).—A study has been made of the factors affecting the viscosity of solutions of viscose (cellulose

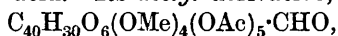
xanthate). By the action of sodium hydroxide solutions on cellulose there appears to be formed a definite compound, having the empirical composition  $C_6H_{10}O_5 \cdot NaOH$ . When solutions containing less than 35% of sodium hydroxide are used, there is an equilibrium set up between cellulose, sodium hydroxide, the compound, and water. The compound is slowly decomposed by absolute ethyl alcohol. The so-called ripening of cellulose xanthate solutions, during which a fall in viscosity takes place, is probably the result of two reactions, the gradual hydrolysis of the cellulose xanthate and the disruptive action of the sodium hydroxide present on the cellulose molecular aggregates. [Cf. *B.*, 1924, 289.]

E. H. R.

**Lignin. I. Flax Lignin and some Derivatives.** W. J. POWELL and H. WHITTAKER (*J. Chem. Soc.*, 1924, 125, 357—364).—Flax lignin, obtained from flax shoves by digestion with 10% sodium hydroxide solution at 130°, can be purified to a homogeneous, light brown product of the composition



by pouring its solution in aqueous acetone into a large volume of dilute hydrochloric acid. Its *acetyl* derivative,



a dark brown, amorphous solid, is insoluble in cold, dilute sodium hydroxide, but is readily hydrolysed by boiling with water, indicating that the acidic properties of the lignin are to be ascribed to phenolic hydroxyl groups. By the action of methyl sulphate under very mild conditions, three methoxyl groups can be introduced into the lignin molecule, forming *methyl-lignin*,



which is insoluble in alkali hydroxide and very resistant to hydrolysis. Attempts to acetylate the methylated product were not successful, indicating some difference between the remaining hydroxyl groups in lignin and those in its derivatives. The product of the action of hydriodic acid on the lignin agrees closely in composition with a demethylated lignin, but it cannot be acetylated, showing that reduction accompanies the demethylation. Cold, concentrated nitric acid, or a mixture of nitric and sulphuric acids, converts the lignin into a *trinitro* derivative,  $C_{42}H_{39}O_{22}N_3$ , a red powder which contains one methoxyl group and behaves as an aromatic nitro compound; six acetyl groups can be introduced, forming *acetyltrinitrolignin*. At higher temperatures, nitration is accompanied by much oxidation. The lignin reacts energetically with chlorine and bromine in absence of sunlight, with evolution of halogen acid. The products, *chlorolignin* and *bromolignin*,  $C_{40}H_{20}O_8Hal_2(OMe)_2(OH)_5 \cdot CHO$ , are soluble in alkali hydroxides, and have suffered partial demethylation. They are not affected by hot nitric acid, and are only partly dehalogenated by boiling with sodium hydroxide solution, indicating that the remaining halogen atoms are attached to aromatic nuclei. *Acetylchlorolignin*,  $C_{53}H_{42}O_{21}Cl_{12}$ , and *acetylbromolignin*,  $C_{42}H_{30}O_{16}Br_{12}$ , as well as the

acetylnitrolignins, are readily hydrolysed. The presence of one aldehyde group in the lignin molecule is deduced from the action of Fehling's solution and of phenylhydrazine. Comparison of these results with those of Cross and Bevan, Klason (A., 1908, i, 707; 1923, i, 187), and Beckmann and Liesche (A., 1921, i, 546; 1922, i, 233), shows that the lignins from jute, flax, and pine are not identical, but that those from flax and winter rye straw are closely related.

On treatment of the neutralised washings from the lignin (see above) with calcium chloride solution, considerable quantities of the calcium salt of a substance resembling lignin, but having a much smaller methoxyl content, are obtained. From the solution of chlorolignin in cold alkali hydroxide, acids precipitate the compound  $C_{43}H_{35}O_{16}Cl_6$ .  
F. G. W.

**Potash Fusion of Lignin, Cellulose, and Wood.** E. HEUSER and F. HERRMANN (*Cellulosechem.*, 1924, 5, 1—6).—The observations of Heuser and Winsvold (A., 1923, i, 541, 900) on the fusion of lignin are confirmed and extended. When iron powder is present the yield of aromatic products is increased and the elimination of carbon dioxide from the protocatechuic acid is promoted, but not to such a large extent as when the fusion is performed in an iron crucible; iron is dissolved. There is only a slightly lower yield when the fusion is carried out at 240—260° instead of 270—280°. In the presence of ammonium carbonate a portion of the pyrocatechol is re-converted into protocatechuic acid. Fusion in an atmosphere of carbon dioxide instead of hydrogen does not have this effect; an atmosphere of carbon dioxide exerts a protective influence in suppressing the formation of oxalic acid, but not so completely as hydrogen. Carbon dioxide also moderates the total reaction, presumably because it combines with the potassium hydroxide; more lignic acid remains in the product. Carbon dioxide is produced to the extent of 27—28% of the weight of lignin when the fusion is carried out in a nickel crucible in the presence of air. Since the decomposition of protocatechuic acid into pyrocatechol is only pronounced in the presence of a catalyst in an atmosphere of hydrogen, the carbon dioxide formed under normal conditions is the result of oxidation at the expense of a portion of the products of reaction. Pure pyrocatechol is substantially resistant under the conditions employed. The fusion of cellulose with potash yields no aromatic products, only oxalic acid, with 21—22% of acetic acid and 1.5—2% of formic acid. The amount of oxalic acid is not substantially altered by the use of an atmosphere of hydrogen or by adding iron as catalyst; thus its formation from cellulose is not a process of oxidation. The fusion of wood gives results exactly compatible with those described for lignin and cellulose.  
J. F. B.

**Nature of Lignin.** E. STRUPP (*Cellulosechem.*, 1924, 5, 6—7).—The cyclo-saccharides or cycloses may be regarded as intermediate links capable of uniting partly with true carbohydrates and partly

directly with one another. The presence of hydroaromatic rings in lignin and its undetermined position between the aromatic and aliphatic systems are cited as arguments in favour of the investigation of this conception. The methyl ether of inositol is a constituent of the cambial sap of certain conifers, and from inositol are obtainable several of the aromatic and aliphatic derivatives which have been detected in the products of decomposition of lignin.

J. F. B.

### Transformation of Ligneous Plant Substances into Coal.

**I. Production of Coal-like Products from Cellulose.** C. G. SCHWALBE and R. SCHEPP (*Ber.*, 1924, 57, [B], 319—322).—Cellulose can be converted into coal-like substances by salts which are present in sea water at a relatively low temperature and with surprising rapidity.

Coal-like substances, the composition and nature of which have not been fully examined, are produced from wood tissue and concentrated magnesium chloride solution at 150—180°, 135°, and 95°, respectively; a similar effect is produced by zinc chloride but not by calcium chloride solutions at 135°. Since in every case hydrochloric acid is produced it remains uncertain whether the effect is to be ascribed to dehydration or to hydrolysis of cellulose to dextrose and carbonisation of the latter.

H. W.

**Synthesis of some New  $\beta$ -Amino-acids, Esters, and Alcohols.** R. BRECKPOT (*Bull. Soc. chim. Belg.*, 1923, 32, 412—433).—Using three alkyl-substituted  $\beta$ -aminobutyronitriles described by Bruylants (*A.*, 1923, i, 762) as a starting-point, the author has effected their hydrolysis and the esterification of the resulting acids, and has studied the reduction of these esters and also their reactions with magnesium ethyl bromide. The following compounds are described:  $\beta$ -Dimethylaminobutyric acid hydrochloride, hygroscopic needles, obtained by the action of concentrated hydrochloric acid on  $\beta$ -dimethylaminobutyronitrile, chloroplatinate, small orange crystals, m. p. 194—195° (decomp.). Ethyl  $\beta$ -dimethylaminobutyrate, b. p. 69.5°/12 mm., 183.5—184.5°/758 mm. (partial decomp.),  $d_4^{20}$  0.91958,  $n_D^{20}$  1.42641, prepared by the action of dry hydrogen chloride on an alcoholic solution of the hydrochloride of the acid, when an oil,  $C_9H_{17}O_4N$ , b. p. 105—110°/12 mm., which could not be identified, was produced simultaneously. The ester yields a methiodide, colourless needles, m. p. 127—128°, and a chloroplatinate, flattened orange-red prisms, m. p. 178—179° (decomp.), whilst on reduction with sodium and absolute alcohol,  $\beta$ -dimethylaminobutyl alcohol, b. p. 178—180°/760 mm.,  $d_4^{20}$  0.896,  $n_D^{20}$  1.4408, is obtained. (The hygroscopic methiodide, m. p. 262—263°, and the non-crystalline hydrochloride are described.) The ester on treatment with magnesium ethyl bromide yields a mixture of diethylpropylenecarbinol,  $CHMe:CH\cdot C(OH)Et_2$ , and  $\alpha\alpha$ -diethyl- $\gamma$ -dimethylaminobutan- $\alpha$ -ol, b. p. 205—212°,  $d_4^{20}$  0.873,  $n_D^{20}$  1.4410 (methiodide, m. p. 140—142°, hydrochloride, a white, extremely hygroscopic solid).  $\beta$ -Ethylaminobutyric acid hydrochloride, a

crystalline mass, m. p. 72—73°, was also prepared by the action of hydrochloric acid on the corresponding nitrile; the corresponding free acid could not be prepared. *Ethyl β-ethylaminobutyrate*, b. p. 74°/12 mm.,  $d_4^{20}$  0.91549,  $n_D^{20}$  1.42531 (*hydrochloride*, m. p. 111—114°), was obtained by passing dry hydrogen chloride through an alcoholic solution of the acid, with simultaneous production of a colourless oil,  $C_{14}H_{27}O_6N$ , b. p. 111—114°/19 mm. On reduction, the ester yields *β-ethylaminobutyl alcohol*, b. p. 187°, and is converted by treatment with magnesium ethyl bromide into the *lactam* of *β-ethylaminobutyric acid*,  $CO < \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ N \end{smallmatrix} > CHMe$ , b. p. 79.5—80.5°/12.5 mm.,  $d_4^{20}$  0.9420,  $n_D^{20}$  1.4478 (*hydrochloride*, m. p. 72—73°); a theoretical explanation of its formation is given. At the same time, an octadiene, a colourless liquid, b. p. 127—130°/761 mm., and a small quantity of hygroscopic white needles, b. p. 255—265°, which were not identified, were produced. *Ethyl β-methylaminobutyrate*, b. p. 72°/12.5 mm., was prepared in a similar manner to its homologue; with magnesium ethyl bromide it yields the *lactam* of *β-methylaminobutyric acid*, b. p. 73—74°/12 mm., together with the same octadiene mentioned above.

The author points out that the three esters described may all be obtained from allyl bromide as a starting point (cf. Bruylants, A., 1922, i, 817), and the yields at each stage are good. H. J. E.

**Salting-out of Amino-acids.** P. PFEIFFER and O. ANGERN (*Z. physiol. Chem.*, 1924, **133**, 180—192).—*L*-Tyrosine, *l*-asparagine, *d*-glutamic acid, and glycylglycine are not salted out by ammonium sulphate and sodium acetate. Glycine and sarcosine are salted out to a greater or less degree by potassium acetate, *l*-cystine by ammonium sulphate, and *dl*-alanine by potassium acetate and ammonium sulphate. *l*-Leucine, *dl*-phenylalanine, and *l*-tryptophan are precipitated by sodium chloride, potassium acetate, and ammonium sulphate. S. S. Z.

**Amino-acids and Polypeptides in Combination with Neutral Salts.** IV. P. PFEIFFER, M. KLOSSMANN, and O. ANGERN (*Z. physiol. Chem.*, 1924, **133**, 22—61).—Compounds of glycine, alanine, sarcosine, betaine, glycylglycine, alanylglycine, and di- and tri-glycylglycine, with a number of metallic salts, mainly alkali halides, were prepared and analysed. S. S. Z.

**Oxidation of Amino-acids with Hydrogen Peroxide and at the Anode.** F. FICHTER and F. KUHN (*Helv. Chim. Acta*, 1924, **7**, 167—172).—The oxidation of glycine in 2*N*-sulphuric acid solution, in presence of ferrous sulphate, with hydrogen peroxide proceeds partly according to the equation,  $NH_2 \cdot CH_2 \cdot CO_2H + 3O = NH_3 + 2CO_2 + H_2O$ , but only about half the theoretical quantity of ammonia and carbon dioxide can be accounted for. When insufficient hydrogen peroxide for the above equation is used, some formic acid is produced. When the oxidation is carried out in presence of ammonia, only minute amounts of carbamide are formed. By

electrochemical oxidation of glycine in presence of ammonia, using ammonium nitrate as the electrolyte, larger quantities of carbamide are formed, and still larger quantities if ammonium carbonate is used instead of the glycine. It is concluded, therefore, that when glycine is used, the carbamide is formed from its decomposition products (cf. Fichter and Schmid, A., 1920, i, 824).

Oxidation of  $\alpha$ -alanine with hydrogen peroxide in dilute sulphuric acid in presence of ferrous sulphate gives ammonia, acetaldehyde, acetic acid, formaldehyde, formic acid, and carbon dioxide; anodic oxidation in acid solution gives the same products. Anodic oxidation of leucine gives a mixture of isovaleraldehyde, isovaleric acid, isobutyric acid, acetone, acetic acid, formic acid, carbon dioxide, and ammonia.

E. H. R.

**Nitrogenous Components of Beetroot and Beetroot Products.** E. O. VON LIPP MANN (*Ber.*, 1924, 57, [B], 256—258).—An account of experiments completed in 1902.

The following substances have been isolated from the solutions obtained after removal of sugar: *d*-arginine, m. p. 207°,  $[\alpha]_D^{20} +11.25^\circ$  in aqueous solution; *d*-lysine, m. p. 193.5°,  $[\alpha]_D^{20} +15.42^\circ$  when dissolved in water; *l*-histidine, m. p. above 280° (decomp.),  $[\alpha]_D^{20} -39.48^\circ$ ; proline, m. p. 203°,  $[\alpha]_D^{20} -3.12^\circ$ ; scatolecarboxylic acid, m. p. 162.5°; *l*-cystine, m. p. about 260° (decomp.),  $[\alpha]_D^{20} +221^\circ$  in hydrochloric acid solution (10%). The juice of freshly-harvested but still unripe beetroot yielded *l*-phenylalanine, m. p. 263°, a substance,  $C_{18}H_{20}O_5N_2$ , m. p. 275°,  $[\alpha]_D^{20} +94.15^\circ$  and  $+38.65^\circ$  in faintly acidic and alkaline solution, respectively, which is probably identical with tyrosine anhydride (A., 1922, i, 184), and a substance,  $C_6H_7O_4N$ , colourless prisms, m. p. 125°, probably the imide of tricarballylic acid (cf. Thole and Thorpe, T., 1911, 99, 1688).

H. W.

### Deamination of Esters of Alanine and Aminoisobutyric Acid.

A. L. BARKER and G. S. SKINNER (*J. Amer. Chem. Soc.*, 1924, 46, 403—414).—*Ethyl  $\alpha$ -aminoisobutyrate hydrochloride*, m. p. 155—157° (corr.), is converted by a slight excess of sodium nitrite in aqueous solution at 0° into ethyl  $\alpha$ -methylacrylate, ethyl  $\alpha$ -hydroxyisobutyrate, and a little  $\alpha$ -methylacrylic acid. Under similar conditions, methyl  $\alpha$ -aminoisobutyrate hydrochloride yields very small amounts of  $\alpha$ -methoxyisobutyric acid which contains a small proportion of  $\alpha$ -hydroxyisobutyric acid and  $\alpha$ -methylacrylic acid together with methyl  $\alpha$ -methylacrylate and methyl  $\alpha$ -hydroxyisobutyrate. Methyl  $\alpha$ -aminopropionate hydrochloride gives methyl acrylate, methyl  $\alpha$ -chloropropionate, and methyl lactate, in addition to a non-volatile residue which is regarded as a pyrazolinedicarboxylic ester; the acidic products include  $\alpha$ -methoxypropionic acid, lactic acid, and unsaturated and chloro acids. Ethyl  $\alpha$ -aminopropionate hydrochloride yields ethyl acrylate, ethyl chloro- and hydroxy-propionates, ethyl diazopropionate, acrylic, lactic,  $\alpha$ -chloropropionic, and  $\alpha$ -ethoxypropionic acids, and certain nitrogenous residues which have not been identified.

A. B. S.

**Attempts to Prepare a Cyanide of Tin.** J. G. F. DRUCE (*Chem. News*, 1924, **128**, 115—116).—No compound of tin with the cyanogen radical could be obtained by boiling an ethereal solution of stannous chloride with silver cyanide or ethyl cyanide. Freshly precipitated stannic hydroxide was dissolved in hot dilute hydrocyanic acid, and the filtered solution on evaporation in a vacuum left a pale brown, amorphous residue insoluble in water, alcohol, or ether. Analysis gave results closely agreeing with the formula  $\text{Sn}(\text{OH})_3\cdot\text{CN}$ . Lead cyanide is produced by adding an excess of potassium cyanide to a saturated solution of lead nitrate; it is a white precipitate slightly soluble in hot 5% hydrocyanic acid, from which it crystallises in colourless needles. A. R. P.

**Oxidation of Saturated Hydrocarbons by Ozone.** R. KOETSCHAU and W. FLEMMING (*Z. angew. Chem.*, 1924, **37**, 42—44).—Saturated cyclic hydrocarbons are attacked by ozone, as is shown by a marked increase in their viscosity and refractive index. The products obtained from decahydronaphthalene are mainly of the nature of peroxides which, unlike normal ozonides, dissolve in saturated hydrocarbons. When they are treated with water, hydrogen peroxide is formed, accompanied, not by aldehydic products, but by hydroxylic and carboxylic compounds. A small proportion of decahydronaphthol was identified in the reaction products, but the constitution of the peroxides and acids is still uncertain. The oxidation is far-reaching, and is complicated by the apparent partial rupture of the ring structure, with liberation of carbon dioxide. W. T. K. B.

**Benzene and the Tetrahedron Formula.** C. W. A. LELY (*Chem. Weekblad*, 1924, **21**, 114—117, 117—124).—Further arguments are quoted in support of the author's triangular formula (A., 1923, i, 99, 313, 767) and criticising the arguments brought against it by Olivier, van Roon, Schoutissen, and Derx and Hermans (*ibid.*, 195, 196, 451). The conclusion is drawn that the benzene formula of Kekulé and van't Hoff's tetrahedron conception of the carbon atom no longer serve to cover all the known facts.

S. I. L.

**Contact Condensation of Acetylene.** N. ZELINSKY.—(See i, 359.)

**Hydrocarbons of Kerosene.** C. R. WAGNER.—(See i, 357.)

**Action of Nitrogen Tetroxide on Aromatic Hydrocarbons, particularly Toluene.** A. SCHAARSCHMIDT and E. SMOLLA (*Ber.*, 1924, **57**, [B], 32—42).—Nitrogen tetroxide scarcely reacts with cold benzene, more readily with toluene or xylene, immediately with mesitylene with evolution of heat. A study of the interaction of the tetroxide (1 part) and the hydrocarbon (3 parts) during extended periods at the atmospheric temperature, shows that benzene gives mainly nitrobenzene, picric acid, and some dinitrobenzene. *p*-Chlorotoluene is oxidised and nitrated to *p*-chlorobenzoic acid and nitro derivatives. Xylene and mesitylene are transformed into resinous products, oxidation occurring to a



particularly marked degree in the case of mesitylene. Toluene is converted into oxalic acid (the yield of which increases greatly with prolongation of the action), benzoic acid, phenols, and benzaldehyde; the residue remaining after the product has been treated successively with water, sodium carbonate, sodium hydroxide, and sodium hydrogen sulphite consists mainly of almost equal proportions of unsaponifiable nitrotoluenes and readily hydrolysed nitrous or nitric esters of dinitrocresol. The unsaponifiable portion contains about 66% of mononitrotoluene; the remainder is a mixture of nitro products of higher boiling point, the least volatile of which decomposes explosively when heated in a vacuum at 200°. In the earlier stages of the reaction, acid, aldehydic, and neutral products are formed the weights of which are approximately in the ratio 3 : 2 : 4; when, however, the reaction is prolonged, the aldehydic components disappear almost completely in favour of the acid substances. The action depends greatly on the purity of the nitrogen tetroxide employed, and is most vigorous in the absence of water. H. W.

**Reaction of Organo-Magnesium Compounds with Cupric Chloride.** E. SAKELLARIOS and T. KYRIMIS (*Ber.*, 1924, 57, [B], 322—326).—Diphenyl, 4 : 4'-ditolyl, 1 : 1'-dinaphthyl, and *s*-diphenylethane have been prepared by treating cupric chloride with the appropriate magnesium monoaryl halide (cf. Krizewsky and Turner, T., 1919, 115, 559). Cupric chloride converts magnesium styryl bromide into  $\alpha\delta$ -diphenyl- $\Delta_{2\gamma}$ -butadiene, m. p. 147°, and magnesium isoamyl bromide into  $\beta\eta$ -dimethyloctane, b. p. 159—160°. Hydrodicamphene, m. p. 86°, is prepared from pinene hydrochloride. H. W.

**Catalytic Effects of Zinc Chloride and Aluminium Chloride.** J. F. NORRIS (*Ind. Eng. Chem.*, 1924, 16, 184).—When the molecular compound of triphenylmethyl chloride and aluminium chloride is treated with ether, triphenylmethane is formed. This reaction is considered to proceed in the following way:  $\text{Ph}_3\text{C}\cdot\text{Cl} + \text{Et}_2\text{O} = \text{Ph}_3\text{C}\cdot\text{OEt} + \text{EtCl}$ ;  $\text{Ph}_3\text{C}\cdot\text{OEt} = \text{Ph}_3\text{CH} + \text{MeCHO}$ . The first reaction is analogous to the action of aluminium chloride on a solution of benzoyl chloride in ether, the second reaction can be effected by heat alone, or in presence of aluminium chloride at the ordinary temperature. Triphenylmethane can therefore be prepared by allowing a mixture of carbon tetrachloride, benzene, and aluminium chloride to stand over-night; ether is then added, and after some hours the mixture decomposed with water. Excellent yields and a pure product are obtained. Primary alcohols are found to react readily with concentrated hydrogen chloride solution in presence of zinc chloride. This seems to indicate that the rôle of zinc chloride in reactions of this type is not that of a dehydrating agent, but of a catalyst operating by means of the formation of a molecular compound with the alcohol. C. I.

**Hexaphenyl, the Linear Chain of Six Benzene Nuclei.** R. PUMMERER and K. BITTNER (*Ber.*, 1924, 57, [B], 84—88).—In continuation of previous work (A., 1922, i, 1196), 1-phenyl-

4-*p*-aminophenylbenzene is described in greater detail together with its transformation into hexaphenyl.

The preparation of 1-phenyl-4-*p*-aminophenylbenzene has been improved in many details; its success depends greatly on the purity of the reagents employed. 1-Phenyl-4-*p*-acetamidophenylbenzene, slender needles, m. p. 294°, 1-phenyl-4-*p*-benzylideneaminophenylbenzene, m. p. 262°, and the compound,  $C_{28}H_{19}O_2N$ , obtained from the base and *p*-naphthaquinone, are described. The amino compound yields a granular, yellow *diazonium sulphate* which is converted by potassium iodide into 1-phenyl-4-*p*-iodophenylbenzene, colourless leaflets, m. p. 247°. The action of silver powder on the iodo compound at about 330° leads to the production of *hexaphenyl*,  $Ph[C_6H_4]_4Ph$ , small, colourless, rhombic leaflets, m. p. 475°.

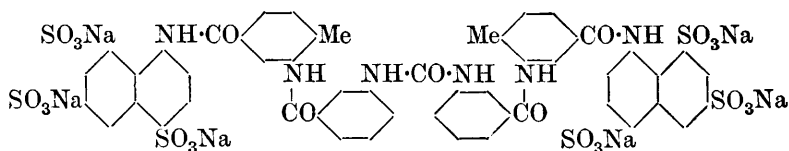
H. W.

**Mechanism of the Reaction of *iso*Cyanates and *iso*Thiocyanates with the Grignard Reagent.** H. GILMAN and C. R. KINNEY (*J. Amer. Chem. Soc.*, 1924, **46**, 493—497).—The reaction between phenyl *isocyanate* and the Grignard reagent may be represented by the scheme : (I)  $PhN:C:O + PhMgBr \rightarrow PhN(MgBr)C(Ph):O \rightarrow PhNH\cdot C(Ph)O$  or (II)  $PhN:C:O + PhMgBr \rightarrow PhN:C(Ph)OMgBr \rightarrow PhN:C(Ph)OH$ , the last compound undergoing rearrangement to benzanilide. To decide between the two schemes, attempts were made to displace the *MgBr* in the additive compound by other radicals before hydrolysis. The introduction of methyl and ethyl groups was attempted, using methyl and ethyl sulphates, but the product obtained on hydrolysis was always benzanilide. The same occurred when diphenylmethyl chloride, triphenylmethyl chloride, methyl iodide, ethyl iodide, allyl bromide, and *p*-nitrobenzyl bromide were used. As the *MgBr* group is more easily replaced when attached to sulphur, the *isothiocyanates* were investigated. When the Grignard compound was treated with methyl sulphate or ethyl sulphate, the products of hydrolysis were always *S*-methylthiobenzanilide and *S*-ethylthiobenzanilide, indicating that the addition of *PhMgBr* had taken place, not on the  $\cdot N:C:$ , but on the  $:C:S$ , group, the *MgBr* going to the sulphur. Scheme (II) represents the action in the case of the *isothiocyanates*, and on account of the similarity of the *isocyanates*, the same scheme probably represents the reaction in their case also.

A. B. S.

**New Series of Trypanocidal Drugs.** E. FOURNEAU, J. TRÉFOUËL, (MME.) J. TRÉFOUËL, and J. VALLÉE (*Compt. rend.*, 1924, **178**, 675—676).—A substance (called 309) resembling Bayer 205 in all physical and trypanocidal properties, has been prepared. It is a grey or flesh-coloured powder, very soluble in water, insoluble in alcohol, and readily hydrolysed by concentrated sulphuric acid. Whilst 20-g. mice are completely unharmed by doses of 10—12 mg., mice infected with *Trypanosoma brucei* (Nagana) are cured by doses of 0.062 mg., infection of 2 days' standing being arrested by half this quantity. The drug is prepared as follows : sodium 1-naphthylamine-4 : 6 : 8-trisulphonate is condensed, in presence of sodium

acetate, with 2-nitro-*p*-toluoyl chloride. The resulting nitro-compound is reduced, the amino compound obtained being condensed with *m*-nitrobenzoyl chloride. The product is reduced, and the amino compound formed condensed with carbonyl chloride. Bayer 205 (or the new compound, 309) is the sodium salt (following formula) of the resulting carbamide :



A large number of allied substances have been prepared, none of which has the physiological action of Bayer 205. The slightest constitutional change, *e.g.*, as obtained by using the above acid chlorides in the reverse order, is accompanied by complete suppression of trypanocidal action. E. E. T.

**Compounds of the 2-Fluorenylmethyl Series.** J. VON BRAUN and H. ENGEL (*Ber.*, 1924, **57**, [B], 191—194; cf. A., 1923, i, 1087).—The cyano group of 2-cyanofluorene can be smoothly reduced to the methylamino group, without the occurrence of hydrogenation of the nucleus, by the action of hydrogen in the presence of nickel on a solution of the compound in decahydronaphthalene at 100°. 2-Fluorenylmethylamine and di-2-fluorenylmethylamine are thereby produced; they are separated from one another by taking advantage of the widely differing solubilities of the respective hydrochlorides in water. The primary base is a colourless, crystalline mass, m. p. 113°, b. p. 215°/10 mm.; the corresponding *hydrochloride*, m. p. 275—278° (decomp.), the *picrate*, m. p. 210°, the *acetyl* derivative, m. p. 171°, and the *phenylthiocarbamide* compound, colourless needles, m. p. 169°, are described. The secondary base, m. p. 147°, gives a *hydrochloride* which does not melt below 360° and a *nitroso* derivative, needles, m. p. 212°. Nitrous acid transforms the primary amine into 2-fluorenylmethyl alcohol, colourless crystals, m. p. 131°, which gives an intense bluish-green coloration with concentrated sulphuric acid; it is converted by the requisite phosphorus halide into 2-fluorenylmethyl chloride, m. p. 100°, and 2-fluorenylmethyl bromide, a pale yellow, crystalline mass, m. p. 95°. With trimethylamine, the bromide yields quantitatively 2-fluorenylmethyltrimethylammonium bromide, m. p. 218—219°, whilst when treated successively with hexamethylenetetramine and water, it is transformed into fluorene-2-aldehyde, colourless crystals, m. p. 174—175° (*semicarbazone*, m. p. 245—247°). 2-Fluorenylacetonitrile, m. p. 124°, is hydrolysed to 2-fluorenylacetic acid, m. p. 178°. H. W.

**Kinetic Behaviour of Mixtures of Isomeric Nitrophenols on Reduction with Stannous Chloride.** A. KLEMENC (*Annalen*, 1924, **435**, 321—322).—The result obtained previously (this vol., i, 36) might have been due to the use of acid at only one concn-

tration. The same result is now obtained varying this concentration, of which it is therefore independent.

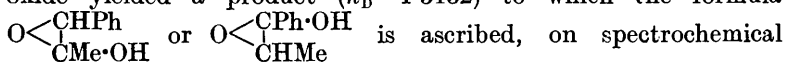
E. E. T.

**Rôle of Weight of Acyl in the Migration from Nitrogen to Oxygen.** L. C. RAIFORD and C. E. GREIDER (*J. Amer. Chem. Soc.*, 1924, **46**, 430—437; cf. Raiford, A., 1920, i, 156).—To investigate the influence of the weight of the acyl group on migration from nitrogen to oxygen, mixed diacyl derivatives of the three aminophenols were prepared, using the acetyl, benzoyl, and  $\alpha$ -naphthoyl radicals. It is concluded that weight is the deciding factor and that migration is independent of substituents in the aminophenol nucleus. The heavier group is always found attached to nitrogen. *o*- $\alpha$ -Naphthoylamidophenyl acetate was obtained when *o*-acetamidophenol in pyridine solution was treated with the calculated quantity of naphthoyl chloride; it forms pink crystals, m. p. 133°. *o*- $\alpha$ -Naphthoylamidophenol is obtained when the acetate is allowed to stand in contact with a 1% solution of potassium hydroxide for 12 hours; very fine needles, m. p. 190°. The constitution of *o*- $\alpha$ -naphthoylamidophenyl acetate was proved by preparing *o*- $\alpha$ -naphthoylamidophenol from *o*-aminophenol and acetylating it, when the same substance was obtained. 5-Bromo-3-naphthoylamido-*p*-tolyl acetate was obtained from 5-bromo-3-acetamido-*p*-cresol by the same method as above; it crystallises in needles, m. p. 218°. 5-Bromo-3-naphthoylamido-*p*-cresol forms colourless needles, m. p. 151°. 4:6-Dibromo-2- $\alpha$ -naphthoylamidophenyl acetate, from 4:6-dibromo-2-acetamidophenol, crystallises in colourless needles, m. p. 226°. 4:6-Dibromo-2- $\alpha$ -naphthoylamidophenol, from the acetate by leaving it in contact with 2% alkali solution for 24 hours, crystallises in needles, m. p. 175°. It was also prepared by benzoylating 4:6-dibromo-2-aminophenol; the product was acetylated and identified with the acetate prepared as above. *o*- $\alpha$ -Naphthoylamidophenyl benzoate was obtained from *o*-benzoylamidophenol by the method described above, the yield being poor; it forms colourless needles, m. p. 176°. 4:6-Dibromo-2- $\alpha$ -naphthoylamidophenyl benzoate, from 4:6-dibromo-2-benzoylamidophenol, by the action of  $\alpha$ -naphthoyl chloride, crystallises poorly, m. p. 235°. Its structure was proved by benzoylating 4:6-dibromo-2- $\alpha$ -naphthoylamidophenol, when the same substance was obtained.

A. B. S.

**Benzoylmethylcarbinol and Acetylphenylcarbinol.** K. VON AUWERS and O. JORDAN (*Biochem. Z.*, 1924, **144**, 31—43).—Benzoylmethylcarbinol has been prepared by the method of Auwers (A., 1918, i, 18), by hydrolysis of the acetyl compound with barium carbonate in water at 100°, and by hydrolysis of  $\alpha$ -bromopropiophenone in aqueous alcohol solution with silver oxide. After purification by distillation in a vacuum, the refractive indices of the various preparations were measured, and these showed no alterations over a period of eight weeks. The purest preparation had  $n_D^{20}$  1.5366, and was not affected by dilute acid or alkali nor by conversion to the acetyl compound and regeneration of the parent

carbinol, which is therefore concluded to be a perfectly stable compound. The observations of Neuberg and Ohle (A., 1922, i, 480, 540) on the partial interchange of benzoylmethylcarbinol ( $\alpha$ -ketol),  $\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$ , into acetylphenylcarbinol ( $\beta$ -ketol),  $\text{OH}\cdot\text{CHPh}\cdot\text{COMe}$ , also obtained biosynthetically by the action of the enzyme carboligase (A., 1921, i, 480), are therefore not confirmed. A mixture of these two compounds ( $\alpha$ - and  $\beta$ -ketols) is obtained by the oxidation of  $\alpha$ -phenylpropylene  $\alpha\beta$ -glycol (Zincke and Zahn, A., 1910, i, 316). Attempts to prepare acetylphenylcarbinol from methylbenzylcarbinol were unsuccessful, and the products obtained from phenylacetone (Carapelle, A., 1904, i, 158) consisted chiefly of derivatives of the  $\alpha$ -ketol. The mechanism of this reaction is discussed. Finally, attempts to obtain acetylphenylcarbinol from methylbromobenzyl ketone by the action of silver oxide yielded a product ( $n_D^{20}$  1.5152) to which the formula



is ascribed, on spectrochemical grounds, and since it does not react with semicarbazide. It is suggested that the slow change of refractive index observed by Neuberg and Ohle (*loc. cit.*) in their preparations may be due to the activity of spores normally present in a biochemical and absent from a chemical laboratory (cf. Auwers and Lange, A., 1922, i, 684).  
J. P.

**The Presence of the Resorcinol Nucleus in the Tannin of Quebracho Wood.** M. NIERENSTEIN (*Ber.*, 1924, 57, [B], 356; cf. Einbeck and Jablonski, A., 1923, i, 1099).—Resorcinol has been obtained previously by the author from quebracho tannin (A., 1906, i, 761).  
H. W.

**Substitution Derivatives of Aurin.** C. H. SPIERS (*J. Chem. Soc.*, 1924, 125, 450—459).—Aurin is most readily isolated from corallin by saturating a solution of the latter in 60% alcohol with sulphur dioxide, and heating the precipitated compound of aurin and sulphurous acid at 130°. The aurin remaining may then be purified by fractional crystallisation from 60% alcohol. *Hexachloroaurin* is obtained as a red powder by boiling with water the product (probably hexachloroaurin sulphate) produced by the action of excess of sulphuryl chloride on aurin in glacial acetic acid solution in presence of ferric chloride. It is insoluble in the usual solvents, but crystallises from anisole in red crystals with a slight golden lustre. *Hexabromoaurin* is obtained similarly from its hydrobromide, which results from the action of excess of bromine on aurin in glacial acetic acid. It dissolves in *o*-chlorophenol, and the solution deposits the compound  $\text{C}_{19}\text{H}_8\text{O}_3\text{Br}_6\cdot\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$  in red crystals with a brassy surface lustre. This loses *o*-chlorophenol at 120° in a vacuum, leaving pure hexabromoaurin as small, red crystals. *Hexabromodiacetylaurin*, obtained by the action of hot acetic anhydride on hexabromoaurin, and also in the cold when a trace of pyridine is present, forms yellow crystals, m. p. 280—290° (decomp.). *Hexabromotriacetylaurin*, colourless crystals of indefinite m. p.

(160—190°), is produced by the action of warm acetic anhydride on the diacetyl derivative in presence of pyridine. *Dibromoaurin* was obtained by the regulated action of bromine on a cold suspension of aurin in glacial acetic acid. It forms deep red, thin, interlocking prisms of a monohydrate, which loses water in a vacuum, leaving small, crimson crystals of the dibromoaurin. By the action of excess of iodine on a solution of aurin in sodium hydroxide, *tetraiododihydroxybenzophenone* (colourless crystals, m. p. 247°, decomp.) was the chief product, together with a little tri-iodophenol, and no iodoaurins could be isolated. *Tetraiododiacetyldihydroxybenzophenone* forms colourless crystals, m. p. 220—222°. *Trimethylaurin* was obtained by diazotising triaminotritolylmethane, and boiling the diazo compound with dilute sulphuric acid. It crystallises from a mixture of ethylene chlorohydrin and water in red crystals with a blue surface colour. *Tribromotrimethylaurin* is obtained by the action of bromine on a solution of trimethylaurin in boiling glacial acetic acid. It crystallises from ethylene chlorohydrin in reddish-brown needles with a slight golden lustre which contain 1 mol. of solvent. The latter is given up at 120° in a vacuum, leaving the tribromotrimethylaurin as small, red crystals. F. G. W.

**Interaction of some Aromatic Hydrocarbons, Alcohols, and Aldehydes with Nitrogen Peroxide.** L. W. BASS and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1924, **46**, 456—461).—Aromatic hydrocarbons show little tendency to interact with nitrogen peroxide at the ordinary temperature. Exposure to sunlight has very little effect. After heating or long exposure, there is slight evidence of nitration and oxidation. *o*-Nitrobenzaldehyde gave, besides *o*-nitrobenzoic acid, a compound which appears to be *o*-diazobenzoic acid nitrate. Benzyl alcohol was oxidised to a mixture of benzaldehyde and benzoic acid in about equal proportions. Aromatic aldehydes oxidised to acids. With *o*-, *m*-, and *p*-nitrotoluenes there was slight oxidation to *o*-, *m*-, and *p*-nitrobenzoic acids. Anthracene was partly oxidised to anthraquinone. A. B. S.

**Chemical Nature of the Naphthenic Acids. I.** N. ZELINSKY (*Ber.*, 1924, **57**, [B], 42—51).—An attempt has been made to settle the vexed question of the nature of the polycyclic ring present in the naphthenic acids. The latter were converted by a series of mild reactions into hydrocarbons containing the same number of carbon atoms. These were subjected to catalytic dehydrogenation (Zelinsky, A., 1911, i, 958; 1912, i, 167) under conditions such that hexamethylene derivatives were converted into hydrogen and aromatic hydrocarbons whereas the *cyclobutane*, *cyclopentane*, and *cycloheptane* rings remained unaffected. It was found that the great majority of the naphthenic acids are not derivatives of *cyclohexane*.

[With A. TSCHUKSANOWA.]—The initial material was a series of fractions of naphthenic acids obtained from Baku petroleum. The acids were converted into their methyl esters, whereby it was found possible to isolate two fractions the analytical composition

of which accorded with that required for methyl heptanaphthene-carboxylate and methyl octanaphthenecarboxylate, respectively, but the wide range of boiling point showed them to be mixtures of isomerides. They were reduced by sodium and alcohol to the corresponding primary alcohols, octanaphthene- and nonanaphthene-alcohols, which were converted by iodine and red phosphorus into the corresponding iodides and subsequently reduced by zinc dust in the presence of aqueous alcohols to the hydrocarbons. The latter were saturated, indifferent towards permanganate and concentrated sulphuric acid, and generally similar to cyclohexane and cyclopentane compounds. When passed over platinum black at 300°, they yielded very little hydrogen.

The preparation of *hexahydro-o-xylene* [1 : 2-dimethylcyclohexane], b. p. 127·5—128°,  $d_{20}$  0·7903,  $d_4^{20}$  0·7893,  $n_D^{20}$  1·4321, is described incidentally; the physical constants of the compound differ widely from those of octanaphthene.

H. W.

**Chemical Nature of the Naphthenic Acids. II.** N. ZELINSKY and E. POKROWSKAJA (*Ber.*, 1924, 57, [B], 51—58).—An investigation of the octa-, nona-, and deca-naphthenecarboxylic acids along the lines indicated in the preceding abstract. The behaviour of nona-, deca-, and undeca-naphthenes towards palladium black at 300—310° shows that they cannot contain more than small amounts of derivatives of cyclohexane.

H. W.

**Naphthenic Acids. IV. Metallic Salts of Naphthenic Acids.** Y. TANAKA, K. HORIUCHI, and G. ŌYAMA (*J. Chem. Ind. Japan*, 1923, 26, 1190—1203).—Pure mixed naphthenic acids derived from the waste lyes from the refining of Kurokawa petroleum were separated by distillation into three fractions consisting chiefly of trideca-, tetradeca-, and pentadeca-naphthenic acids, respectively. Metallic salts of these fractions have been prepared, and their solubilities and some other properties have been studied. The solubility increases with decreasing molecular weight of the acid. The lead salts are transparent, resinous solids, m. p. 110—118°. Manganese tridecanaphthenate is a pink powder, soluble in ether, slightly soluble in absolute alcohol (about 2% at 15°), and practically insoluble in cold or hot water. This result contradicts that of von Kozicke and von Pilat (*A.*, 1916, i, 814). Manganese tetradecanaphthenate melts at 61—63°. The lead and manganese salts have a drying action on linseed oil. Chromium salts were obtained in two different modifications, one being a violet powder and the other a green, viscous mass; the former is changed into the latter by heating. Aluminium naphthenate forms a transparent, colourless, and porous mass which can be powdered; it has a waterproofing action. The calcium salts are white, lustrous solids and the magnesium and zinc salts white powders.

K. K.

**Solid Constituents of Low-temperature Coal Tar.** J. MARCUSSE and M. PICARD (*Brennstoff-Chem.*, 1924, 5, 68—69).—The solid carboxylic acids, isolated from low-temperature coal tar, may be divided into three classes, according as they are soluble

in ether, insoluble in ether but soluble in acetone, or insoluble in ether or acetone. They are all aromatic in character and may be sulphonated and nitrated. The content of solid phenols in a tar varies with the method of distillation employed. Naphthalene or anthracene is not present in the primary tar, which contains up to 2% of solid paraffins, a considerable proportion of which is unsaturated. The acetyl value of the neutral portion of the tar both before and after hydrogenation was low, indicating that only small quantities of aldehydes and ketones were present. [Cf. *B.*, 1924, 287.] T. S. W.

**Action of Esters on Magnesium Alkyl Halides.** G. STADNIKOFF (*Ber.*, 1924, 57, [B], 1—8).—An investigation of the abnormal course of the action of Grignard's reagents on esters whereby esters, ethers, and hydrocarbons are produced in addition to alcohols.

The formation of esters is attributed to the action of the iodomagnesium compounds of the alcohols, formed primarily, on the unchanged ester, thus:  $2RMgI + R' \cdot CO_2Et \rightarrow R_2R'CO \cdot MgI + EtO \cdot MgI$  and  $R_2R'CO \cdot MgI + R' \cdot CO_2Et \rightarrow R' \cdot CO_2 \cdot CR_2R' + EtO \cdot MgI$ . Under somewhat unusual conditions, a preparative method of obtaining the esters of complex alcohols is thereby afforded; the examples cited are benzhydryl acetate, b. p. 169—170°/11 mm., m. p. 40—42°, 3-methylcyclohexyl acetate, b. p. 187—188°/784 mm., menthyl formate, b. p. 110°/20 mm., menthyl acetate, b. p. 131°/40 mm.,  $[\alpha]_D -79.2^\circ$ , menthyl benzoate, b. p. 189—190°/16 mm., m. p. 54.5—55°, menthyl iminodiacetate,  $C_{24}H_{43}O_4N$ , b. p. 263°/15 mm., m. p. 48—50°, and menthyl cyanotriacetate,  $C_{36}H_{63}O_6N$ , m. p. 80—81°. The iodomagnesium derivatives of the phenols do not react with esters.

The production of simple and mixed ethers is ascribed to the interaction of halogenomagnesium alkoxides on iodides or bromides in accordance with the scheme:  $R \cdot O \cdot MgI + CHR'_2I \rightarrow MgI_2 + R \cdot O \cdot CHR'_2$ , whilst the iodides are themselves formed by the action of magnesium iodide on esters of alcohols of high molecular weight as exemplified by the scheme:  $R \cdot CO_2CHPh_2 + MgI_2 = R \cdot CO_2 \cdot MgI + CHPh_2I$ . The small proportion of magnesium iodide normally present in a Grignard solution is sufficient to account for the change, since the material which enters into reaction is regenerated. If this explanation be accepted, it is to be expected that hydrocarbons would be formed when an excess of magnesium is employed as indicated by the scheme:  $2CHPh_2I + Mg \rightarrow CHPh_2 \cdot CHPh_2 + MgI_2$ . The following experimental evidence in favour of this interpretation is cited. Magnesium ethyl iodide when treated successively with benzhydrol and ethyl acetate in ethereal solution yields benzhydryl ethyl ether, b. p. 157—157.5°/14 mm., and dibenzhydryl ether, m. p. 108—109°. The same products with the addition of tetraphenylethane, m. p. 208—209°, are formed when ethyl acetate is replaced by ethyl formate; the yield of the hydrocarbon is increased by the use of an excess of magnesium. The iodomagnesium compound of triphenylcarbinol is converted

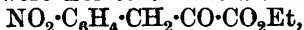


to a small extent by ethyl acetate into triphenylmethyl ethyl ether, m. p. 84—85°; the intermediate production of triphenylmethyl iodide is placed beyond doubt by the isolation of triphenylmethyl peroxide from the products of the reaction.

When, in contrast to the usual conditions, the reaction between magnesium phenyl bromide and methyl benzoate is conducted vigorously, considerable amounts of triphenylmethyl methyl ether, m. p. 83—84°, are produced in addition to triphenylcarbinol. The formation of ethers can be considerably restricted, however, by a suitable choice of radicals. Thus magnesium phenyl bromide and benzyl benzoate give only a very small proportion of *triphenylmethyl benzyl ether*, m. p. 106—107°, in boiling ethereal solution, although the yield may be increased by working under increased pressure. Magnesium phenyl bromide and ethyl benzoate give triphenylcarbinol and triphenylmethyl ethyl ether in yields of 42% and 31%, respectively, whereas ethyl formate and magnesium phenyl bromide produce dibenzhydryl ether, benzhydryl ethyl ether, and tetraphenylethane.

Ethyl formate and magnesium  $\alpha$ -naphthyl bromide give *di- $\alpha$ -naphthylmethyl ethyl ether*,  $C_{23}H_{20}O$ , m. p. 134—135°. H. W.

**Condensation of Ethyl Oxalate with Nitrotoluenes. I. *o*-Nitrotoluene.** W. WISLICENUS and E. THOMA (*Annalen*, 1924, 436, 42—68).—By condensing *o*-nitrotoluene with ethyl oxalate in presence of potassium ethoxide, the authors have obtained *o*-nitrophenylpyruvic acid in a better yield (80 as against 55% of the theoretical) than resulted from Reissert's experiments (A., 1897, i, 417; 1898, i, 315). The product was first isolated as a *potassium* derivative, probably of the *acinitro* form,  $NO_2 \cdot K \cdot C_6H_4 \cdot CH \cdot CO \cdot CO_2Et$ , a dark red substance. In aqueous solution, the colour gradually disappears and potassium *o*-nitrophenylpyruvate is formed. The two desmotropic forms of *o*-nitrophenylpyruvic acid were isolated. The *keto* form,



was obtained by decomposing the above red potassium derivative in aqueous solution and formed needles or prisms, m. p. 46—47°. The *enol* form,  $NO_2 \cdot C_6H_4 \cdot CH : C(OH) \cdot CO_2Et$ , m. p. 70—71°, was produced when the decomposition was carried out in ethereal suspension. In alcoholic solution, the two forms exist together as an equilibrium mixture containing 20% of enol, as determined by titration with bromine in the usual way. *Ethyl  $\beta$ -bromo-*o*-nitrophenylpyruvate*, obtained by brominating the enol, forms white crystals melting at about 76—82°. It regenerates the parent ester when treated with sodium bisulphite, and with aqueous or alcoholic alkali is partly transformed to a compound,  $C_{16}H_{13}O_6N_2Br$ , m. p. 121—122°. *Ethyl *o*-nitrophenylpyruvate phenylhydrazone* forms yellow needles, m. p. 103.5°, and the *oxime*, colourless needles, m. p. 121—122°. When the ester was treated with ammonia during 4 days, *o*-nitrophenylpyruvamide,  $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot CO \cdot NH_2$ , colourless needles, m. p. 165—166°, was obtained. The ester reacts with aniline and various substituted anilines (but not with

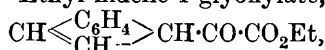


methyl oxalate was used, nor from *p*-nitrotoluene and potassium or sodium ethoxide alone under the same conditions. *Ethyl p-nitrophenylpyruvate* forms a red *potassium* derivative resembling the *o*-isomeride described above. The free ester appears to exist solely in the enolic form as an intensely yellow substance, crystallising in rectangular prisms, m. p.  $106^{\circ}$ . The *acid* has m. p.  $194^{\circ}$  and gives a *pyridine* salt, yellowish-green needles, m. p.  $150^{\circ}$ . When the ethyl ester is reduced with tin and hydrochloric acid, it gives *p*-aminophenyl-lactic acid, m. p.  $188^{\circ}$  (Erlenmeyer, A., 1883, 994). *Ethyl p-nitrophenylpyruvate phenylhydrazone* forms yellowish-green prisms, m. p.  $113^{\circ}$ , and when heated with alcoholic sulphuric acid suffers intramolecular condensation, forming *ethyl 3-p-nitrophenylindole-2-carboxylate*, yellow, rectangular leaflets, m. p.  $216^{\circ}$ . The *anil* of ethyl *p*-nitrophenylpyruvate forms orange-red scales, m. p.  $76^{\circ}$ ; the corresponding derivative with *o*-toluidine, orange-yellow needles, m. p.  $85^{\circ}$ ; with *p*-toluidine, scarlet-red prisms, m. p.  $97^{\circ}$ ; with  $\alpha$ -naphthylamine, orange-red leaflets, m. p.  $113^{\circ}$ ; with  $\beta$ -naphthylamine, scarlet-red, rectangular scales, m. p.  $137^{\circ}$ ; with anthranilic acid, yellow needles, m. p.  $194^{\circ}$ . When the ester is treated with *o*-diamines quinoxalines are formed; thus with 1:3:4-tolylenediamine *2-hydroxy-3-p-nitrobenzyl-7-methylquinoxaline* was obtained, m. p.  $270^{\circ}$ . With *o*-aminophenol *2-keto-3-p-nitrobenzylbenzoxazine*, a deep red substance, m. p.  $192^{\circ}$ , was produced. By interaction of *p*-nitrotoluene and methyl oxalate, *methyl p-nitrophenylpyruvate* was prepared. This compound resembles the ethyl ester and crystallises in yellow pyramids, m. p.  $149^{\circ}$ . The  $\beta$ -*bromo* derivative has m. p.  $114$ – $115^{\circ}$ , the *oxime*,  $172$ – $173^{\circ}$ , and the *phenylhydrazone* about  $136$ – $145^{\circ}$ .

**III. Condensation of Ethyl Oxalate and 1-Nitro-2-methylnaphthalene.** [With E. MUNDINGER.]—The sole product of this reaction under normal conditions was *ethyl 1-nitro-2-naphthylpyruvate*, but if double the usual quantity of potassium ethoxide were used 1:1'-*dinitro-2:2'-dinaphthylethane*, yellow prisms, m. p.  $251^{\circ}$ , was chiefly formed (cf. Mayer and Oppenheimer, A., 1916, i, 816). *Ethyl 1-nitro-2-naphthylpyruvate* was isolated in the two desmotropic forms. The *ketonic* form was obtained by decomposing its bisulphite compound and formed colourless needles, m. p.  $84^{\circ}$ . The *enol* was prepared by treating the potassium compound in ethereal suspension with mineral acid and separated as yellow crystals, m. p.  $135^{\circ}$ . In alcoholic solution, the two forms exist as an equilibrium mixture containing about 58% of enol. The *ketonic* form yields an additive compound with methyl alcohol, m. p.  $76^{\circ}$ . The ester forms a *copper* compound when treated with copper acetate, a brown precipitate, m. p.  $182^{\circ}$ . Its *O-benzoyl* derivative crystallised in yellow prisms, m. p.  $107^{\circ}$ ; its *O-methyl* derivative in pearly prisms, m. p.  $114$ – $115^{\circ}$ ; the corresponding methoxy *acid* melts at  $178^{\circ}$ . The *anil* of ethyl nitronaphthylpyruvate forms yellow prisms, m. p.  $116$ – $117^{\circ}$ . When the ester is treated with *o*-aminophenol an *oxazine* corresponding with the one described under II is formed (yellow prisms, m. p.  $179^{\circ}$ ), and when it is reduced with zinc amalgam *ethyl  $\alpha$ -naphthindolecarboxylate*

(m. p. 173—174°, free *acid*, m. p. 213°) is obtained (cf. Mayer and Oppenheimer, A., 1919, i, 17). W. A. S.

**Studies in the Indene Series. I. Derivatives of Indene-glyoxylic Ester and of Indene-1-carboxylic Acid [Indene-3-carboxylic Acid].** W. WISLICENUS and W. HENTRICH (*Annalen*, 1924, 436, 9—41).—Ethyl indene-1-glyoxylate,



is methylated less readily than the corresponding fluorene derivative (see p. 398) and gives a product which cannot be isolated in a pure condition and was therefore directly hydrolysed; 55% of the calculated yield of 3-methylindene (b. p. 198·5°,  $d_4^{20}$  0·9640) was thus obtained together with tarry by-products, transference of the double bond having occurred (cf. Courtot, A., 1915, i, 392). In the same way, 3-ethylindene was prepared; yield 43% of the theoretical, b. p. 215—216° (cf. von Braun, A., 1918, i, 111). The intermediate ethyl indeneglyoxylate could not be obtained in a pure state. 1-Benzylidene-3-ethylindene crystallises in yellow, rectangular scales, m. p. 57—58°. The benzylidene derivative of 3-benzylindene has m. p. 137·5°; the corresponding derivative from *p*-tolualdehyde forms bundles of yellow needles, m. p. 94°, and from cinnamaldehyde orange prisms, m. p. 161—162°. Ethyl 3-benzylidene-1-glyoxylate forms orange, rectangular tablets, m. p. 130°. This compound, unlike its congeners, is stable. 3-Allylindene, b. p. 138°/27 mm., prepared by the same general method, is very easily oxidised by the air. Attempts to prepare *s*-diindenylethane failed.

Ethyl indeneglyoxylate behaves in a similar way to the corresponding fluorene compound when treated with primary amines (cf. p. 398). The *anil*,  $\text{C}_9\text{H}_7\text{C}(\text{NPh})\cdot\text{CO}_2\text{Et}$ , forms brownish-red prisms, m. p. 142°; the *o*-toluidine derivative (unstable), dark brown prisms, m. p. 107—108°; the  $\alpha$ -naphthylamine derivative, reddish-brown crystals, m. p. 127°. The phenylhydrazone forms dull yellow cubes, m. p. 69°; it decomposes when kept. The *oxime* forms a yellow, crystalline powder, m. p. 204° (decomp.).

When ethyl indeneglyoxylate reacts with one molecular proportion of hydrazine hydrate, an additive compound is formed to which the authors ascribe the formula  $\text{C}_9\text{H}_7\text{C}(\text{OH})(\text{NH}\cdot\text{NH}_2)\cdot\text{CO}_2\text{Et}$ . This is quite stable, m. p. 184°, and decomposes when heated above its melting point. When two molecular proportions of hydrazine hydrate were used the product was the *hydrazide* of the above, m. p. 218° (decomp.). Bromination of the ester gave a definite product only when four atomic proportions of bromine were taken up, 1:2:3-tribromohydrindene-3-glyoxylic acid, white rosettes, m. p. 101°, being formed. For this reason, attempts to determine the proportion of enol in ethyl indeneglyoxylate by Meyer's bromine titration method failed.

Ethyl indeneglyoxylate reacts with diazonium compounds, giving, not a hydrazone of the hitherto unknown indenone like the corresponding fluorene derivative (Wislicenus and Densch,

A., 1902, i, 291), but a compound for which the structure  $\text{CH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > \text{C} \begin{smallmatrix} \text{CO} \cdot \text{CO}_2\text{Et} \\ \text{N} : \text{NR} \end{smallmatrix}$  is proposed.

Ethyl 3-methylindene-1-glyoxylate gives a similar compound. This formula explains the fact that the compound dissolves readily in aqueous alkali with loss of the carbethoxy group. *Ethyl 1-benzene-azoidene-1-glyoxylate* forms dark red crystals, m. p. 146°. Similar products were obtained by interaction with *p*-nitrobenzenediazonium chloride (scarlet-red needles, m. p. 209°, decomp.), and with *m*-nitrobenzenediazonium chloride (red, amorphous powder, m. p. 201—202°, decomp.). From the latter an *acid* was obtained by dissolving it in cold dilute aqueous potassium hydroxide and reprecipitating, m. p. 151—153° (decomp.).

*Indene-3-carboxylic acid* was prepared by oxidising sodium indene-1-glyoxylate (Thiele, A., 1901, i, 76) with hydrogen peroxide (yield variable, 30—65%). The product melted at 160° and was found to be identical with that obtained by Weissgerber (A., 1911, i, 623). Transposition of the double bond has again taken place. The *hydrazide*,  $\text{C}_9\text{H}_7 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , forms rectangular, colourless leaflets, m. p. 186°; its *hydrochloride*, needles, darkens at 245° and decomposes at 263°. The hydrazide reacts readily with aromatic aldehydes, but not so smoothly with ketones, to give well crystallised *hydrazones*; thus with benzaldehyde, it forms white needles, m. p. 272—273°; with *o*-nitrobenzaldehyde, pale yellow needles, m. p. 215° (decomp.); with *p*-tolualdehyde, long, colourless needles, m. p. 254—255° (decomp.); with salicylaldehyde, flexible, yellow needles, m. p. 267° (decomp.); with cinnamaldehyde, sulphur-yellow leaflets, m. p. 239—242° (decomp.); with furfuraldehyde, yellow, rectangular, prismatic needles, m. p. 234°; with oxindole-3-aldehyde, yellow, clustered needles, darkening at 280°, m. p. 293° (decomp.). The *diacetyl* derivative of the hydrazide forms colourless needles, m. p. 147°; the *benzoyl* derivative, leaflets, m. p. 212—213°; a by-product, presumably the *dibenzoyl* derivative, has m. p. 253—255°. The  $\beta$ -*phenylhydrazide* of indene-3-carboxylic acid,  $\text{C}_9\text{H}_7 \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPh}$ , forms yellow needles, m. p. 188°. The *amide*,  $\text{C}_9\text{H}_7 \cdot \text{CO} \cdot \text{NH}_2$ , forms yellow leaflets, m. p. 180°. The *anilide* crystallises in yellow prisms, m. p. 158°. Indene-3-carboxylic acid readily reacts with aldehydes in methyl-alcoholic potassium hydroxide solution to form highly coloured fulvene derivatives of the general formula,  $\text{CO}_2\text{H} \cdot \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} > \text{C} : \text{CHR}$ .

*1-Benzylideneindene-3-carboxylic acid* forms yellow needles, m. p. 222°; the *3-furfurylidene* derivative, brownish-red, prismatic needles, m. p. 250°; the *3-cinnamylidene* derivative is an orange powder, m. p. 235°. *Ethyl 3-carboxyindene-1-glyoxylate* forms orange-red prisms, m. p. 138.5° (decomp.). The *acid* forms a red precipitate, m. p. 199°. Its *ethyl* ester, obtained by interaction of ethyl indenecarboxylate with ethyl oxalate, crystallises in rectangular prisms, m. p. 116°. By treating the potassium derivative of potassium indene-3-carboxylate with ethyl bromide it was hoped to obtain 1-ethylindene-3-carboxylic acid, but actually

the product was mainly 3-ethylindene. The potassium compound of ethyl indenecarboxylate reacts with two molecular proportions of benzenediazonium chloride, giving an orange-red substance, m. p. 163°. A similar compound with *p*-nitrodiazobenzene forms a red powder, m. p. 223—225° (decomp.).

Ethyl 3-methylindene-2-carboxylate (Thiele and Rüdiger, A., 1906, i, 586) reacts with ethyl oxalate in presence of potassium ethoxide to give *ethyl 3-methyl-2-carbethoxyindene-1-glyoxylate*,  $\text{CO}_2\text{Et} \cdot \text{C}_9\text{H}_5\text{Me} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , the potassium compound of which forms pearly leaflets darkening at 200° and melting with decomposition at 215°. The free ester crystallises in pale yellow needles, m. p. 123—125° (only if rapidly heated). The corresponding compound from the methyl methylindenecarboxylate forms yellow needles, m. p. 134—135°.

**II. Indene-3-carboxylic Acid.** [With G. MANTHE.]—Methyl indene-3-carboxylate (Weissgerber, A., 1911, i, 623) on methylation readily gave (yield 66%) *methyl 1-methylindene-3-carboxylate*, a yellow oil, b. p. 127°/14 mm., which forms an unstable *dibromide*, m. p. 87—88°, b. p. 170—185°/11 mm. When the ester was hydrolysed 3-methylindene was obtained. In the same way, *ethyl 1-methylindene-3-carboxylate* was prepared (yield 80%, b. p. 132—136°/16 mm.) and likewise hydrolysed. *Ethyl 1-ethylindene-3-carboxylate* (yield 70%, b. p. 148—150°/19 mm.) gave similarly ethylindene in 70% yield. *Ethyl 1-benzylindene-3-carboxylate* (yellow, viscous oil, b. p. 240°/20 mm.) gave a good yield (80%) of benzylindene. Attempts to prepare by this method both *s*-di-indenylethane and 1:1'-di-indenyl failed. When the potassium compound of ethyl indenecarboxylate was treated with one molecular proportion of benzoyl chloride, a blue compound still containing potassium was produced, whilst when an excess of benzoyl chloride was used a *dibenzoyl* derivative was formed (yellow prisms, m. p. 166°). A similar derivative was produced when *m*-nitrobenzoyl chloride was used (yellow needles, m. p. 164°). The *dibenzoyl* derivative of the methyl ester forms a yellow powder, m. p. 182°. Indene-3-carboxylic acid, but not its ethyl ester, reacts with ethyl nitrate in presence of potassium ethoxide to give *di-potassium 1-nitroindene-3-carboxylate*,  $\text{CO}_2\text{K} \cdot \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{C} \cdot \text{NO}_2\text{K}$ , of which the lead salt was also prepared.

**III. 1-Nitroindene.** [With K. PFEILSTICKER.]—Indene was treated with ethyl nitrate and potassium ethoxide and the hitherto unknown 1-nitroindene obtained as a *potassium* derivative,  $\text{CH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{C} \cdot \text{NO}_2\text{K}$ , an unstable, yellow, crystalline substance.

The free nitroindene was obtained as a crystalline, greenish-yellow precipitate, m. p. 50°, which was too easily decomposed to be recrystallised. This is the *aci*-form. It decomposes without changing over into the true nitro compound. It forms more stable condensation products with aromatic aldehydes, but not with ketones, in presence of sulphuric acid. 3-Nitro-1-benzylidene-indene forms orange leaflets, m. p. 139°; 3-nitro-1-tolylideneindene.

red crystals, m. p.  $105^{\circ}$ ; similar derivatives with *p*-nitrobenzaldehyde (red needles, m. p.  $218-220^{\circ}$ ) and cinnamaldehyde (deep red crystals, decomposing at  $208^{\circ}$ ) were prepared. Potassium nitroindene was converted by treatment with benzoyl chloride into 1-nitro-3-benzoylindene, yellow rhombs, m. p.  $121^{\circ}$ . The above benzylidene derivatives were reduced with tin and hydrochloric acid, giving the corresponding benzylaminoindenes. Nitroindene itself gave an unstable product. 1:3- (or 3:1-)Benzylaminoindene is a rapidly oxidising oil; its hydrochloride, microscopic crystals, m. p.  $237^{\circ}$ ; its acetyl derivative, needles, decomposing at  $243^{\circ}$ . Cinnamylaminoindene hydrochloride melts at  $242-245^{\circ}$ , and its acetyl derivative decomposes at  $267^{\circ}$ .  
W. A. S.

**Condensations in the Arylacetonitrile Series. I. Formyl- $\alpha$ -naphthylacetonitrile, Ethyl Formyl- $\alpha$ -naphthylacetate, and Ethyl  $\alpha$ -Naphthylloxalacetate.** W. WISLICENUS, G. BUTTERFASS, and G. KOKEN (*Annalen*, 1924, 436, 69—100).—Formyl- $\alpha$ -naphthylacetonitrile was obtained by interaction of naphthylacetonitrile (Mayer and Oppenheimer, A., 1916, i, 816) and ethyl formate. The potassium compound forms a yellow powder. The free nitrile is an imperfectly crystalline, colourless mass, m. p.  $130^{\circ}$ , giving a brown copper salt. Titration with bromine indicated that from 95.8 to 99.7% (in different preparations) existed in the enolic form. It should therefore be formulated as hydroxymethylene-naphthylacetonitrile,  $C_{10}H_7 \cdot C(CN) : CH \cdot OH$  (cf. Wislicenus, A., 1896, i, 522). It forms an anilide, white leaflets, m. p.  $152-154^{\circ}$ ; *p*-toluidide, prisms, m. p.  $142^{\circ}$ ; semicarbazide, diamond-shaped scales, m. p.  $172-173^{\circ}$ ; and hydroxylamide, needles, m. p.  $111^{\circ}$ . It reacts with phenylisocyanate only at a much higher temperature than similar compounds (cf. Wislicenus, *loc. cit.*) to form the carbanilate,  $NHPh \cdot CO \cdot O \cdot CH : C(C_{10}H_7) \cdot CN$ , pale yellow needles, m. p.  $158-159^{\circ}$  (decomp.).

Various derivatives of ethyl formyl- $\alpha$ -naphthylacetate (Wislicenus and Elvert, A., 1917, i, 202) which could not be obtained directly by simultaneous hydrolysis and esterification of the nitrile, were prepared. The anilide forms quadratic prisms, m. p.  $94-96^{\circ}$ ; the *p*-toluidide, glistening crystals, m. p.  $90-91^{\circ}$ . The latter derivative when heated at  $250-260^{\circ}$  suffered intramolecular condensation and 3- $\alpha$ -naphthyl-4-hydroxy-6-methylquinoline was formed (needles, m. p.  $302-305^{\circ}$ , subliming at a somewhat higher temperature; picrate, m. p.  $140-145^{\circ}$ ). When ethyl formyl-naphthylacetate was reduced by Clemmensen's method, it gave a mixture of  $\alpha$ -( $\alpha$ -naphthyl)hydracrylic acid (crystalline powder, m. p.  $112^{\circ}$ ) and ethyl  $\alpha$ -naphthylacrylate (an oil, b. p.  $220-230^{\circ}/12$  mm.).  $\alpha$ -Naphthylacrylic acid forms needles, m. p.  $152-154^{\circ}$ . Ethyl formyl- $\alpha$ -naphthylacetate was alkylated and found to give invariably *O*-derivatives. The methyl derivative formed an indefinitely crystalline mass, m. p.  $63-64^{\circ}$ , and the ethyl derivative needles, m. p.  $75^{\circ}$ .

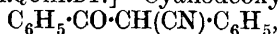
Ethyl  $\alpha$ -naphthylacetate and ethyl oxalate were condensed together in the usual way to produce ethyl  $\alpha$ -naphthylloxalacetate,

$C_{10}H_7 \cdot CH(CO_2Et) \cdot CO \cdot CO_2Et$ , a yellow oil which decomposes when distilled. Its *potassium* salt forms silky leaflets which decompose at  $220-223^\circ$ ; its *copper* salt has a m. p. dependent on the solvent from which it is recrystallised. With phenylhydrazine, *ethyl 1-phenyl-4- $\alpha$ -naphthyl-5-pyrazolone-3-carboxylate* is obtained as microscopic leaflets, m. p.  $213-214^\circ$ . When the ester is heated at  $180-186^\circ$  it loses carbon monoxide, forming *ethyl  $\alpha$ -naphthyl-malonate* (clustered prisms, m. p.  $59-60^\circ$ ), the sodium derivative of which, by interaction with ethyl bromoacetate and subsequent hydrolysis, gives  *$\alpha$ -naphthylsuccinic acid*, rectangular scales, m. p.  $206^\circ$  (decomp.).

**II. Formyl- $\beta$ -naphthylacetonitrile and Ethyl Formyl- $\beta$ -naphthylacetate.** [With H. RIETHMÜLLER.]—The  $\beta$ -naphthyl derivative resembles the  $\alpha$ -isomeride described above. It crystallises in leaflets, m. p.  $181-182^\circ$ , gives a brown *copper* salt, and appears to exist mainly in the *enolic* form. Its *O-benzoyl* derivative forms needles, m. p.  $188^\circ$ ; the *anilide*, yellow needles, m. p.  $185^\circ$ ; *p-toluidide*, yellowish-green leaflets and needles, m. p.  $199-201^\circ$ ; *oxime*, leaflets, m. p.  $135-136^\circ$ ; compound with *phenylcarbimide*, needles, m. p.  $178^\circ$  (decomp.). It reacts with benzenediazonium chloride to form  *$\beta$ -naphthylglyoxylonitrile phenylhydrazone* (yellow needles, m. p.  $195-196^\circ$ ), the formyl group being displaced. When formyl- $\beta$ -naphthylacetonitrile is treated with bromine, an impure *bromo* derivative, m. p.  $162-164^\circ$ , is obtained, whilst with iodine its *potassium* compound in methyl-alcoholic solution gives *s-di- $\beta$ -naphthylsuccinonitrile*,  $C_{10}H_7 \cdot CH(CN) \cdot CH(CN) \cdot C_{10}H_7$ , colourless prisms, m. p.  $246-249^\circ$ . The free nitrile in aqueous methyl alcohol with iodine and sodium hydroxide gives *s-di- $\beta$ -naphthyl-dicyanoethylene*,  $C_{10}H_7 \cdot C(CN) : C(CN) \cdot C_{10}H_7$ , yellow needles, m. p.  $204^\circ$ . The latter compound was also obtained by treating  $\beta$ -naphthylacetonitrile in a similar way.

Ethyl formyl- $\beta$ -naphthylacetate gave on reduction and hydrolysis the corresponding  *$\alpha$ -( $\beta$ -naphthyl)- $\beta$ -hydroxypropionic acid*,  $OH \cdot CH_2 \cdot CH(C_{10}H_7) \cdot CO_2H$ , which formed clustered crystals, m. p.  $154-156^\circ$ . Ethyl formyl- $\beta$ -naphthylacetate gives an *anilide*, yellow needles, m. p.  $91-92^\circ$ ; with phenylhydrazine it forms, not the expected phenylhydrazone, but *1-phenyl-4- $\beta$ -naphthyl-5-pyrazolone*, colourless needles, m. p.  $219-220^\circ$ , yet with 2:4-dinitrophenylhydrazine the second reaction does not take place and the corresponding *dinitrophenylhydrazone* only is formed, orange-yellow crystals, sintering at  $110^\circ$  and melting between  $115^\circ$  and  $118^\circ$ .

**III. Ester Condensations with Benzyl Cyanide.** [With H. EICHERT and M. MARQUARDT.]—Cyanodeoxybenzoin,



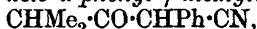
was obtained by interaction of ethyl benzoate, benzyl cyanide, and metallic potassium in yields superior to those of earlier workers (Walther and Schickler, A., 1897, i, 522; Bodroux, A., 1911, i, 545). It forms colourless scales, m. p.  $91-92^\circ$ , and gives an *anil*, yellow needles, m. p.  $201^\circ$ . By simultaneous hydrolysis and esterification *ethyl benzoylphenylacetate* (needles, m. p.  $90-91^\circ$ ; b. p.  $220-225^\circ$  /



13 mm.) and the corresponding *methyl* ester (rosettes of colourless prisms, m. p. 74—75°) were obtained. Both compounds exist in solution in the two desmotropic forms; in the case of the *methyl* ester, the enolic form accounts for 4—5% of the whole. Ethyl benzoylphenylacetate heated with aniline forms *benzoylphenylacetanilide*,  $\text{Bz}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NHPh}$ , colourless needles, m. p. 168°; with phenylhydrazine it gives either the *phenylhydrazone* (needles, m. p. 173—174°) or, at a higher temperature, 1:3:4-*triphenyl-5-pyrazolone*, leaflets, m. p. 193—194°. When it was treated with phosphorus pentachloride, a mixture of 3-*chloro-2-phenylindone*,  $\text{CCl}\cdot\text{C}_6\text{H}_4\cdot\text{CO}$ , orange-red needles, m. p. 93—94°, b. p. 205—210°/13 mm., and *ethyl chlorobenzoylphenylacetate*, needles, m. p. 44—45°, b. p. 225—230°/12 mm., was formed. The latter compound was also obtained by direct chlorination of the ester.

Ethyl benzoylbenzoate (A., 1908, i, 994) was similarly condensed with benzyl cyanide to form *benzoylbenzoylphenylacetoneitrile*, crystallising from alcohol in colourless needles or scales, m. p. 214°, and from benzene in irregular crystals, m. p. 188°. Neither is the enolic form. The compound resists hydrolysis, and forms a loose compound with hydrogen chloride. It is unaffected by hydrazine, aniline, and the like, and the only derivative obtained was *benzoylbenzoylphenylmethylacetoneitrile*,  $\text{Bz}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CMePh}\cdot\text{CN}$ , prisms, m. p. 145°.

Ethyl isobutyrate and benzyl cyanide condensed to form *phenylisobutyroacetoneitrile* ( $\beta$ -*keto- $\alpha$ -phenyl- $\gamma$ -methylvaleronitrile*),



a yellow oil, b. p. 154—156°/13 mm. The *bromo* derivative (needles, m. p. 192°), *phenylhydrazone* (needles, m. p. 109°), *hydrazone* (needles, m. p. 102°), *oxime* (needles, m. p. 85°), and *semicarbazone* (needles, m. p. 147°) were prepared. By simultaneous hydrolysis and esterification, *ethyl  $\alpha$ -phenylisobutyroacetate* (oil, b. p. 150—160°/13 mm.) and the corresponding *methyl* ester (leaflets, m. p. 52°) were obtained. The *acid*,  $\text{CHMe}_2\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ , forms colourless needles, m. p. 159°. From the ester with phenylhydrazine 1:4-*diphenyl-3-isopropylpyrazolone* (colourless needles, m. p. 191°) and with hydrazine 4-*phenyl-3-isopropylpyrazolone* (m. p. 192°) were obtained, whilst with semicarbazide, 4-*phenyl-3-isopropyl-5-pyrazolone-1-carboxylamide*,  $\text{Pr}^i\text{C}\cdot\text{N}=\text{N}\cdot\text{CONH}_2$ , m. p. 187°,  $\text{CHPh}\cdot\text{CO}$

solidified again at 188—189°, remelted at 318—320°, was produced. When the ester was hydrolysed with dilute sulphuric acid, benzyl isopropyl ketone (b. p. 232—235°; cf. Blaise, A., 1901, i, 252) was obtained.

Ethyl diphenylacetate and benzyl cyanide condense to give *diphenylacetophenylacetoneitrile* ( $\beta$ -*keto- $\alpha\gamma$ -triphenylbutyronitrile*),  $\text{CPh}_2\cdot\text{CO}\cdot\text{CHPh}\cdot\text{CN}$  (needles, m. p. 97°), which gives a *phenylhydrazone* (needles, m. p. 167°) and a *hydrazone* (needles, m. p. 135°). *Ethyl  $\beta$ -keto- $\alpha\gamma$ -triphenylbutyrate* forms scales, m. p. 109—110°, and gives 4-*phenyl-3-diphenylmethyl-5-pyrazolone*, m. p. 232—233°, with hydrazine.

W. A. S.

p\*

**Fluorene- and 2-Nitrofluorene-9-glyoxylic Esters.** W. WISLICENUS and H. WETTEMAYER (*Annalen*, 1924, **436**, 1—9).—*Fluorene-9-glycollic acid*, which the authors (A., 1921, i, 511) failed to obtain from its ester, prepared by reducing ethyl fluorene-9-glyoxylate with aluminium amalgam, owing to simultaneous dehydration to dibenzofulvene- $\omega$ -carboxylic acid, is produced directly when the reduction is carried out by Clemmensen's method. *Methyl fluorene-9-glycollate* forms white needles, m. p. 96°. When ethyl fluorene-9-glyoxylate or the free acid is oxidised with hydrogen peroxide following Reissert's procedure, it gives, not the expected fluorene-9-carboxylic acid, but exclusively fluorenone. The product obtained by Wislicenus and Densch (A., 1902, i, 291) by methylating ethyl fluoreneglyoxylate is the *C*-methyl derivative, as it may be easily hydrolysed to 9-methylfluorene. Ethyl fluoreneglyoxylate may be nitrated: the glyoxylyl group is displaced and 2:9-dinitrofluorene formed. This substance crystallises in white needles which turn yellow on exposure to light, m. p. 136°. It decomposed when heated above its melting point, giving 2-nitrofluorene. The same compound was obtained, and its constitution proved, by further nitrating both 9-nitrofluorene (Wislicenus and Waldmüller, A., 1908, i, 973) and ethyl 2-nitrofluorene-9-glyoxylate. Although 9-nitrofluorene reacts with alcoholic potassium hydroxide, the 2:9-dinitro derivative is insoluble in this reagent and is unable to pass over into an *aci*-form. Ethyl fluorene-9-glyoxylate yields an *anil*,  $C_{13}H_9 \cdot C(NPh) \cdot CO_2Et$ , orange-yellow crystals, m. p. 137°, and corresponding derivatives with *p*-toluidine and  $\beta$ -naphthylamine (m. p. 156°). With hydrazine, on the other hand, the ethoxy group is displaced and a *hydrazide* formed,  $C_{13}H_9 \cdot CO \cdot CO \cdot NH \cdot NH_2$ , small, yellow crystals, m. p. above 350°. This compound reacts with benzaldehyde to form a *benzylidene* derivative, crystallising in needles which decompose above 350°, and with acetone to give the *hydrazone*,  $C_{13}H_9 \cdot CO \cdot CO \cdot NH \cdot N : CMe_2$ , m. p. 216°.

In 2-nitrofluorene, as in 2:7-dibromofluorene (Siegltz, A., 1920, i, 605), the methylene group is more reactive than in fluorene itself. Thus when a warm solution of 2-nitrofluorene in benzene is added to a mixture of ethyl oxalate and potassium ethoxide, the potassium salt of 2-nitrofluorene-9-glyoxylic ester is immediately thrown down. *Ethyl 2-nitrofluorene-9-glyoxylate* forms yellow crystals, m. p. 143°. It gives coloured precipitates with heavy metals. The ester must be hydrolysed at temperatures below 80°, otherwise scission takes place and 2-nitrofluorene is reproduced. The free acid,  $NO_2 \cdot C_{13}H_8 \cdot CO \cdot CO_2H \cdot H_2O$ , forms minute yellow crystals, m. p. 183°. The *methyl* ester has an indefinite melting point, about 120°. The ethyl ester yields a *phenylhydrazone*, yellowish-brown crystals, m. p. 192°; an *anil*, dark red crystals, m. p. 162°, and corresponding derivatives with *p*-toluidine and  $\beta$ -naphthylamine, m. p. 164° and 187°, respectively. Like the unsubstituted fluoreneglyoxylic ester, it gives a *benzoyl* derivative,  $NO_2 \cdot C_{13}H_7 \cdot C(OBz) \cdot CO_2Et$  (cf. Wislicenus and Densch, *loc. cit.*), minute yellow crystals, m. p. 137—138°, easily decomposed again by solution in alcoholic potassium hydroxide.

W. A. S.

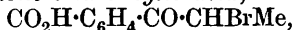
**Equilibrium in the System, Sodium Phthalate-Sodium Sulphate-Water.** H. W. FOOTE and S. B. SMITH (*J. Amer. Chem. Soc.*, 1924, **46**, 84—88).—The solubility relations of the system, sodium phthalate-sodium sulphate-water have been determined at 0°, 25°, and 35°. The transition temperature at the quintuple point, where the solid phases are anhydrous sodium sulphate, the decahydrate of sodium sulphate, and hydrated sodium phthalate, has been found to be 23°. When crystallised from water at the ordinary temperature, sodium phthalate has the composition represented by  $2\text{Na}_2\text{C}_8\text{H}_4\text{O}_4 \cdot 7\text{H}_2\text{O}$ . J. F. S.

**Unsaturated Lactones.** S. GABRIEL, L. KORNFELD, and C. GRUNERT (*Ber.*, 1924, **57**, [B], 302—306).—An investigation of the behaviour of arylidene- and alkylidenephthalides containing a bromine atom in the side chain towards sodium methoxide.

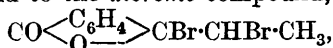
$\alpha$ -Bromobenzylidenephthalide,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C}:\text{CBr} \cdot \text{Ph}$ , quadratic leaflets, m. p. 193°, is obtained by heating the corresponding dibromide in a current of carbon dioxide at 140—150° until hydrogen bromide ceases to be evolved. It is transformed by a solution of sodium in methyl alcohol into *hydroxydiketophenylhydrindene*,  $\text{C}_6\text{H}_4 \langle \text{CO} \rangle \text{C}(\text{OH})\text{Ph}$ , yellow needles, m. p. 192° (in a vacuum), which, when dissolved in alkali hydroxide and exposed to the air, passes into *benzil-o-carboxylic acid*,  $\text{COPh} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , m. p. 140—141°. *Methoxydiketophenylhydrindene* crystallises in needles, m. p. 114°.  $\alpha$ -Bromobenzylidenephthalide is not appreciably affected by boiling water, but is transformed by boiling potassium hydroxide solution (20%) into *benzhydroldicarboxylic acid*,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}(\text{OH}) \cdot \text{CO}_2\text{H}$ .

$\alpha$ -Bromo-*p*-tolylidenephthalide is converted in a similar manner into 4'-methylbenzil-2-carboxylic acid, small needles, m. p. 143°.

$\alpha$ -Bromopropiophenone-*o*-carboxylic acid,



needles, m. p. 110°, is transformed by potassium hydroxide into *hydroxydiketomethylhydrindene*, which readily becomes oxidised on exposure to air and by a saturated solution of hydrogen bromide in glacial acetic acid to the *dibromo* compound,



rhombic crystals, m. p. 97—99°.  $\alpha\alpha$ -Dibromopropiophenone-*o*-carboxylic acid, needles, m. p. 140°, when treated successively with boiling water and phenylhydrazine, gives a *phenylhydrazone*,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}(\text{N} \cdot \text{NHPh}) \cdot \text{Me}$ , or  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{N} \cdot \text{NHPh}) \cdot \text{CO} \cdot \text{Me}$ , quadratic plates, m. p. 219° (decomp.).

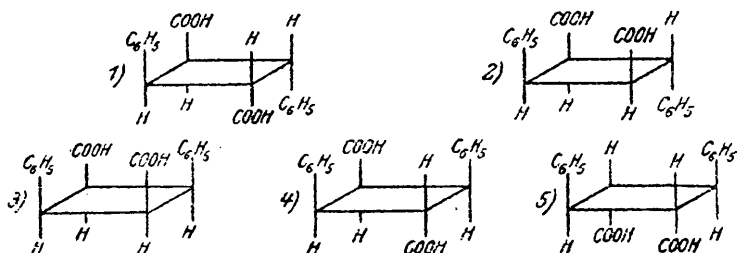
Phthalylideneacetic acid is converted by phosphoryl chloride and phosphorus pentachloride into *phthalylideneacetyl chloride*,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C}:\text{CH} \cdot \text{COCl}$ , long needles, m. p. 158°, which is transformed by a small quantity of the respective alcohols into the corresponding *methyl ester*, quadratic leaflets, m. p. 168° (decomp.),

and *ethyl* ester, m. p. 132—134°; when boiled with an excess of the alcohols, however, it yields *methyl o-carboxybenzoylacetate*,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , m. p. 73°, or the corresponding *ethyl* ester. *Methyl diketohydrindenecarboxylate*,  $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{CH}\cdot\text{CO}_2\text{Me}$ , is prepared by the action of potassium hydroxide solution at 0° on the dimethyl ester or of sodium methoxide on methyl phthalylideneacetate. The diethyl ester is converted similarly into ethyl diketohydrindenecarboxylate, m. p. 76°. H. W.

**Fluorene Series. VIII. Synthesis of Fluorenone-1-carboxylic Acid.** A. SIEGLITZ (*Ber.*, 1924, 57, [B], 316—317).—2'-Aminobenzophenone-2-carboxylic acid is diazotised in sulphuric acid solution and the diazonium solution is warmed, thus giving anthraquinone, fluorenone, and fluorenone-1-carboxylic acid, m. p. 192—193° (cf. Mayer and Freitag, A., 1921, i, 248); the main product of the change, however, is 2'-hydroxybenzophenone-2-carboxylic acid, colourless needles, m. p. 170—171°, which is converted by methyl sulphate and potassium hydroxide into 2'-methoxybenzophenone-2-carboxylic acid, colourless crystals, m. p. 144—145°, and by concentrated sulphuric acid into 1-hydroxyanthraquinone, m. p. 191°. H. W.

**Synthesis of Depsides of isoFerulic Acid [3-Hydroxy-4-methoxycinnamic Acid].** F. MAUTHNER (*J. pr. Chem.*, 1923, 106, 333—335; cf. A., 1922, i, 936).—Carbomethoxyisoferulic acid, obtained by the action of methyl chlorocarbonate on isoferulic acid in alkaline solution, forms crystals, m. p. 223—224° (decomp.). It is converted by phosphorus pentachloride into carbomethoxyisoferulyl chloride, colourless needles, m. p. 84°. With *p*-hydroxybenzoic acid, this gives *p*-carbomethoxyisoferulyloxybenzoic acid, colourless crystals, m. p. 206—207°. The carbomethoxy group is removed by the slow action of ammonia in pyridine solution. The depside, *p*-isoferulyloxybenzoic acid, forms colourless crystals, m. p. 217—218°. *m*-Carbomethoxyisoferulyloxybenzoic acid forms colourless crystals, m. p. 203—204°, and *m*-isoferulyloxybenzoic acid, colourless crystals, m. p. 191—192°. E. H. R.

**Stereoisomerism of the Truxillic Acids and the Discovery of the Remaining Acid of this Group. VIII.** R. STOERMER and F. BACHER (*Ber.*, 1924, 57, [B], 15—23).—Theoretically five truxillic acids should exist, the configurations of which are shown by the formulæ :



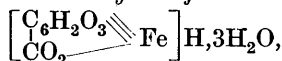
The configurations 1 and 2 have been assigned definitely to  $\alpha$ - and  $\gamma$ -truxillic acids respectively (cf. A., 1923, i, 929).  $\epsilon$ -Truxillic acid is characterised as a *cis*-compound since it yields a unimolecular, crystalline imide from which it is smoothly regenerated. The *cis*-nature of  $\eta$ -truxillic acid follows from its ready conversion into the anhydride (cf. Stobbe and Zschoch, A., 1923, i, 337); since it is shown that the heavy groups lie on the same side of the cyclobutane ring, it is proposed to designate the compound *peri*-truxillic acid (configuration 3). The action of hydrochloric acid at 180° or of an excess of boiling sodium hydroxide on the *peri*-acid yields the outstanding member of the group, which is termed *epi*-truxillic acid owing to its production by a type of epimeric change. The conversion of the *epi*-acid by acetic anhydride into  $\epsilon$ -truxillic acid (5) shows it to be a *trans*-compound to which the constitution 4 must necessarily be assigned.

The following individual compounds are described: *peri*-truxillic anhydride, prepared by a modification of the method of Stobbe and Zschoch (*loc. cit.*), m. p. 285°; *peri*-truxillic acid, m. p. 266° (decomp.) (Stobbe and Zschoch give m. p. 280°); *methyl peri-truxillate*, obtained by treatment of the acid with an ethereal solution of diazomethane or by the rapid action of methyl sulphate and alkali hydroxide, colourless crystals, m. p. 104–105°; *methyl hydrogen peri-truxillate*, from the anhydride and methyl alcohol at 180–200°, m. p. 192°; *peri*-(? *epi*-)truxillamic acid, small, quadratic plates or needles, m. p. 264° (decomp.); *peri-truxillanilic acid*, m. p. 247° (decomp.), from the *peri*-anhydride and boiling aniline whereby  $\epsilon$ -truxilldianilide, m. p. 283°, is also produced; *methyl peri-truxillanilate*, m. p. 131°; *methyl  $\epsilon$ -truxillanilate*, m. p. 159°; *epi-truxillic acid*, prepared most conveniently by heating the *peri*-acid with an excess of sodium hydroxide solution (10%), m. p. 285–287° (with transformation into  $\epsilon$ -truxillic acid); *methyl epi-truxillate*, from the acid by means of diazomethane, methyl sulphate, or methyl-alcoholic hydrogen chloride, m. p. 111–112°; *methyl hydrogen epi-truxillate*, prepared by the partial hydrolysis of the normal ester with alcoholic potassium hydroxide solution, m. p. 204.5°. *epi*-Truxillic acid is converted by aniline at 190–210° into  $\epsilon$ -truxilldianilide, and, apparently, a mixture of the two theoretically possible *epi*-truxillanilic acids which has not been separated satisfactorily into its components. H. W.

**Formation and Ageing of Written Characters. The Primary Ink-salts of Iron Inks.** F. ZETZSCHE, G. VIELI, G. LILLJEQVIST, and A. LOOSLI (*Annalen*, 1924, 435, 233–264).—The primary ink salts have been prepared by the following method: the parent hydroxy compound (*e.g.*, salicylic acid) was treated with the theoretical quantity (see below) of a solution of ferrous sulphate in dilute sulphuric acid, the mixture neutralised with sodium hydroxide, and then shaken in an atmosphere of oxygen and carbon dioxide, until no more oxygen was absorbed. In the case of hydroxy compounds which are readily oxidised in alkaline solution (*e.g.*, pyrogallol), neutralisation was effected in the above

oxygen-carbon dioxide atmosphere. In this manner, the formation of the ink salts can be followed and controlled, and that of secondary (oxidation) products avoided. The experimental procedure adopted follows very closely the mechanism of the formation of written characters.

Gallic acid gives rise to *monogallatoferric acid*,



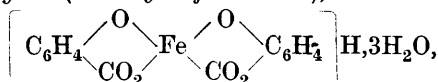
a violet, microcrystalline powder, affording gallic acid on being treated with acids, dissolving in alkali to a blue, red, or yellow solution, according to the concentration, the latter solution being oxidised by air to give a yellow substance (galloflavine?). The conversion of yellow, soluble ferrous gallate,  $(\text{C}_6\text{H}_2[\text{OH}]_3\text{CO}_2)_2\text{Fe}$ , into the above violet compound is reversed in presence of hydrogen and a platinum catalyst.

Using a greater proportion of ferrous sulphate to gallic acid,

*ferric monogallatoferrate* (?),  $\left[ \begin{array}{c} \text{C}_6\text{H}_2 \text{---} \text{O}_3 \text{---} \\ \diagup \quad \diagdown \\ \text{CO}_2 \end{array} \right] \text{Fe} \cdot 12\text{H}_2\text{O}$ , results,

as a bluish-violet powder. It is readily oxidised, gives ferric oxide on heating at 85–90° and ferric hydroxide on treating with alkali.

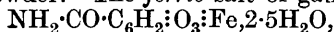
*Ferric disalicylate (disalicylatoferric acid)*,



red needles, gives a bluish-red solution in hot water, carbon dioxide being evolved on boiling. Unless care is taken in the preparation of this compound, Weinland's hexasalicylatotri-ferric disalicylatoferrate (cf. A., 1917, i, 649, and previous papers) is obtained. Alkali converts the disalicylate into alkali di- and trisalicylatoferrates.

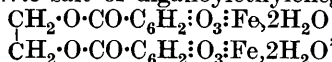
*Ferric protocatechuate*,  $\text{C}_6\text{H}_3 \begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{CO}_2 \end{array} \text{Fe} \cdot 3\text{H}_2\text{O}$ , is a violet-blue,

microcrystalline powder. The *ferric* salt of gallamide,



is a dark blue, microcrystalline powder; the *ferric* salt of gallanilide,  $\text{NHPh} \cdot \text{CO} \cdot \text{C}_6\text{H}_2 \text{---} \text{O}_3 \text{---} \text{Fe} \cdot 3\text{H}_2\text{O}$ , a dark violet powder and the *ferric* salt of ethyl gallate,  $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_2 \text{---} \text{O}_3 \text{---} \text{Fe} \cdot 2\text{H}_2\text{O}$ , a dark blue powder. The last four compounds give wine-red solutions in aqueous alkali.

The *ferric* salt of tribromopyrogallol,  $\text{C}_6\text{Br}_3 \text{---} \text{O}_3 \text{---} \text{Fe} \cdot 2\text{H}_2\text{O}$ , is a dark blue powder, rapidly becoming brown owing to decomposition. The *diferic* salt of digalloyl-ethyleneglycol,



is a bluish-violet powder, and the *triferic* salt of trigalloylglycerol,  $\text{C}_{24}\text{H}_{11}\text{O}_{15}\text{Fe}_3 \cdot 2\text{H}_2\text{O}$  (having a constitution similar to that of the glycol derivative) a bluish-violet powder, affording a red solution with alkali. The *pentaferic* salt of pentagalloyl-β-glucose,  $\text{C}_{41}\text{H}_{37}\text{O}_{36}\text{Fe}_5 \cdot 10\text{H}_2\text{O}$ , and *pentaferritannate*,  $\text{C}_{76}\text{H}_{37}\text{O}_{46}\text{Fe}_5 \cdot 10\text{H}_2\text{O}$ , have similar properties.

The proportions of phenolic compound to iron (mols. of phenolic compound : atoms of iron) in other primary ferric ink salts (which have not been actually isolated) are as follows: pyrocatechol (violet, 2 : 1), protocatechuic aldehyde (violet, 2 : 1),  $\beta$ -resoreylic acid (reddish-yellow, 1 : 1), gentisic acid (violet-red, 1 : 1), dibromopyrogallol (blue, 1 : 1), dibromogallic acid (dark blue, 1 : 1), and pyrogallolcarboxylic acid (dark violet, 1 : 1).

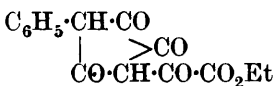
When ink is applied to paper, neutralisation of the acid present occurs first, followed by atmospheric oxidation of the ferrous salts, which are converted into bluish-violet insoluble primary ink salts (e.g., of the gallic acid type). By the further action of atmospheric oxygen and moisture, the primary salts undergo oxidation, carbonyl or carbethoxyl groups being removed, with formation of carbon dioxide and brown secondary ink salts (e.g., of the pyrogallol type). The black shade acquired by writing ink a week or so after use is due to the presence of a mixture of primary and secondary salts, or, in the case of salts rich in iron, to the presence, also, of ferric hydroxide. The addition of gum arabic to inks hinders atmospheric oxidation and loss of carbon dioxide.

Complete oxidation to the secondary ink salt type takes, on the average, twenty or thirty years. After a much longer time, ferric oxide or hydroxide alone will remain on the paper. E. E. T.

#### ***o*-Cresoltetrachlorophthalein and some of its Derivatives.**

E. L. ARNOLD (*J. Amer. Chem. Soc.*, 1924, **46**, 489—493).—*o*-Cresoltetrachlorophthalein was prepared by condensing tetrachlorophthalic acid with *o*-cresol, using stannic chloride. It forms colourless crystals, m. p. 292—293° (decomp.). It resembles phenolphthalein and phenoltetrachlorophthalein, acting as an indicator, purple in alkaline solution; the end-point is between  $p_H$  8.5 and 9. It forms a colourless *diacetyl* derivative, m. p. 207—208°, and a *dimethyl ether*, m. p. 212—213°. In concentrated sulphuric acid it gives a red solution probably due to sulphate formation. The spectrum of *o*-cresoltetrachlorophthalein in absolute ethyl alcohol is very similar to that of phenoltetrachlorophthalein, showing four weak bands in the ultra-violet, whereas that of phenolphthalein has only two bands, which correspond with the more prominent bands of the other two spectra. These bands are of frequency 3523 and 3613. A. B. S.

**Ring Syntheses with Ethyl Oxalate.** W. WISLICENUS and F. MELMS (*Annalen*, 1924, **436**, 101—112).—Continuing the work of Wislicenus and Schollkopf (A., 1917, i, 700), *ethyl triketophenylcyclopentaneglyoxylate* (annexed formula), was prepared by interaction of benzyl methyl ketone and ethyl oxalate (2 mols.) in presence of potassium ethoxide. This substance (yellow needles, m. p. 169—170°) is strongly enolised. It forms a red *di-potassium* salt and a dark red *copper* salt. The acid was obtained by mild alkaline hydrolysis as an orange powder, m. p. 214° (decomp.). When the ester was subjected to acid hydrolysis,

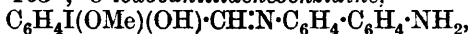


scission took place and 2:4:5-triketo-1-phenylcyclopentane was formed, crystallising from benzene in yellow needles, from alcohol in colourless needles, whilst an orange modification was obtained when the compound was fused and again cooled, or boiled with water. All three forms melted at 167°. An aqueous solution of the substance is strongly acid to litmus and reduces Fehling's solution. The phenylhydrazone (only one keto group enters into these reactions) forms greenish-yellow scales, m. p. 241°, the anil orange-red scales, m. p. 172°, the *p*-toluidine derivative, red crystals, m. p. 195—196°. The quinoxaline formed by interaction with *o*-phenylenediamine forms brown needles, m. p. 251°. The methyl ether, 2:4-diketo-5-methoxy-1-phenylcyclopentene, in preparing which diazomethane was used, forms colourless crystals, m. p. 54—55°. The benzylidene derivative of triketophenylcyclopentane forms yellow crystals, m. p. 219°; similar derivatives with *p*-tolualdehyde (m. p. 206—207°) and *p*-nitrobenzaldehyde (m. p. 262—264°) were prepared; the latter is noteworthy in that the colour of the solution varies with the solvent employed. The dibromo derivative has m. p. 185°. When triketophenylcyclopentane was dissolved in alkali and reprecipitated, it was found to have been converted apparently into a bis-product of high melting point. A preliminary investigation of the condensations of ethyl  $\beta$ -ethoxyglutaconate, ethyl acetonedicarboxylate, and ethyl acetoacetate is described. W. A. S.

**Polymorphic Forms and Thermotropic Properties of Schiff's Bases derived from 5-Iodo-4-hydroxy-3-methoxybenzaldehyde.** R. M. HANN (*J. Washington Acad. Sci.*, 1924, 14, 79—86).—Derivatives of the Schiff base type have been prepared from 5-iodo-4-hydroxy-3-methoxybenzaldehyde and aromatic amines. These 5-iodovanillidene compounds are not phototropic, but on vigorous trituration they change colour owing to the production of polymorphic forms. The introduction of iodine into *p*-hydroxy-*m*-methoxybenzaldehyde results in the disappearance of the power to undergo thermotropic change in the vanillidene derivatives. The following compounds are described: 5-iodovanillideneaniline, deep red bipyramids, changing to an orange powder, m. p. 152—153°; 5-iodovanillidene-*o*-chloroaniline, yellowish-brown crystals, m. p. 143°; 5-iodovanillidene-*p*-chloroaniline, red needles, changing to an orange powder, m. p. 110—111° (decomp.); 5-iodovanillidene-*p*-bromoaniline, yellowish-brown powder, changing to yellowish-green, with metallic lustre, m. p. 108° (partial decomp.); 5-iodovanillidene-*p*-iodoaniline, yellowish-brown powder, changing to yellowish-green with metallic lustre, m. p. 98°; 5-iodovanillidene-*o*-toluidine, light yellow needles, changing to deep yellow, m. p. 120—121°; 5-iodovanillidene-*m*-toluidine, orange-red granules, darkening on trituration, m. p. 103—104°; 5-iodovanillidene-*p*-toluidine, brilliant golden-yellow crystals, becoming nearly colourless on trituration, m. p. 160—161°; 5-iodovanillidene- $\alpha$ -naphthylamine, yellowish-brown crystals, changing to bright yellow, decomposes at 226°; 5-iodovanillidene- $\beta$ -naphthyl-



*amine*, light yellow needles, changing to deep yellow, m. p. 163°; *5-iodovanillidene-ψ-cumidine*, chocolate-brown powder, changing to yellow, m. p. 165°; *5-iodovanillidenebenzidine*,



bright orange flocks, crimson on trituration, m. p. 160–161° (incipient decomp.). R. B.

### ***o*-Methoxydiphenylacetaldehyde and its Transformations.**

R. STOERMER and F. FRICK (*Ber.*, 1924, 57, [B], 23–29).— $\alpha\alpha$ -*o*-Methoxydiphenylethylene glycol,  $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , long needles, m. p. 96°, prepared in moderate yield by the action of magnesium *o*-anisyl bromide on benzoylcarbinol, is smoothly converted by hot sodium hydrogen sulphite solution into *o*-methoxydiphenylacetaldehyde, a viscous liquid, b. p. 198°/16 mm.; the corresponding semicarbazone has m. p. 175°, whereas an oxime or a phenylhydrazone could not be isolated. The aldehyde is converted by glacial acetic and hydrobromic acids into 1-phenylcoumarone, m. p. 120°, instead of the expected 2-phenyl derivative. Probably the migration of the phenyl group takes place in an intermediately formed tolane derivative which could not be isolated. The aldehyde is transformed by phosphorus pentachloride into  $\alpha$ -chloro- $\beta\beta$ -*o*-methoxydiphenylethylene, b. p. 190°/11 mm., which, however, is converted by sodium ethoxide at 200° immediately into 1-phenylcoumarone.

*o*-Methoxydiphenylacetaldehyde is decomposed by an excess of alcoholic potassium hydroxide solution at 180–200° into potassium formate and *o*-methoxydiphenylmethane, long, colourless needles, m. p. 30°, the constitution of which is established by its formation from *o*-methoxybenzophenone by Clemmensen's method; the corresponding phenylurethane has m. p. 115°. The methoxy derivative is converted by glacial acetic and hydrobromic acids at 150° into *o*-hydroxydiphenylmethane, b. p. 175°/18 mm., m. p. 15°.

The aldehyde is oxidised in acetone solution by potassium permanganate in the presence of potassium carbonate to *o*-methoxydiphenylacetic acid, m. p. 125°; it is reduced by aluminium amalgam in the presence of moist ether to *o*-methoxydiphenylethyl alcohol, a colourless, very viscous liquid, b. p. 220°/30 mm. (*phenylurethane*, m. p. 107°; *benzoate*, m. p. 98°), which is converted by acetic and hydrobromic acids into 2-phenylcoumaran, m. p. 39°, together with much resinous matter.

*as-o*-Methoxydiphenylethylene oxide, m. p. 90°, is obtained as a by-product of the preparation of  $\alpha\alpha$ -*o*-methoxydiphenylethylene glycol; it is transformed by dilute hydrochloric acid at 180° into methoxydiphenylacetaldehyde. H. W.

**Action of Piperidine on Phenyl  $\alpha$ -Bromostyryl Ketone. Production of a New Ketone, Phenylbenzylglyoxal.** C. DUFRAISSE and H. MOUREU (*Compt. rend.*, 1924, 178, 573–575; cf. A., 1922, i, 843; 1923, i, 113).—Piperidine converts phenyl  $\alpha$ -bromostyryl ketone into *phenyl  $\alpha$ -bromo- $\beta$ -phenyl- $\alpha$ -piperidinoethyl ketone*,  $\text{COPh}\cdot\text{CBr}(\text{NC}_5\text{H}_{10})\cdot\text{CH}_2\text{Ph}$ , a pale yellow, sparingly

soluble substance, m. p.  $164^{\circ}$ , very unstable, but forming stable salts with acids. This ketone, with 1 mol. of alkali in alcoholic solution, affords the red piperidinobenzylideneacetophenone described by Watson (T., 1904, 85, 1322) and now shown to be phenyl  $\alpha$ -piperidinostyryl ketone,  $\text{COPh}\cdot\text{C}(\text{NC}_5\text{H}_{10})\text{:CHPh}$ . The latter substance, on hydrolysis by acid, is converted into *phenylbenzylglyoxal*,  $\text{Bz}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ , a pale yellow solid, m. p.  $67-68^{\circ}$ , unstable in air, but stable in a vacuum. E. E. T.

**Additive Compounds of Metallic Salts and Doubly Unsaturated Aromatic Ketones.** W. DILTNEY and O. RAUCHHAUPT (*Ber.*, 1924, 57, [B], 309—310).—Concentrated solutions of di-*p*-methoxystyryl ketone and ferric chloride in glacial acetic acid yield the additive compound,  $[(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\text{:CH})_2\text{CO}]_2\text{FeCl}_3$ , dark violet needles, m. p.  $146^{\circ}$  after previous decomposition. In a similar manner, *o*-chlorostyryl methoxystyryl ketone, yellow crystals, m. p.  $109^{\circ}$ , gives the compound,  $\text{C}_{36}\text{H}_{30}\text{O}_2\text{Cl}_4\text{Fe}$ , dark violet needles, m. p.  $155-156^{\circ}$  (decomp.). Uranyl chloride and distyryl ketone yield the product,  $[(\text{CHPh}\text{:CH})_2\text{CO}]_2\text{UO}_2\text{Cl}_2$ , small, golden-yellow leaflets, m. p.  $264^{\circ}$  after incipient decomposition at  $200^{\circ}$ ; the corresponding compound,  $\text{C}_{38}\text{H}_{36}\text{O}_8\text{Cl}_2\text{U}$ , from di-*p*-methoxystyryl ketone, crystallises in violet-red, hexagonal leaflets, m. p. about  $258^{\circ}$  (incipient decomp.  $150^{\circ}$ ). The additive compound,  $[(\text{C}_6\text{H}_4[\text{OMe}]\text{:CH}\text{:CH})_2\text{CO}]_2\text{VCl}_2$ , brownish-yellow needles, is prepared from its components dissolved in glacial acetic acid.

H. W.

**Synthesis of Nitranilic Acid.** H. O. MEYER (*Ber.*, 1924, 57, [B], 326—328).—Nitranilic acid [3:6-dinitro-2:5-dihydroxy-*p*-benzoquinone] is obtained in 72—78% yield by the action of fuming nitric acid ( $d$  1.459) on *p*-benzoquinone at  $-5^{\circ}$  to  $-10^{\circ}$ . It crystallises in lemon-yellow needles, m. p.  $86-87^{\circ}$ , whereas Nietzki (A., 1911, i, 69) gives m. p.  $100^{\circ}$ . The potassium salt,  $\text{C}_6\text{O}_8\text{N}_2\text{K}_2$ , exists in two distinct crystalline forms. The *rubidium* salt,  $\text{C}_6\text{O}_8\text{N}_2\text{Rb}_2$ , yellow needles, is described.

H. W.

**Action of Potassium Ferricyanide on Purpurin in Alkaline Solution.** R. SCHOLL and P. DAHL (*Ber.*, 1924, 57, [B], 80—83).—Purpurin is readily oxidised in alkaline solution by potassium ferricyanide at the atmospheric temperature to *o*-phthalic acid and 2:5-dihydroxy-*p*-benzoquinone, *o*-2:5-dihydroxy-*p*-benzoquinonoylbenzoic acid being apparently produced initially. The first stage of the oxidation of purpurin is therefore similar to that of alizarin (Scholl and Zinke, A., 1919, i, 25; 1920, i, 169) and quinizarin (this vol., i, 178). Dihydroxyanthraquinones which contain the hydroxy group attached to different nuclei and monohydroxyanthraquinones are not affected by potassium ferricyanide in alkaline solution at the atmospheric temperature. The hypothesis that oxidative fission occurs through the diquinones therefore receives further support.

In addition to the orange-yellow modification described in the

literature, 2 : 5-dihydroxy-*p*-benzoquinone exists in a pale yellow, metastable *modification* which is stable only in the presence of acetic acid. The substance is readily converted by methyl-alcoholic hydrogen chloride into the dimethyl ether. H. W.

**Dyestuffs of the Phenanthrene Series.** K. BRASS (*Z. angew. Chem.*, 1924, **37**, 67—69).—Phenanthraquinonyl azides behave in a similar manner to phenyl azides towards sulphuric acid. Thus, 2-azidophenanthraquinone yields 2-amino-3-hydroxyphenanthraquinone, from which 2 : 3-dihydroxyphenanthraquinone is prepared in the usual manner, some 2-aminophenanthraquinone being formed at the same time. Under certain conditions 4-azidophenanthraquinone yields, with sulphuric acid, 4-amino-1-hydroxyphenanthraquinone, and under others 1 : 4-dihydroxyphenanthraquinone. These compounds are dyestuffs for wool and cotton. The presence of a hydroxyl group in the *o*-position to an amino- or a hydroxyl group has little or no effect on the tinctorial properties of the parent compounds, whereas its presence in the *p*-position to such groups greatly enhances their value. As mordant dyestuffs the 4-amino-1-hydroxy and 1 : 4-dihydroxy compounds are more powerful than the 2-amino-3-hydroxy and 2 : 3-dihydroxy compounds. The simple aminophenanthraquinones are also dyestuffs for wool, and possess more powerful tinctorial properties than the simple aminoanthraquinones. [Cf. *B.*, 1924, 246.]

W. T. K. B.

**Azido-, Aminohydroxy-, and Dihydroxy-phenanthraquinones.** I. K. BRASS, E. FERBER, and J. STADLER (*Ber.*, 1924, **57**, [B], 121—128).—2-Aminophenanthraquinone behaves as an amine of the benzene series, in which the basic character is repressed by the presence of acidic groups; its diazotisation and the conversion of its diazonium hydrogen sulphate into a series of derivatives are described.

2-Aminophenanthraquinone is conveniently diazotised in accordance with the method of Schmidt and Soll (*A.*, 1908, i, 996), somewhat less advantageously in the presence of concentrated sulphuric acid. *Phenanthraquinone-2-diazonium perbromide*,  $C_{14}H_7O_2N_2Br_3$ , orange-yellow crystals which lose bromine at the atmospheric temperature, is prepared by treating a solution of the diazonium sulphate with an excess of bromine dissolved in potassium bromide solution. It is transformed by ice-cold ammonia solution (25%) into 2-azidophenanthraquinone, cinnabar-red leaflets, m. p. 186° (decomp.) after darkening at 175°, which is converted by *o*-phenylenediamine hydrochloride into 2-azidophenanthraphenazine,  $C_{20}H_{11}N_5$ , long, yellow needles, m. p. 190° (decomp.) after softening at 180°. The action of sulphuric acid on the azide gives a mixture of 2-aminophenanthraquinone and 2-amino-3-hydroxyphenanthraquinone, bluish-black needles, which softens at 120°, but does not melt in a capillary tube at a higher temperature. The mixture of products yields phthalic acid when oxidised. 2 : 3-Dihydroxyphenanthraquinone, prepared by diazotisation of the hydroxy-

amine in concentrated sulphuric acid solution, crystallises in slender, reddish-brown needles which have no definite melting point; it yields a *mono-sodium* salt and a *quinoxaline* derivative, small, orange-yellow needles, m. p. 162° (decomp.). H. W.

**Azido-, Aminohydroxy-, and Dihydroxy-phenanthraquinones.** II. K. BRASS and J. STADLER (*Ber.*, 1924, 57, [B], 128—136).—4-Aminophenanthraquinone is converted by sodium nitrite in the presence of concentrated sulphuric acid into the corresponding diazonium salt, which is relatively unstable in comparison with phenanthraquinone-2-diazonium sulphate (preceding abstract). It is transformed by a solution of bromine in concentrated potassium bromide solution into *phenanthraquinone-4-diazonium perbromide*, an orange-red, crystalline powder, from which 4-azidophenanthraquinone, red needles, is obtained by the action of aqueous ammonia (10%). 4-Azidophenanthraphenazine, prepared from the azide and *o*-phenylenediamine hydrochloride, crystallises in slender, yellow needles, m. p. 197° (decomp.). 4-Azidophenanthraquinone reacts with dilute sulphuric acid with unexpected ease, and after prolonged treatment at the temperature of boiling water yields solely 1:4-dihydroxyphenanthraquinone, very slender, bluish-violet needles (1:4-diacetoxypheanthraquinone, prisms, m. p. 183°; 1:4-dihydroxyphenanthraphenazine, brownish-red, lustrous needles, m. p. 288°). The attachment of the two hydroxy groups to the same benzene nucleus is established by the observation that phthalic acid is the only isolable product of its oxidation. The compound must therefore be either 1:4- or 3:4-dihydroxyphenanthraquinone, and, since the latter constitution has already been assigned to morpholquinone, from which the present compound is quite distinct, the former alternative is selected. It appears, however, to be quite exceptional for a substituent to enter the phenanthraquinone nucleus in the 1-position. Oxidation of 1:4-dihydroxyphenanthraquinone in ethereal solution with silver oxide or lead tetra-acetate leads to the formation of a yellow *op-diquinone* which has not been isolated in the homogeneous condition.

4-Amino-1-hydroxyphenanthraquinone is prepared by the action of sulphuric acid on the azide at a temperature not exceeding 90°. It crystallises in violet-black aggregates of needles, decomp. 218° after subliming at 165°. The *sulphate* and the *hydrochloride* are described; the *sodium* salt is hydrolysed by water. It is transformed by hot, dilute sulphuric acid into 1:4-dihydroxyphenanthraquinone. H. W.

**Formation of Diketocamphane (Ketocamphor) and of Diketofenchane (Ketofenchone) by the Oxidation of Camphor and Fenchone with Chromic Acid.** J. BREDT (*J. pr. Chem.*, 1923, 106, 336—347).—The *p*-diketocamphane described by Bredt and Goeb (*A.*, 1921, i, 257) has now been obtained by the oxidation of both natural and inactive synthetic camphor with chromic acid. The product in both cases melts at 210° and the yield is only 4—5% of the theoretical. In its physiological action, *p*-di-

ketocamphane is similar to camphor, and it has the advantage of greater solubility in water.

By oxidation of fenchone in glacial acetic acid solution with chromic acid below  $15^{\circ}$  (the reaction takes about 5 weeks), *ketofenchone* is obtained, probably having the annexed formula. It forms long, thin needles, m. p.  $42.5-43^{\circ}$ , has a typical lactone odour, and is readily volatile in steam; b. p.  $108^{\circ}/10.5$  mm. The new keto group is more active than the original keto group of fenchone, and there are readily formed a *monophenylhydrazone*, white needles, m. p.  $149-150^{\circ}$  (decomp.), and a *monosemicarbazone*, thin needles, m. p.  $222-223^{\circ}$ . Ketofenchone has  $[\alpha]_D^{25} +75.78^{\circ}$  in benzene. E. H. R.

**Solubility of Sulphur in Caoutchouc.** W. J. KELLY and K. B. AYERS (*Ind. Eng. Chem.*, 1924, **16**, 148—150).—The distribution of dissolved sulphur between unvulcanised rubber and amyl or *n*-butyl alcohol obeys Henry's law. The sulphur consequently is present in the rubber in a state of solution and not of adsorption. For the determination of the solubility of sulphur in rubber it is convenient to suspend strips of the latter in a saturated solution of sulphur in butyl alcohol in the presence of solid sulphur; when equilibrium is attained, the dissolved sulphur is extracted from the rubber with acetone and its amount determined. [Cf. *B.*, 1924, 266.] D. F. T.

**Reduction Products of 1-Acylcoumarones.** R. STOERMER, C. W. CHYDENIUS, and E. SCHINN (*Ber.*, 1924, **57**, [B], 72—80).—1-Acetylcoumarone, b. p.  $136^{\circ}/11$  mm., m. p.  $76^{\circ}$  (cf. Stoermer and Schäffer, A., 1903, i, 846), is prepared conveniently by the action of chloroacetone on salicylaldehyde and potassium hydroxide dissolved in alcohol; the *phenylhydrazone*, pale yellow crystals, m. p.  $153-154^{\circ}$ , and the *semicarbazone*, colourless needles, m. p.  $217^{\circ}$ , are described. Reduction of the ketone by sodium amalgam in the presence of alcohol acidified with acetic acid yields coumaranylmethylcarbinol,  $C_6H_4<\overset{O}{CH_2}>CH\cdot CHMe\cdot OH$ , and *acetylcoumarane*,

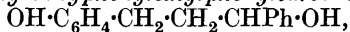
$C_6H_4<\overset{O}{CH_2}>CHAc$ , a colourless liquid, b. p.  $132-133^{\circ}/12$  mm. (the sodium hydrogen sulphite compound, the *oxime*, m. p.  $111-112^{\circ}$ , the *phenylhydrazone*, yellow leaflets, m. p.  $113^{\circ}$ , and the *semicarbazone*, m. p.  $192^{\circ}$ , are described). *Diacetylbiscoumarane*,  $C_{20}H_{18}O_4$ , m. p.  $183^{\circ}$ , gives a *mono-oxime*, m. p.  $177^{\circ}$ . Reduction of acetylcoumaraneoxime by sodium amalgam and alcohol leads to the formation of small quantities of 1- $\alpha$ -aminoethylcoumarane,  $C_6H_4<\overset{O}{CH_2}>CH\cdot CHMe\cdot NH_2$ , a fairly mobile liquid, b. p.  $153^{\circ}/15$  mm. (*hydrochloride*, colourless, lustrous leaflets, m. p.  $117-118^{\circ}$ ; *picrate*, yellow leaflets, decomp.  $209^{\circ}$ ).

Reduction of acetylcoumarone with sodium and alcohol according to the method of Stoermer and Schäffer (*loc. cit.*) gives acetylcoumarane, coumaranylmethylcarbinol, and *o*-hydroxyphenyl-

butan- $\gamma$ -ol, m. p. 66—67°; the latter substance may also be obtained by reduction of coumaranylmethylcarbinol. It is converted by bromine in chloroform solution into 4-bromo-2-hydroxyphenylbutan- $\gamma$ -ol, long, colourless needles, m. p. 94—95°. o-Methoxyphenylbutan- $\gamma$ -ol, a colourless, viscous liquid, b. p. 143°/12 mm., is prepared by the action of methyl iodide and potassium hydroxide on an alcoholic solution of the corresponding phenol. It is converted by zinc chloride at 150° into o- $\Delta^{\beta}$ -butenylanisole, b. p. 104—106°/12 mm.,  $d_4^{19}$  0.9721,  $n_D^{19}$  1.5255 (cf. von Braun and Schirmacher, A., 1923, i, 286), which is isomerised when heated with a small quantity of potash-lime to o- $\Delta^{\alpha}$ -butenylanisole, b. p. 106—108°/12 mm.,  $d_4^{18}$  0.9819,  $n_D^{18}$  1.5346.

1-isoPropenylcoumarane,  $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown CH_2 \end{smallmatrix} CH \cdot CMe \cdot CH_2$ , a mobile liquid, b. p. 106—108°/12 mm., is obtained together with much resinous matter by the action of magnesium methyl iodide on acetylcoumarane.

1-Benzoylcoumarone, m. p. 90—91° (*semicarbazone*, m. p. 137°), is conveniently obtained by the action of bromoacetophenone and potassium hydroxide on salicylaldehyde in alcoholic solution. Somewhat unexpectedly, it is reduced by sodium and alcohol mainly to 1-benzylcoumarane, m. p. 26°, b. p. 185°/15 mm.; small quantities of  $\beta$ -o-hydroxyphenylethylphenylcarbinol,



slender needles, m. p. 94° (*phenylurethane*, m. p. 124°; *diphenylurethane*, m. p. 52°), are simultaneously produced. Coumaronyl-

phenylcarbinol,  $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown CH \end{smallmatrix} \geq C \cdot CHPh \cdot OH$ , m. p. 76°, is obtained

by the reduction of benzoylcoumarone with sodium amalgam in acid-alcoholic solution at the atmospheric temperature; the corresponding phenylurethane has m. p. 126°. Benzoylcoumarone-oxime, m. p. 132°, is reduced by sodium amalgam in faintly acid, alcoholic solution to coumaronylphenylaminomethane, a colourless liquid, b. p. 200°/11 mm. (*hydrochloride*, m. p. 210°). It is converted by one molecular proportion of sodium nitrite into coumarylphenylcarbinol and by two molecular proportions into benzoylcoumarone; it is reduced by sodium and alcohol to benzoylcoumarane. 1-Benzylcoumarone, b. p. 180—185°/15 mm., cannot be prepared from the benzoyl compound by Clemmensen's method, but is obtained when the hydrazone is heated with an alcoholic solution of sodium ethoxide at 220—230°. Attempts to prepare it by converting coumarylphenylcarbinol by means of thionyl chloride into coumarylphenylmethyl chloride and reduction of the latter substance with zinc dust and acetic acid yielded a compound,  $C_{30}H_{26}O_2$ , m. p. 98°, probably 1:1'-dibenzyl-2:2'-dicoumarane. H. W.

**Synthesis of 4-Ketochroman [Chromanone].** F. MAYER and L. VAN ZÜTPHEN (*Ber.*, 1924, 57, [B], 200—202; cf. Arndt and Källner; Krollpfeiffer and Schultze, succeeding abstracts).— $\beta$ -Chloropropionyl chloride is converted by phenol in the presence of carbon disulphide and aluminium chloride or phosphoryl chloride

into a mixture of phenyl  $\beta$ -chloropropionate, b. p. 132—135°/12 mm., and a substance,  $C_9H_{10}O_3$ , m. p. 141—142°, which is regarded provisionally as *o*(? *p*)-hydroxyphenyl  $\beta$ -hydroxyethyl ketone. The ester is transformed by aluminium chloride into *o*-hydroxyphenyl  $\beta$ -chloroethyl ketone, colourless prisms, m. p. 70°, and *p*-hydroxyphenyl  $\beta$ -chloroethyl ketone, colourless, lustrous leaflets, m. p. 90° (m. p. 75—80°, directly after crystallisation from water), which are separated from one another by distillation with steam, with which only the ortho-derivative is volatile; the compound  $C_9H_{10}O_3$  (above) is also formed in small amount. The ortho-compound is converted by aluminium chloride at 160—180° into 4-ketochroman [chromanone],  $C_6H_4 \begin{smallmatrix} < CO \cdot CH_2 \\ O - CH_2 \end{smallmatrix}$ , colourless, slender needles, m. p. 111°, b. p. 128°/13 mm. (the sodium salt, yellow crystals, the oxime, long, colourless needles, m. p. 144—145°, and the benzylidene derivative, m. p. 147—150°, are described). H. W.

**Chromanone and Chromonol.** F. ARNDT and G. KÄLLNER (*Ber.*, 1924, 57, [B], 202—206; cf. Mayer and van Zütphen, preceding abstract; Krollpfeiffer and Schultze, succeeding abstract).— $\beta$ -Phenoxypropionic acid is converted by concentrated sulphuric acid or, more advantageously from the point of view of yield, by successive treatment with phosphorus pentachloride and aluminium chloride in the presence of benzene, into chromanone, colourless plates, b. p. 127—128°/13 mm., m. p. 38° (Mayer and van Zütphen, *loc. cit.*, give m. p. 111°); 3-benzylidenechromanone, almost colourless crystals, has m. p. 113° (Mayer and van Zütphen give m. p. 147—150°). Chromanone condenses with *p*-nitrosodimethylaniline in alcoholic solution in the presence of potassium hydroxide and the product is reduced by hydrazobenzene to (?3-*p*-dimethylaminophenylamino)chromanone,  $C_6H_4 \begin{smallmatrix} < CO \cdot CH \cdot NH \cdot C_6H_4 \cdot NMe_2 \\ O - CH_2 \end{smallmatrix}$ ,

golden-yellow leaflets, m. p. 154° (the colourless hydrochloride is described), which is oxidised by potassium ferricyanide to the corresponding, very unstable anil. The latter substance is converted by boiling, concentrated hydrochloric acid into chromonol (3-hydroxy-1:4-benzopyrone),  $C_6H_4 \begin{smallmatrix} < CO \cdot C(OH) \\ O - CH \end{smallmatrix}$ , coarse, colourless needles, m. p. 181°; the sodium, calcium, and magnesium derivatives are described. The benzoate crystallises in colourless needles, m. p. 177.5°. 3-Bromochromanone has m. p. 69—70°. H. W.

**Ring Closures from  $\beta$ -Phenoxypropionic Acids to Chromanones.** F. KROLLPFEIFFER and H. SCHULTZE (*Ber.*, 1924, 57, [B], 206—207; cf. Mayer and van Zütphen; Arndt and Källner, preceding abstracts).—The formation of chromanones from  $\beta$ -phenoxyphenylpropionic acids is most conveniently effected by heating mixtures of the latter and phosphoric anhydride under diminished pressure; the action of concentrated sulphuric acid or of phosphoric oxide in the presence of benzene is less suitable. Chromanone crystallises in colourless leaflets, m. p. 39—40°, b. p.

124°/14 mm.; the *semicarbazone*, small, colourless needles, has m. p. 227°.  $\beta$ -*p-Toloxypionic acid*, colourless needles, m. p. 147—148°, yields 6-methylchromanone, m. p. 34—36° (cf. von Auwers and Krollpfeiffer, A., 1915, i, 442). H. W.

**Syntheses of Chromones and Coumarins.** G. WITTIG (*Ber.*, 1924, 57, [B], 88—95).—Chromones are readily obtained by condensation of *o*-acetylphenols with sodium and ethyl acetate, followed by ring closure of the diketones thus produced.

The displacement of the acetyl group into the ortho position to the hydroxy radical is effected by heating the phenolic esters with aluminium chloride at 110—115°; 4-chloro-6-acetylphenol (3-chloro-6-hydroxyphenyl methyl ketone), m. p. 53·5—54·7°, 4-chloro-6-acetyl-*m-cresol*, colourless needles, m. p. 69—70°, and 6-acetyl-*p-cresol*, m. p. 45—46°, are described.

4-Chloro-6-acetylphenol is converted by acetic anhydride and sodium acetate at 160—170° into a mixture of 6-chloro-4-methylcoumarin, m. p. 186—187°, and 6-chloro-2-methylchromone,

$\text{C}_6\text{H}_3\text{Cl} \begin{array}{l} \diagup \text{CO} \cdot \text{CH} \\ \diagdown \text{O} - \text{CMe} \end{array}$ , colourless needles, m. p. 115—116°. The

substances are separated from one another by means of an alcoholic solution of sodium ethoxide, which causes fission of both rings with the production of 5-chloro- $\beta$ -methylcoumaric acid, m. p. 156° (decomp.), and 4-chloro-6-acetylacetophenol. Addition of acid converts the former into its lactone, whereas the latter can be removed by aqueous sodium hydroxide and subsequently reconverted into its cyclic compound by sulphuric acid. The mixture of chromone and coumarone is converted by boiling 2*N*-sodium hydroxide solution into 5-chlorosalicylic acid, m. p. 173—174°, which owes its formation to fission of the intermediately formed diketone,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COMe}$ .

A similar series of reactions has been applied to 4-chloro-6-acetyl-*m-cresol*, whereby the following compounds are produced: 6-chloro-4:7-dimethylcoumarin, needles, m. p. 206—207°; 4-chloro-6-acetyl-aceto-*m-cresol*, pale yellow, lustrous leaflets, m. p. 115·5—116·5°; 6-chloro-2:7-dimethylchromone, needles, m. p. 144·5—145·5°; 5-chloro-4-methylsalicylic acid, m. p. 203—204°. Similarly, 6-acetyl-*p-cresol* gives 2:6-dimethylchromone, m. p. 99·5—100°, 4:6-dimethylcoumarin, m. p. 147·5—148°, and 5-methylsalicylic acid, m. p. 148·5—149°.

*p*-Chlorophenyl methyl ether is converted by acetyl chloride and aluminium chloride in the presence of carbon disulphide into 4-chloro-6-acetylphenyl methyl ether, needles, m. p. 29—30°, which is transformed by sodium and ethyl acetate into 4-chloro-6-acetylacetophenyl methyl ether, yellow prisms, m. p. 76·5—77·5°; the latter compound is converted by concentrated hydriodic acid or, less advantageously, by hydrobromic and glacial acetic acids into 6-chloro-2-methylchromone.

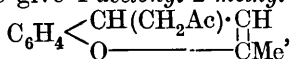
The preparation of 6-chloro-2-methylchromone, 6-chloro-2:7-dimethylchromone, and 2:6-dimethylchromone by the action of sodium and ethyl acetate on the requisite phenol is described.



4-Chloro-6-acetylacetophenol crystallises in pale yellow leaflets, m. p. 110—111°; 6-acetylaceto-p-cresol has m. p. 94·5—96°.

H. W.

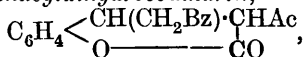
**Interaction of Ethyl Acetoacetate with o-Hydroxystyryl Ketones.** T. A. FORSTER and I. M. HEILBRON (*J. Chem. Soc.*, 1924, 125, 340—347).—2-Hydroxystyryl methyl ketone condenses with ethyl acetoacetate, in presence of sodium ethoxide or aqueous sodium hydroxide, to give 4-acetonyl-2-methyl- $\gamma$ -pyran,



colourless needles, m. p. 134—135° (*phenylhydrazone*, colourless needles, m. p. 200°). Condensation of 2-hydroxystyryl phenyl ketone with ethyl benzoacetate similarly affords 2-phenyl-4-phenacyl- $\gamma$ -pyran, colourless crystals, m. p. 130°, together with 2-phenyl-4-phenacyl- $\gamma$ -pyran-3-carboxylic acid, colourless prisms, m. p. 157°. Condensation of 2-methoxystyryl methyl ketone with ethyl acetoacetate affords ethyl 3-o-methoxyphenyl-5-methyl- $\Delta^5$ -cyclo-

hexen-1-one-2(or 4)-carboxylate,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \begin{array}{c} \text{CH}_2 \text{-----} \text{CMe} \cdot \text{CH} \\ \text{CH} \text{-----} \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CO} \end{array}$  or  $\begin{array}{c} \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CMe} \cdot \text{CH} \\ \text{CH} \text{-----} \text{CH}_2 \text{-----} \text{CO} \end{array}$ , pale yellow needles, m. p. 139°.

2-Methoxystyryl phenyl ketone (colourless needles, m. p. 60°) condenses with ethyl acetoacetate to give ethyl 5-phenyl-3-o-methoxyphenyl- $\Delta^5$ -cyclohexen-1-one-2-carboxylate, colourless prisms, m. p. 95°, whilst 2-hydroxystyryl phenyl ketone under similar conditions affords 3-acetyl-4-phenacyldihydrocoumarin,



colourless needles, m. p. 175°, together with a small quantity of a colourless crystalline substance, m. p. 214°.

6-, 7-, and 8-Methoxy-4-acetonyl-2-methyl- $\gamma$ -pyran respectively form feathery needles, m. p. 119°, colourless crystals, m. p. 149°, and colourless needles, m. p. 168°, the 8-compound affording a colourless, crystalline *phenylhydrazone*, m. p. 186°.

Spectrographic measurements support certain of the above constitutional formulæ.

F. G. W.

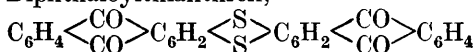
**The Brazilin and Hæmatoxylin Question. III. The Degradation Product of Brazilin obtained by Schall and Dralle.** P. PFEIFFER and J. OBERLIN (*Ber.*, 1924, 57, [B], 208—213; cf. A., 1917, i, 661; 1920, i, 561).—The compound,  $\text{C}_9\text{H}_6\text{O}_4$ , isolated by Schall and Dralle (A., 1892, 502) by the action of atmospheric oxygen on an alkaline solution of brazilin has been considered by Feuerstein and von Kostanecki (A., 1899, i, 538) to be 3:7-dihydroxychromone,  $\text{HO} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{O} \text{-----} \text{CH} \\ \text{CO} \cdot \text{C} \text{-----} \text{OH} \end{array}$ . This is confirmed by the observation that synthetic 3:7-dimethoxychromone is identical with the dimethyl ether of the degradation product.

$\beta$ -3-Methoxyphenoxypionic acid,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ ,

colourless, lustrous crystals, m. p. 81—83°, is prepared in poor yield (17%) from resorcinol methyl ether and  $\beta$ -iodopropionic acid. It is converted by treatment with zinc chloride at 145°, with phosphoric anhydride at about 100°, or by the successive action of phosphorus pentachloride and aluminium chloride, into 7-methoxychromanone, identical with the product obtained by Pfeiffer and Grimmer by the reduction of 7-methoxychromone (cf. A., 1917, i, 661). The chromanone is transformed by amyl nitrite and potassium amoxide in amyl alcoholic solution into 3-oximino-7-methoxychromanone (3-oximino-7-methoxy-2 : 3-dihydro-1 : 4-benzopyrone), almost colourless, microscopic leaflets, m. p. 146—147° (decomp.), which, when treated with glacial acetic and dilute sulphuric acids, gives 3-hydroxy-7-methoxychromone (3-hydroxy-7-methoxy-1 : 4-benzopyrone), colourless, microscopic needles, m. p. 171—172°. 3 : 7-Dimethoxychromone, prepared from the preceding compound and methyl sulphate, forms colourless crystals, m. p. 169—170°. H. W.

**Linear and Angular Diphthaloylthianthrens.** K. BRASS and K. HEIDE (*Ber.*, 1924, 57, [B], 104—121).—An extension of the work on compounds containing the dithiin ring to anthracene derivatives. In these, the stability of the ring is much greater than in the corresponding naphthalene compounds (cf. Brass and Köhler, A., 1922, i, 1050), and its conversion by loss of an atom of sulphur into the thiophen ring is effected only under drastic conditions. Contrary to the views of Scholl and Seer (A., 1911, i, 557), both linear and angular diphthaloylthianthrens are well-defined vat dyes.

2 : 3 : 6 : 7-Diphthaloylthianthren,



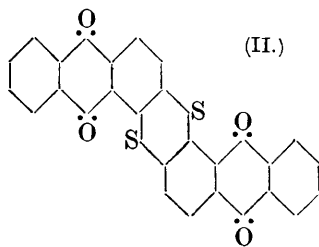
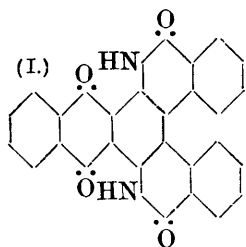
(cf. Scholl and Seer, *loc. cit.*), is prepared by heating a mixture of molecular proportions of 2 : 3-dibromoanthraquinone and crystalline sodium sulphide gradually to 210° under pressure; it crystallises in small, brown needles which do not melt below 360°. It is remarkably stable towards nitric acid. It is reduced by alkaline sodium hyposulphite or by zinc dust and alkali hydroxide to tetrahydroxydianaphthalthianthren, pale greenish-yellow needles; the tetrabenzoate, golden-yellow needles, which darken at 320° but do not melt below 350°, is hydrolysed and oxidised by concentrated sulphuric acid to benzoic acid and diphthaloylthianthren.

2 : 3-Dibromoquinizarin is transformed by boiling acetic anhydride in the presence of fused zinc chloride into the corresponding diacetate, pale yellow needles, m. p. 242° (indefinite), and by benzoyl chloride in the presence of nitrobenzene into the dibenzoate, yellow needles. It is converted by an equimolecular proportion of crystalline sodium sulphide at a temperature not exceeding 190° into 1 : 4 : 5 : 8-tetrahydroxy-2 : 3 : 6 : 7-diphthaloylthianthren, dark green needles with a metallic lustre which do not melt below 360°; the dithiin is more advantageously prepared by the action of sodium sulphide on an aqueous suspension of 2 : 3-dibromo-1 : 4 : 9 : 10-anthra-

diquinone (cf. Dimroth, Friedmann, and Kämmerer, A., 1920, i, 444) in the absence of air. When heated with nitric acid (*d* 1.52) on the steam-bath it loses almost exactly a molecular proportion of sulphur and is doubtless transformed into diquinizarinthiophen, which, however, has not been more closely investigated. The dithiin yields a *monosodium* salt,  $C_{28}H_{11}O_8S_2Na$ , a *di-sodium* salt, and a *di-potassium* salt; greater proportions of base could not be introduced into the molecule. It is converted by alkaline hyposulphite solution or by zinc dust and alkali hydroxide into a blood-red vat from which *octahydroxydianthracenedithiin* separates in brown flocks after addition of acid; it has m. p. 238—244°. The corresponding *octabenzoate* crystallises in pale yellow needles, m. p. 240—244°. Tetrahydroxydiphthaloylthianthren is converted by benzoyl chloride in the presence of boiling nitrobenzene into the corresponding *tetrabenzoate*, a greenish-yellow, crystalline powder which does not melt below 360°, and by acetic anhydride in the presence of dehydrating agents into the *diacetate*, brown leaflets.

2 : 3-Dichloro-1 : 4-diaminoanthraquinone is converted by crystalline sodium sulphide at 210° into 1 : 4 : 5 : 8-*tetra-amino-2 : 3 : 6 : 7-diphthaloylthianthren*,  $C_{28}H_{16}O_4N_4S_2$ , small, dark blue needles which do not melt below 360°; with alkaline sodium hyposulphite solution it yields a red vat from which ammonia is evolved at 50—60°. Benzoylation of the vat leads to the production of the expected *octabenzoyl* derivative,  $C_{34}H_{52}O_{12}S_2$ , long, pale yellow, prismatic needles, m. p. 302° (decomp.). 1 : 4 : 5 : 8-*Tetrabenzoylamino-2 : 3 : 6 : 7-diphthaloylthianthren* crystallises in small, greenish-yellow, lustrous needles, which do not melt below 360°.

The presence of two benzoylamino groups in the vicinal position to the halogen atoms of 2 : 3-dichloro-1 : 4-dibenzoylaminoanthraquinone appears to inhibit the formation of the dithiin ring, since the substance is converted by sodium sulphide at 180° into the phenanthridone (I), microscopic, green needles which do not melt below 300°.



3 : 4 : 7 : 8-*Diphthaloylthianthren* [*thioindanthren*] (II), dark green, coppery needles, which do not melt below 360°, is prepared from 1 : 2-dibromoanthraquinone and sodium sulphide at 190°. With alkaline sodium hyposulphite solution, it gives a blood-red vat from which the expected *tetrabenzoate*, yellow needles, is obtained by the action of benzoyl chloride.

H. W.

**Hydroxypyrrole Derivatives [IV] and certain Reactions of Chloroacetyldiacetonitriles.** E. BENARY and G. SCHWOCH (*Ber.*, 1924, 57, [B], 332—339; cf. Benary and Lau, A., 1923, i, 366).—The remarkable formation of dyes when treated with alcoholic or liquid ammonia appears to be a general property of halogeno-acyl derivatives of dinitriles containing an aromatic substituent and an unsubstituted imino group; when the latter contains a substituent, the normal formation of hydroxypyrroles is observed.

Chloroacetyldiacetonitrile,  $\text{NH}_2\cdot\text{CMe}\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , is converted by methyl-alcoholic ammonia into 4-hydroxy-2-methylpyrrole-3-nitrile,  $\text{HN} < \begin{smallmatrix} \text{CMe}\cdot\text{C}\cdot\text{CN} \\ \text{CH}=\text{C}\cdot\text{OH} \end{smallmatrix}$ , which is too unstable to permit

its isolation in the homogeneous condition; it is characterised by its conversion into 5-benzeneazo-4-keto-2-methylpyrroline-3-nitrile, orange needles, decomp.  $240^\circ$ , by benzenediazonium solution, and by formaldehyde into methylenebis-4-keto-2-methylpyrroline-3-nitrile, an orange precipitate, decomp. about  $250^\circ$ .

C-Chloroacetyl-p-toluacetodinitrile,

$\text{NH}_2\cdot\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , matted needles, m. p.  $166\text{--}168^\circ$ , is prepared from p-toluacetodinitrile and chloroacetyl chloride in the presence of pyridine; it is converted by methyl-alcoholic ammonia into the dye,  $\begin{smallmatrix} \text{C}(\text{CN})\text{---CO} \\ \text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{NH} \end{smallmatrix} > \text{C}:\text{C} < \begin{smallmatrix} \text{C}(\text{CN})\cdot\text{C}\cdot\text{C}_6\text{H}_4\text{Me} \\ \text{CH}_2\text{---NH} \end{smallmatrix}$ ,  $\text{H}_2\text{O}$ , a dark, violet-red powder, decomp. about  $200^\circ$ . The chloro compound is transformed by potassium hydrogen sulphide in alcoholic solution into the corresponding sulphide,  $[\text{NH}_2\cdot\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2]_2\text{S}$ , colourless prisms, decomp.  $218\cdot5\text{--}220^\circ$ .

p-Methoxybenzoacetodinitrile, coarse, colourless prisms, m. p.  $118^\circ$ , is prepared by the action of sodium wire on anisonitrile and acetonitrile dissolved in hot benzene. It is converted by treatment in warm alcoholic solution with dilute hydrochloric acid into p-methoxyphenyl cyanomethyl ketone,  $\text{C}_6\text{H}_4(\text{OMe})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$ , prisms, m. p.  $130\cdot5^\circ$ ; this ketone, with phenylhydrazine and glacial acetic acid in cold alcoholic solution, affords the phenylhydrazone, soft needles, m. p.  $135\text{--}136^\circ$ , which when heated above its m. p. or boiled with dilute acetic acid passes into 5-imino-1-phenyl-3-p-methoxyphenylpyrazolone,  $\text{PhN} < \begin{smallmatrix} \text{N}=\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \\ \text{C}(\text{NH})\cdot\text{CH}_2 \end{smallmatrix}$ , lustrous leaf-

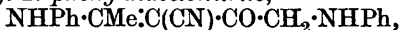
lets, m. p.  $188^\circ$ . The dinitrile is converted by hydroxylamine hydrochloride in boiling, aqueous-alcoholic solution into 5-imino-3-p-methoxyphenylisooxazolone, prisms, m. p.  $136\text{--}137^\circ$ . C-Chloroacetyl-p-anisylacetodinitrile,  $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}_2\text{Cl}$ , needles, m. p.  $164^\circ$ , is converted by methyl-alcoholic ammonia into the dark, violet-red dye,  $\text{C}_{24}\text{H}_{18}\text{O}_3\text{N}_4$  (cf. formula above), decomp.  $200^\circ$  after darkening at  $185^\circ$ , and by potassium hydrogen sulphide into the sulphide,  $[\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{CH}_2]_2\text{S}$ , a crystalline powder, m. p.  $196\text{--}197^\circ$  (decomp.) after darkening and softening at  $190^\circ$ .

C-Chloroacetyl-N-p-anisylldiacetonitrile,  $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}_2\text{Cl}$ , lustrous needles, m. p.  $80\text{--}81\cdot5^\circ$ , is converted by alcoholic potassium

hydroxide solution into 3-hydroxy-1-p-anisyl-5-methylpyrrole-4-nitrile, matted needles, m. p. 190—192° (decomp.).

N-Phenyl- $\alpha$ -anilinoacetylbenzoacetodinitrile, prepared from chloroacetylbenzoacetodinitrile and aniline, decomposes at 258—260° when rapidly heated; with mercuric chloride and dilute hydrochloric acid it yields the additive compound,  $C_{23}H_{19}ON_3 \cdot HCl \cdot HgCl_2$ , pale yellow needles, m. p. 172°. When boiled with an excess of glacial acetic acid the base yields  $\alpha$ -acetanilidoacetyl- $\beta$ -anilino- $\beta$ -phenylacrylamide,  $NHPh \cdot CPh \cdot C(CO \cdot CH_2 \cdot NAcPh) \cdot CO \cdot NH_2$ , colourless prisms, decomp. 296—298°, which is also obtained from chloroacetylbenzoacetodinitrile, aniline, and glacial acetic acid at 115—120°.

C-Anilinoacetyl-N-phenyldiacetonitrile,



small needles, m. p. 214—216° when rapidly heated, is obtained from chloroacetyldiacetonitrile and aniline or from the latter and C-chloroacetyl-N-phenylbenzoacetodinitrile; it gives a lemon-yellow picrate, m. p. 165—166° after previous softening, and the additive compound,  $C_{18}H_{17}ON_3 \cdot HCl \cdot HgCl_2$ , colourless needles, decomp. 230° after darkening at 215°.

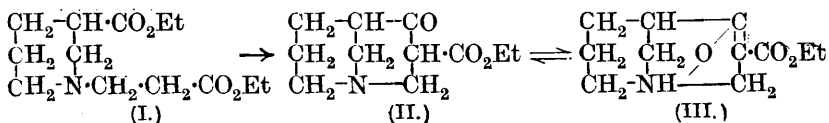
The action of phenylhydrazine on chloroacetyldiacetonitrile leads somewhat unexpectedly to the production of 5-chloromethyl-

1-phenyl-3-methylpyrazole-4-nitrile,  $PhN \begin{array}{c} \diagup N \\ \diagdown C(CH_2Cl) \cdot C \cdot CN \end{array} \begin{array}{c} = \\ = \\ = \\ \end{array} CMe$ , needles,

m. p. 130.5° after softening, which is also obtained from cyanoacetone phenylhydrazone and chloroacetyl chloride. It is hydrolysed to 5-hydroxymethyl-1-phenyl-3-methylpyrazole-4-carboxylic acid (cf. Benary, A., 1910, i, 434). Treatment with alcoholic potassium hydroxide solution transforms it into 5-ethoxymethyl-1-phenyl-3-methylpyrazole-4-nitrile, slender needles, m. p. 68.5°, which is unaffected by boiling, concentrated hydrochloric acid. The chloride is converted by methyl-alcoholic ammonia at 50—60° into 5-aminomethyl-1-phenyl-3-methylpyrazole-4-nitrile, long, colourless needles, m. p. 58—59° (picrate, pale yellow leaflets, m. p. about 250—251° [decomp.]) from which 5-hydroxymethyl-1-phenyl-3-methylpyrazole-4-nitrile, needles, m. p. 114—116°, is obtained by means of nitrous acid.

H. W.

**Synthesis of a New Bicyclic Nitrogen Ring. isoGranat-  
anine Derivatives.** Preparation of an Isomeride of Homococaine. S. M. McELVAIN and R. ADAMS (*J. Amer. Chem. Soc.*, 1923, 45, 2738—2750).—Ethyl nipecotinate (piperidine-3-carboxylate) on condensation with ethyl  $\beta$ -chloropropionate in alcoholic solution in the presence of silver oxide yields ethyl (3-carbethoxy-piperidino)-propionate (I), this being converted by sodium in xylene solution into ethyl isogranatonine carboxylate (II).



Reduction of the ketone converts it into ethyl granatolinecarboxylate, and benzoylation of the latter yields a compound isomeric with homococaine. It is a less efficient local anæsthetic than cocaine, and is considerably more toxic than the latter.

Nicotinic acid nitrate was obtained by adding nicotine to nitric acid ( $d$  1.42) and heating at  $100^\circ$  for several hours. The nitrate was converted into the hydrochloride by heating with hydrochloric acid, removing excess of the latter in a vacuum, dissolving the product in water, and precipitating with alcohol. Pure nicotinic acid was then obtained in the usual manner. Ethyl nicotinate was obtained by treating nicotinic acid (or its hydrochloride) successively with thionyl chloride and alcohol (excess of chloride being removed intermediately). Nipecotinic acid was prepared by the reduction of nicotinic acid hydrochloride with hydrogen in the presence of platinum oxide catalyst (cf. Freudenberg, A., 1919, i, 93). *Ethyl nipecotinate* is a colourless, water-soluble liquid, b. p.  $102-104^\circ/7$  mm.,  $d_{20}^{20}$  1.0121,  $n_D^{19}$  1.4592 (*hydrochloride*, needles, m. p.  $110-111^\circ$ ); it may also be obtained (less satisfactorily) by the catalytic reduction of ethyl nicotinate hydrochloride in alcoholic solution, and by the reduction of ethyl nicotinate in alcoholic acetic acid. *Ethyl (3-carbethoxypiperidino)acetate*, obtained from ethyl nipecotinate and ethyl chloroacetate in presence of finely powdered silver oxide, has b. p.  $147-149^\circ/5$  mm.,  $d_{20}^{20}$  1.0684,  $n_D^{18}$  1.4607. The free acid, obtained by hydrolysis of the ester or by condensing nipecotinic acid with chloroacetic acid in the presence of hydrochloric acid, forms white crystals, m. p.  $268-270^\circ$  (decomp.). *Ethyl (3-carbethoxypiperidino)propionate*, obtained similarly from ethyl nipecotinate and ethyl- $\beta$ -chloropropionate or from nipecotinic acid and  $\beta$ -chloropropionic acid, has b. p.  $159-161^\circ/5$  mm.,  $d_{20}^{20}$  1.0452,  $n_D^{18}$  1.4605. *Ethyl isogranatoninecarboxylate hydrochloride* forms white, microscopic crystals, m. p.  $187-189^\circ$ ; it is extremely soluble in water and gives a deep reddish-purple coloration with ferric chloride. The keto-ester hydrochloride can be obtained crystalline by adding dry ether to its alcoholic solution until a faint cloudiness appears and then cooling to about  $-12^\circ$ . *Ethyl isogranatoninecarboxylate* is a thick, colourless oil, b. p.  $137-139^\circ/8$  mm.,  $d_{20}^{20}$  1.1381,  $n_D^{18}$  1.5070; it gives a pronounced colour with acidified ferric chloride solutions. *Ethyl isogranatolinecarboxylate hydrochloride*, obtained by the reduction of the ketone with sodium amalgam in acid solution or by catalytic reduction in alcoholic solution in the presence of the platinum oxide catalyst, melts at  $199-201^\circ$ . An *isomeride* appears to be present in the mother-liquors left after crystallisation. The *benzoyl* derivative of the alcohol is obtained in the form of its hydrochloride as a white, crystalline powder.

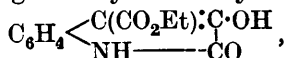
An ethereal solution of the crude keto-ester (II) gradually deposits crystals which from their solubility in organic solvents probably consist of compound (III). F. G. P.

### Pepper-substances. III. The Chavicine of Black Pepper.

II. E. OTT and O. LÜDEMANN (*Ber.*, 1924, 57, [B], 214-216).—Chavicine is purified by dissolution in benzene, addition of stannic

bromide, and precipitation of the additive compound (as a resinous mass) by means of ether. Analysis of the chavicine, regenerated after further dissolution in benzene and precipitation with ether, confirms the previous conclusion (Ott and Eichler, A., 1922, i, 1026) that it is stereoisomeric with piperine. Treatment of purified chavicine with alcoholic alkali hydroxide solutions yields unchanged material, isochavicine acid, and piperidine; wax alcohols and fatty acids are not produced as is the case when crude chavicine is employed. H. W.

**Ester Condensations with Ethyl o-Aminophenylacetate and Oxindole.** W. WISLICENUS and H. BUBECK (*Annalen*, 1924, 436, 113—124).—It was expected that by condensing ethyl o-aminophenylacetate (Neber, A., 1922, i, 545) with ethyl formate, indole-3-carboxylic acid would be formed, but actually the product was oxindole-3-aldehyde (Friedländer, A., 1910, i, 592). Ethyl oxalate with the amino ester gave ethyl 2 : 3-dihydroxycinchoninate,



together with a little oxindole-3-glyoxylic ester. Oxindole-3-aldehyde, obtained as above or from oxindole itself, forms yellow needles, m. p. 205—206°, and its anil has m. p. 254°. Oxindole-3-glyoxylic acid, the ester of which was obtained by condensing oxindole and ethyl oxalate, forms orange-yellow leaflets, m. p. 262—265° (decomp.); anilide, yellow leaflets, m. p. 261° (decomp.). The ethyl ester crystallises in orange needles, m. p. 187—188°, gives a green, crystalline copper salt, a benzoyl derivative (yellow needles, m. p. 160—161°), an anil (yellow prisms, m. p. 191—193°), and the corresponding compound with α-naphthylamine (m. p. 190°). Titration with bromine indicates that ethyl oxindole-3-glyoxylate exists solely in the enolic form. When treated with phenylhydrazine, it gives a mixture of the phenylhydrazide of the acid (needles, m. p. 238—239°) and the phenylhydrazone of the ester (yellow prisms, m. p. 160—164°), but at higher temperatures a substance, C<sub>16</sub>H<sub>11</sub>O<sub>2</sub>N<sub>3</sub>, crystallising in colourless needles, which decomposes at 265°. The phenylmethylhydrazone of the ethyl ester forms yellowish-brown prisms, m. p. 139°. Methyl oxindole-3-glyoxylate forms yellow needles, m. p. 167—169° (decomp.), and gives a phenylhydrazone, m. p. 197° (decomp.), which again gives the above compound, C<sub>16</sub>H<sub>11</sub>O<sub>2</sub>N<sub>3</sub>, when boiled with glacial acetic acid.

Ethyl 2 : 3-dihydroxycinchoninate forms needles, sintering about 210°, melting at 227—228°, and decomposing at 230°. It is a weak acid, giving crystalline ammonium and hydrazine salts. The acid forms white needles and decomposes without melting at 180°, giving 2 : 3-dihydroxyquinoline (Madelung, A., 1913, i, 92). Its anilide forms needles, m. p. 260° (decomp.). The benzoyl and acetyl derivatives of the ester (only the 3-hydroxy group reacted in each case) melt at 182—183° and 190°, respectively.

W. A. S.

[Tri-indolylmethanes and Aldehydes, Ketones, Ketonic Esters, and Keto-nitriles of Substituted Indoles.] H. FISCHER (*Ber.*, 1924, 57, [B], 356).—2-Methylindole-3-aldehyde (cf. Fischer and Pisbor, this vol., i, 86) has been obtained previously by Barger (*A.*, 1917, i, 476). H. W.

**Mechanism of Diazo Coupling Reactions. IV. Azo Dyes from 2-Methylenetrialkylindolines.** W. KÖNIG and J. MÜLLER (*Ber.*, 1924, 57, [B], 144—149; cf. *A.*, 1923, i, 862).—2-Methylene-1:3:3-trialkylindolines couple with diazonium salts to yield azo dyes whereby the alkyl group in position 1 is removed as the corresponding alcohol. The new compounds are of the general type,  $\begin{pmatrix} (\text{Alk})_2\text{C}:\text{CH}:\text{N}:\text{NAr} \\ \text{C}_6\text{H}_4-\text{NH} \end{pmatrix}$ , which becomes somewhat modified when a chromophoric group is present in the para-position in the diazonium component. The facility with which coupling occurs depends on the nature of the 3-alkyl groups.

The following compounds are described: 1:2:3:3-Tetramethylindoleninium bromide, pale yellow crystals, m. p. 252° (decomp.), and the corresponding perchlorate, long, colourless needles, m. p. 192° (decomp.). 2-Methyl-1:3:3-triethylindoleninium picrate, yellow needles, m. p. 180°, and the very hygroscopic chloride, slender, colourless needles, m. p. 131°. 1:2-Dimethyl-3:3-diethylindoleninium picrate, dark yellow needles, m. p. 167° (the corresponding chloride and perchlorate are extremely hygroscopic). 2:3:3-Trimethyl-1-ethylindoleninium perchlorate, needles, m. p. 197° (decomp.).

2-Benzeneazomethylene-3:3-dimethylindoline is isolated as the hydrochloride,  $\text{C}_{17}\text{H}_{18}\text{N}_3\text{Cl}$ , m. p. 186° (decomp.), by treatment of a solution of 1:2:3:3-tetramethylindolinium iodide (or bromide) with sodium hydroxide and addition of benzenediazonium chloride to the emulsion of the methylene base. 2-p-Nitrobenzeneazomethylene-3:3-dimethylindoline, prepared in a similar manner from 2-methylene-1:3:3-trimethylindoline or 2-methylene-1-ethyl-3:3-dimethylindoline, crystallises in reddish-brown leaflets, m. p. 168°; the corresponding hydrochloride, brownish-red needles, decomp. about 286°, the hydrobromide, brownish-red needles, decomp. 250°, and the acetate, leaflets, are described. 2:4'-Nitro-2'-methoxybenzeneazomethylene-3:3-dimethylindoline forms lustrous, steel-blue needles, m. p. 211° (hydrochloride [ $+\text{CH}_3\cdot\text{CO}_2\text{H}$ ], m. p. 128°, and subsequently decomp. about 290°). 2-p-Nitrobenzeneazomethylene-3:3-diethylindoline could not be caused to crystallise; the hydrochloride, brownish-yellow needles, has m. p. 280° (decomp.). 2-p-Acetylbenzeneazomethylene-3:3-dimethylindoline crystallises in lustrous, red needles, m. p. 191°; the hydrobromide forms reddish-brown needles, m. p. 264°. H. W.

**Supposed Syntheses from Ethyl Isatin-1-carboxylate.** A. HANTZSCH (*Ber.*, 1924, 57, [B], 195—199).—A criticism of the work of Heller (*A.*, 1918, i, 309). Heller's 2:3-dihydroxy-2:3-dihydroindole-2-carboxylic acid is shown to be formylisatoic acid,  $\text{CHO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , since its production from ethyl isatin-



1-carboxylate by the action of warm water or cold sulphuric acid (50%) is accompanied by that of acetaldehyde whilst, also, it is hydrolysed in alkaline solution to isatoic and formic acids; this conclusion is confirmed by the analysis of the ethyl ester, m. p. 67°. The supposed "lactone-like anhydride," m. p. 108°, is proved to be 1-formylisatin, since its optical properties are almost identical with those of 1-acetylisatin; attempts to prepare it directly from isatin and formic acid in the presence of dehydrating agents were, however, unsuccessful. Heller's 2:4-dihydroxy-1:2:3:4-tetrahydroquinoline-2-carboxylic acid is, in reality, formylanthranilic acid, which is transformed by acetic anhydride and sodium acetate into acetylanthranilic acid (Heller's hydroxydihydroquinoline-2-carboxylic acid, m. p. 184°). The observed formation of yellow solutions of the colourless formylisatoic acid in water and anhydrous solvents is due to the ready production of 1-formylisatin. H. W.

**Catalytic Hydrogenation of Pyridine.** N. ZELINSKY and P. BORISOFF (*Ber.*, 1924, 57, [B], 150—153).—Pyridine is very readily hydrogenated to piperidine in the presence of platinised asbestos (40%) at 150°. The catalyst does not become poisoned, since it retains its ability to cause the hydrogenation of benzene. At about 250°, it smoothly effects the dehydrogenation of piperidine, but, after use, it is no longer capable of bringing about the reduction of benzene or pyridine or the dehydrogenation of *cyclohexane*. Palladised asbestos is a still more effective agent for the hydrogenation of pyridine at 150°; after use, however, it is found to have lost all activity towards benzene. It readily causes the dehydrogenation of piperidine, but not of *cyclohexane* at 250°; after use, it is incapable of effecting hydrogenation.

The preparation of the highly active catalyst is effected in the following manner. Asbestos, which has been washed with acid and ignited, is soaked in a concentrated, faintly acid solution of platinum or palladium chloride at the temperature of boiling water and subsequently immersed in cold formaldehyde solution (35—40%). It is then treated with concentrated sodium hydroxide solution (40—50%), initially at 0° and finally on the water-bath. The product is washed thoroughly with water, immersed in dilute acetic acid solution, and again washed until the filtrate is neutral in reaction. It is dried for a short period at 110°. H. W.

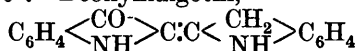
**Complex [Pyridine, Pyrazine, and Quinoxaline] Salts of Bivalent Iron.** H. LEY, C. SCHWARTE, and O. MÜNNICH.—(See ii, 228.)

**The Product of the Action of Acidic Reducing Agents on Indigotin.** W. MADELUNG and P. SIEGERT (*Ber.*, 1924, 57, [B], 222—233).—The reduction of indigotin in the presence of acids leads to the opening of the ring with formation of 2:2'-diamino- $\omega$ -styrylacetophenone.

The gradual addition of indigotin and finely-divided iron to an almost saturated solution of hydrogen chloride in alcohol leads to the separation of 2:2'-diamino- $\omega$ -styrylacetophenone hydrochloride,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{HCl}$ , pale brown

crystals; the corresponding *picrate*, *sulphate*, and *perchlorate* are described. The hydrochloride is converted by acetic anhydride in the presence of pyridine into the *acetyl* derivative,  $C_{20}H_{20}O_3N_2$ , colourless leaflets, m. p.  $181^\circ$  (the *perchlorate* is described). With formaldehyde and benzaldehyde, respectively, the base gives the *compounds*,  $C_{17}H_{16}ON_2$ , greenish-yellow crystals, and  $C_{23}H_{20}ON_2$ , slender, greenish-yellow crystals. The conversion of indigotin into 2:2'-diamino- $\omega$ -styrylacetophenone can be effected by ferrous chloride or by the addition of indigo-white to alcoholic hydrogen chloride, whereby disproportionation occurs accompanied by precipitation of indigotin.

2:2'-Diamino- $\omega$ -styrylacetophenone is very easily dehydrogenated. The hydrochloride is converted by solution in warm pyridine and exposure to air into 2-o-aminostyrylindoxyl,  $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{NH} \end{smallmatrix} > C:CH:CH \cdot C_6H_4 \cdot NH_2$ , small needles, m. p.  $161^\circ$ , which is readily oxidised further; it gives a *monoacetyl* derivative, decomp. above  $250^\circ$ . Deoxyindigotin,



(cf. Borsche and Meyer, A., 1922, i, 55), is also obtained by the action of air on solutions of 2:2'-diamino- $\omega$ -styrylacetophenone in pyridine and is the sole product of the action of alcoholic solutions of potassium hydroxide or sodium alkoxide on the base. The ultimate product of the dehydrogenation of 2:2'-diamino- $\omega$ -styrylacetophenone is the *substance*,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} > C:C < \begin{smallmatrix} \text{CH} \\ \text{NH} \end{smallmatrix} > C_6H_4$ ,

cocoa-brown, rhombic leaflets (*monoacetyl* derivative, pale yellow leaflets, decomp.  $245\text{--}250^\circ$ ). When its solution in pyridine is exposed to air for 3—4 days the dimeric *compound*,  $(C_{16}H_{10}ON_2)_2$ , separates in the form of dark violet-blue, slender needles. A second dimeric *compound*,  $(C_{16}H_{10}ON_2)_2$ , is obtained by the action of concentrated acids on a solution of the monomeric substance,  $C_{16}H_{10}ON_2$ ; the latter, which forms orange crystals, is immediately coloured green, probably owing to the formation of an unstable salt, and subsequently rapidly passes into the tile-red salt of the dimeride, which can also be obtained by dehydrogenation or disproportionation from the compounds  $C_{16}H_{16}ON_2$ ,  $C_{16}H_{14}ON_2$ , and  $C_{16}H_{12}ON_2$ . It has well-marked basic properties and gives sparingly soluble salts with mineral acids, the most characteristic of which is the *hydriodide*,  $C_{32}H_{20}O_2N_4 \cdot HI$ . The *diacetyl* derivative,  $C_{36}H_{24}O_4N_4$ , is a red, crystalline powder. When boiled with an alcoholic solution of formaldehyde, the base is converted into the *substance*,  $C_{33}H_{22}O_2N$  (orange-yellow crystals), whereas it is transformed by a boiling solution of sodium methoxide in methyl alcohol into the *compound*  $C_{32}H_{28}O_2N_4$ , canary-yellow, rhombic leaflets. H. W.

**Imines, Anils, and Hydrazones of Indigotin and the Stereochemical Configuration of the Indigoids.** W. MADE-LUNG and O. WILHELM (*Ber.*, 1924, 57, [B], 234—241).—The carbonyl and imino groups of indigotin are so indifferent towards

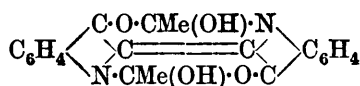
the usual reagents that their presence cannot be established in the customary manner. On the other hand, derivatives such as the oximes, phenylhydrazones, and azines can easily be prepared when di-iminoindigotin (Madelung, A., 1913, i, 904) is used as initial material; of these, indigotindioxime has already been described (Madelung, A., 1914, i, 738). The stability of indigotin suggests that there is an intimate connexion between the carbonyl and imino groups such as has been indicated by the constitutions proposed by Claasz (A., 1916, i, 840) and by Lifschitz and Lourié (A., 1917, i, 586). These formulæ do not, however, appear to be satisfactory, since they are valid only for indigotin itself, and cannot be extended to the derivatives of it which are now described; these are very closely related (optically) to indigotin. It is suggested that the oxygen atom of the carbonyl group is joined by a subsidiary valency either to the hydrogen atom of the imino group in the opposite half of the molecule, thus yielding a new six-membered ring, as has been proposed by Scholl (Georgievics, "Die Beziehungen zwischen Farbe u. Konstitution von Farbstoffen," 1920), or to the imino nitrogen atom, thus giving a new five-membered ring.

*Indigotinbisphenylhydrazone*,  $C_{16}H_{10}N_2 \cdot (N \cdot NPh)_2$ , red needles, m. p. 219—220° (decomp.), is prepared by the gradual addition of phenylhydrazine to a solution of di-iminoindigotin acetate in glacial acetic acid and subsequent treatment of the hot saturated solution of the product in alcohol with anhydrous potassium carbonate; it separates from acetic acid in green crystals (+2CH<sub>3</sub>·CO<sub>2</sub>H), m. p. 202—204°. The *hydrochloride*,  $C_{28}H_{22}N_6 \cdot HCl$ , green needles, and the *picrate*,  $C_{28}H_{22}N_6 \cdot 2C_6H_3O_7N_3$ , green needles, are described. In a similar manner, di-iminoindigotin acetate is converted by hydrazine hydrate into *indigotinazine acetate*,  $C_{16}H_{10}O_4 \cdot C_2H_4O_2$ , long, somewhat unstable needles, m. p. above 300° after previous change; the free base is too unstable to isolate. *Indigotindianilide acetate*,  $C_{28}H_{20}N_4 \cdot C_2H_4O_2$ , dark, bluish-green crystals, is obtained from di-iminoindigotin acetate, aniline, and glacial acetic acid in boiling alcoholic solution; when dissolved in xylene and treated with anhydrous sodium carbonate, it gives the corresponding free base (cf. Grandmougin and Dessoulavy, A., 1910, i, 73). *Dimethyl-iminoindigotin acetate*, prepared from di-iminoindigotin acetate and methylamine in boiling alcoholic solution, has m. p. 252—254°; the corresponding base crystallises in blue needles. The action of acetic anhydride on the imino acetate affords *diacetyl-iminoindigotin*, aggregates of dark blue needles, m. p. 202°.

*Indoleazobenzene*,  $C_{11}H_{11}N_3$ , yellowish-brown crystals, m. p. 133—134°, is prepared by the gradual addition of a methyl-alcoholic solution of indole to an alkaline solution of diazotised aniline. H. W.

**Alkyl and Acyl Derivatives of Leuco-indigotin and Indoxyl.** W. MADELUNG (*Ber.*, 1924, 57, [B], 241—252).—A study of the action of benzyl chloride on alkaline solutions of leuco-indigotin leads the author to the conclusion that, contrary to previous views, alkylation leads primarily to the production of *C*-substituted derivatives which readily undergo fission to substituted indoxyls. The

formation of two diacetyl-leuco-indigotins is very difficult to interpret; it is suggested that the acetyl groups are not present as such



but form a bridge between the hydroxy and imino groups as indicated in the annexed formula. The stereoisomerism

is due to the presence of two asymmetric carbon atoms in the two new rings (cf. Madelung and Hagen, A., 1916, i, 840).

[With O. HALLER.]—Indigo white is converted by methyl sulphate in the presence of sodium hydroxide into a dimethyl derivative, rhombic leaflets, m. p. above 235° (decomp.) after darkening at 200° (cf. Grandmougin, A., 1922, i, 470); it gives a *picrate*, dark violet needles, m. p. 173°, and is converted by nitrous acid in the presence of glacial acetic acid into indigotin.

*Monobenzyl-leuco-indigotin*,  $\text{C}_{23}\text{H}_{18}\text{O}_2\text{N}_2$ , ochre-yellow needles, m. p. 183°, is prepared by the action of benzyl chloride on leuco-indigotin at the ordinary temperature. When an excess of benzyl chloride is used under similar conditions, two isomeric *dibenzyl-leuco-indigotins* are formed. The main product, pale greenish-yellow crystals, m. p. 203°, resembles the dimethyl compound in yielding fluorescent solutions; it is unstable in hot solutions in the presence of acids. It is regarded as the *C*-dibenzyl compound,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C}(\text{CH}_2\text{Ph}) \cdot \text{C}(\text{CH}_2\text{Ph}) \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C}_6\text{H}_4$ . The second substance, colourless needles, m. p. 192°, is stable in organic media, but more sensitive towards permanganate than its isomeride; it is considered to be the dibenzyl ether of leuco-indigotin. The substance, m. p. 203°, is converted by boiling glacial acetic acid into benzyldeneindoxyl,  $\text{C}_{15}\text{H}_{11}\text{ON}$ .

When treated in alkaline solution with an excess of benzyl chloride at 70–80°, leuco-indigotin suffers fission and the primary products become further benzylated, whereby 2 : 2'-dibenzylindoxyl, yellow crystals, m. p. 174–175° (*nitroso* derivative, pale yellow, lustrous leaflets, m. p. 135°), and 2-benzylindoxyl benzyl ether, colourless, slender needles, m. p. 198–199°, are formed; the latter substance is readily oxidised by permanganate, but is stable towards nitrous acid.

1-Acetylinidoxyl gives a *phenylhydrazone*,  $\text{C}_{16}\text{H}_{15}\text{ON}_3$ , pale yellow needles, m. p. 154°, and an *oxime hydrochloride*,  $\text{C}_{10}\text{H}_{10}\text{O}_2\text{N}_2 \cdot \text{HCl}$ , colourless needles, m. p. 139°.

Indigotin is converted when heated with acetic anhydride, zinc dust, and acetyl chloride into a compound,  $\text{C}_{20}\text{H}_{14}\text{O}_3\text{N}_2$ , yellow needles, m. p. 209–210°, which is regarded as *diacetylanhydroleuco-indigotin*; the success of the preparation depends greatly on the purity of the materials and appears to be governed largely by experimental conditions.

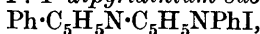
H. W.

**Spectroscopy of the Sulphonated Indigotins.** W. C. HOLMES (*J. Amer. Chem. Soc.*, 1924, 46, 208–214).—The absorption spectra of the pure potassium salts of sulphonated indigotin in the visible spectrum have been measured under various conditions. The absorption maxima of the potassium salts in aqueous solution were :



is almost exclusively produced if the solution is made alkaline from the commencement of the experiment. The action of iodine on 1:1'-diphenyltetrahydro-4:4'-dipyridyl proceeds in a complex manner, yielding 1:1'-diphenyl-4:4'-dipyridinium di-iodide, red prisms, m. p. about 360° (cf. König, A., 1923, i, 382); the corresponding perchlorate and picrate have m. p. 311° and 244°, respectively, whereas König (*loc. cit.*) gives m. p. 299° and 170°; 1-phenylpyridinium iodide, colourless, flattened prisms or anhydrous leaflets, m. p. 210° after darkening above 100°, is also produced, whilst about half the original material remains in the chloroform.

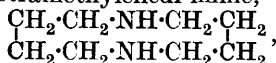
1:1'-Diphenyl-4:4'-dipyridinium,  $\text{Ph}\cdot\text{N}\cdot\text{C}_5\text{H}_4\text{N}\cdot\text{C}_5\text{H}_4\text{N}\cdot\text{Ph}$ , is most conveniently prepared by dissolving 1:1'-diphenyltetrahydro-4:4'-dipyridyl in a warm mixture of pyridine and methyl alcohol and preserving the mixture in a closed, half-filled flask for about a week; it separates from the solution in red, rhombic crystals with a vivid blue reflex, decomp. above 180°. It decomposes readily when exposed to air. It is converted by iodine in all solvents with the exception of benzene, primarily into the subiodide (below) and finally into the red di-iodide. The radical may also be prepared by the reduction of an aqueous solution of the di-iodide with zinc dust. 1:1'-Diphenyl-4:4'-dipyridinium subiodide,



is most conveniently prepared by mixing equivalent quantities of diphenyldipyridinium di-iodide and the corresponding leuco compound dissolved in acetone or chloroform; it crystallises in lustrous, steel-blue prisms, m. p. 318—319° (decomp.).

1:1'-Diphenyltetrahydro-4:4'-dipyridyl dissolved in chloroform is converted by a mixture of oxygen and carbon dioxide into 1:1'-diphenyl-4:4'-dipyridinium hydrogen subcarbonate, short prisms which appear violet by reflected, nearly black by transmitted light. The product is also obtained when a mixture of nitric oxide and carbon dioxide is used. H. W.

**Cyclic Di-imines and their Decomposition. III.** J. VON BRAUN, G. BLESSING, and F. ZOBEL (*Ber.*, 1924, 57, [B], 185—191; cf. A., 1923, i, 840).—The catalytic hydrogenation of  $\gamma$ -phenoxy-*n*-butyronitrile in amyl-alcoholic solution (cf. A., 1923, i, 1088) gives a mixture of  $\delta$ -phenoxybutylamine and di- $\delta$ -phenoxybutylamine; when subjected to slow distillation, the secondary base is transformed into phenol and *phenoxybutylpyrrolidine*, a colourless liquid, b. p. 170°/13 mm. (the hygroscopic *hydrochloride*, the *picrate*, yellow needles, m. p. 110°, and the *methiodide*, m. p. 123°, are described). It is converted by fuming hydrobromic acid at 100° into  $\delta$ -bromobutylpyrrolidine (identified as the *chloroplatinate*, m. p. 133—134° after softening at about 130°), which is readily transformed into dipyrrolidinium bromide (cf. von Braun, A., 1916, i, 631). The salt is slowly converted by concentrated ammonia at 170—180° into ditetramethylenedi-imine,



a colourless liquid, b. p.  $95^{\circ}/12$  mm.,  $d_4^{18}$  0.902; the hygroscopic *hydrochloride*, the *chloroplatinate*, yellowish-red crystals, decomp.  $207^{\circ}$ , the *picrate*, m. p.  $203$ — $204^{\circ}$ , the *benzenesulphonyl* compound, the *nitroso* derivative, the exceedingly hygroscopic *dimethiodide*, and the corresponding *chloride* and *chloroplatinate*, decomp.  $257^{\circ}$ , are described.

*Tetramethylenepentamethylenedi-imine*, a liquid, b. p.  $110$ — $112^{\circ}/14$  mm.,  $d_4^{17}$  0.920, is prepared similarly from the corresponding bromide; it yields a non-crystalline *benzenesulphonyl* derivative and *picrate*, a hygroscopic *hydrochloride*, a *chloroplatinate*, decomp.  $190^{\circ}$ , and a *di-methiodide*,  $C_{13}H_{30}N_2I_2$ , m. p.  $247^{\circ}$ , which is transformed through the *chloride* into the corresponding *chloroplatinate*, decomp.  $248^{\circ}$ .

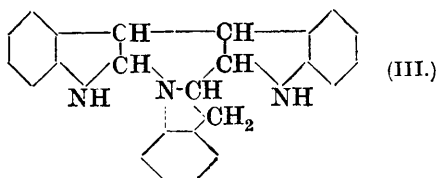
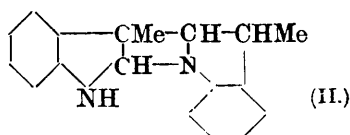
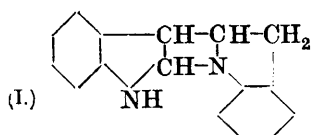
Treatment of dipiperidinium bromide with aqueous ammonia (cf. A., 1907, i, 151) leads to the isolation of very small yields of *dipentamethylenedi-imine* (*dipiperidine*), b. p.  $108$ — $110^{\circ}/12$  mm.,  $d_4^{17}$  0.9195. The non-crystalline *picrate* and *nitroso* derivative, the hygroscopic *hydrochloride*, and the *chloroplatinate*, an orange-coloured, crystalline powder, decomp.  $180^{\circ}$ , are described. The *dimethiodide*, m. p.  $272^{\circ}$  (decomp.), and the corresponding *chloroplatinate*, decomp.  $247^{\circ}$ , have been prepared.

H. W.

**Discatole.** B. ODDO and G. B. CRIPPA (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 31—34).—*Discatole*,  $C_{18}H_{18}N_2$ , obtained as hydrochloride by subjecting scatole, in anhydrous ethereal solution, to the action of a slow current of hydrogen chloride, forms white needles, m. p.  $130^{\circ}$ , and is free from the faecal odour of scatole itself. Its *hydrochloride*,  $C_{18}H_{18}N_2 \cdot HCl$ , forms microscopic, highly refractive, prismatic crystals, m. p.  $173^{\circ}$ ; its orange-red *picrate*,

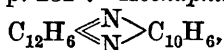
$C_{18}H_{18}N_2 \cdot C_6H_3O_7N_3$ , m. p.  $170^{\circ}$ , and its colourless *oxalate*,  $(C_{18}H_{18}N_2)_2 \cdot C_2H_2O_4$ , m. p.  $180^{\circ}$ , are described. It has not been found possible to obtain a triscatole.

These results, in conjunction with the facts that indole gives both a dimeride and a trimeride, that 2-methylindole undergoes no such polymerisation, and that any of these polymerides yields only a mono-hydrochloride, indicate for di-indole, discatole, and tri-indole the formulæ (I), (II), and (III), respectively:

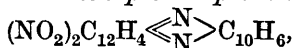


T. H. P.

**Dyes derived from Acenaphthenequinone.** A. C. SIRCAR and S. K. GUHA (*J. Chem. Soc.*, 1924, **125**, 335—340).—Azines produced by the condensation of acenaphthenequinone and of its 3:4-dinitro derivative with *o*-diamines, possess tinctorial properties not inferior to those of the corresponding derivatives of phenanthraquinone. Although insoluble in water, they can be used when freshly precipitated for dyeing wool. The azine sulphonic acids and azonium derivatives are also satisfactory dye-stuffs. The reduction products of the 3:4-dinitroazines have probably the diaminodihydroazine structure (cf. T., 1922, **121**, 1950). Attempts to prepare 3-nitroacenaphthenequinone by the method of Rowe and Davies (T., 1920, **117**, 1349) always yielded a product containing the dinitro derivative. The following substances are described *acenaphthatholazine*,  $C_{12}H_6 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} C_6H_3Me$ , light brown needles, m. p. 232°. *Acenaphthanaphthazine*,

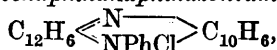


brownish-yellow needles, m. p. 290°. 3:4-Dinitroacenaphthatholazine,  $(NO_2)_2C_{12}H_4 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} C_6H_3Me$ , orange-yellow needles, m. p. not below 290°. 3:4-Dinitroacenaphthanaphthazine,

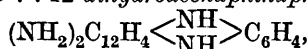


scarlet-red, shining needles, m. p. not below 290°. 3:4-Dinitroacenaphthaphenazine,  $(NO_2)_2C_{12}H_4 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} C_6H_4$ , orange-yellow plates, m. p. not below 290°. 3:4-Dinitroacenaphthaphenazinazine,  $(NO_2)_2C_{12}H_4 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} C_6H_2 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} C_6H_4$ , red, prismatic needles, no m. p.

*Acenaphthanaphthazine-5'-sulphonic acid*,  $C_{12}H_6 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} C_{10}H_5 \cdot SO_3H$ , microscopic, brownish-yellow needles, m. p. not below 300°. 3:4-Dinitroacenaphthaphenazine-5'-sulphonic acid, brown, amorphous precipitate. *Phenylacenaphthaphthazonium chloride*,



greenish-black powder, m. p. not below 290°. *Phenyl-3:4-dinitroacenaphthaphthazonium chloride*, similar, m. p. 270°. *Naphthylacenaphthaphenazonium chloride*, dull, black powder, m. p. not below 290°. 3:4-Diamino-7:12-dihydroacenaphthaphenazine,



orange-red prisms, m. p. (with sublimation) above 290°. 3:4-Diamino-7:12-dihydroacenaphthanaphthazine, scarlet-red, rectangular plates. 3:4-Dihydroxy-7:12-dihydroacenaphthaphenazine, brick-red powder, subliming above 290°. F. G. W.

**Action of Hydrazine on Uracil and Thymine.** R. FOSSE, A. HIEULLE, and L. W. BASS (*Compt. rend.*, 1924, **178**, 811—813).—Uracil reacts with hydrazine to give carbamide and pyrazolone,



the latter with xanthhydrol affording 1:2- or 1:4-*dixanthylpyrazolone*, colourless filaments, colouring at 195° and melting at 210—213° to a red liquid. Thymine, treated successively with hydrazine hydrate and xanthhydrol, affords *dixanthylcarbamide* and *dixanthyl-4-methylpyrazolone* (colourless crystals, m. p. about 202°), this substance also resulting by the action of xanthhydrol on the crude condensation product from hydrazine and ethyl formylpropionate.

E. E. T.

### Oxidation Products of Bilirubin. Detection of Urobilin.

A. ADLER.—(See ii, 280.)

**5-Nitrobarbituric Acids.** H. BILTZ and K. SEDLATSCHKE (*Ber.*, 1924, 57, [B], 339—349).—Violuric acid, decomp. 240—241° after darkening at 220° (cf. Biltz and Hamburger, A., 1916, i, 505) is converted by concentrated nitric acid into 5-nitrobarbituric acid, decomp. 180—181°, the yield being about 95% of that theoretically possible. The latter acid when suspended in ice-cold water and treated with chlorine yields *5-chloro-5-nitrobarbituric acid*,  $\text{CO} < \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} > \text{CCl} \cdot \text{NO}_2$ , colourless, slender needles, decomp. 86—87°, which is decomposed by warm water into nitrobarbituric acid, carbamide, and chloropicrin and by bleaching powder solution into chloropicrin and carbamide. *5-Bromo-5-nitrobarbituric acid*, long, slender needles, decomp. 108°, is decomposed by warm water in the same manner as the chloro compound. The position of the halogen atom in these acids is established by the observation that they are transformed by diazomethane into 5-halogeno-5-nitro-1:3-dimethylbarbituric acids (see later).

*5-Nitro-1-methylbarbituric acid*,  $\text{C}_5\text{H}_5\text{O}_5\text{N}_3 \cdot 2\text{H}_2\text{O}$ , colourless, slender needles, decomp. 142—143°, is prepared in 92% yield from methylvioluric acid; the *ammonium*, *potassium*, *sodium* (+ $\text{H}_2\text{O}$ ), and *barium* (+ $\text{H}_2\text{O}$ ) salts are described. The acid is remarkably stable towards solutions of alkali hydroxides. *5-Chloro-5-nitro-1-methylbarbituric acid*, colourless, hexagonal plates, decomp. 122—123°, is decomposed completely by boiling water into nitromethylbarbituric acid, methylcarbamide, chloropicrin, and carbon dioxide. *5-Bromo-5-nitro-1-methylbarbituric acid* forms colourless, four-sided prisms, m. p. 137—138°.

*5-Nitro-1:3-dimethylbarbituric acid*, small, colourless needles, decomp. 148—149° (the *sodium* and *potassium* salts are described), is converted into 5-chloro-5-nitro-1:3-dimethylbarbituric acid, decomp. 150°, and 5-bromo-5-nitro-1:3-dimethylbarbituric acid, decomp. 152°.

*5-Nitro-1-ethylbarbituric acid*,  $\text{C}_6\text{H}_7\text{O}_5\text{N}_3 \cdot \text{H}_2\text{O}$ , forms colourless needles, decomp. 132—133°; the *ammonium*, *potassium*, *sodium*, *calcium*, and *strontium* salts are described. *5-Chloro-5-nitro-1-ethylbarbituric acid* crystallises in colourless, rhombic leaflets, decomp. 127—128°. *5-Bromo-5-nitro-1-ethylbarbituric acid* is a heavy, microcrystalline powder, decomp. 138—139°.

*5-Nitro-1:3-diethylbarbituric acid*, colourless octahedra, decomp. 116—117°, is prepared from diethylvioluric acid; it may also be

obtained in poorer yield by the direct nitration of 1:3-diethylbarbituric acid, whereby diethylalloxan and tetraethylalloxantin are also produced; the *ammonium* salt, long, colourless needles, is described. 5-Chloro-5-nitro-1:3-diethylbarbituric acid, a heavy, crystalline precipitate, decomp.  $53^{\circ}$ , and 5-bromo-5-nitro-1:3-diethylbarbituric acid, a heavy, micro-crystalline powder, decomp.  $63-64^{\circ}$ , have been prepared.

Evidence is adduced against the existence of violantin and its alkyl derivatives. H. W.

#### Acetonylbarbituric Acid and some of its Derivatives.

A. W. DOX and B. HOUSTON (*J. Amer. Chem. Soc.*, 1924, **46**, 252—256).—The acetonyl group may be introduced directly at carbon atom 5 of barbituric acid by means of chloroacetone. Further substitution by halogen is readily effected, or by allyl, benzyl, and acetonyl. The less reactive alkyl halides, such as butyl bromide, do not react readily with acetonylbarbituric acid, but the acetonyl and alkyl groups may be introduced in the reverse order by treatment of the monoalkylbarbituric acid with chloroacetone. The acetonylalkylbarbituric acids are much less effective as hypnotics than the dialkylbarbituric acids with the same length of side chains.

It was not found possible to prepare ethyl acetonylmalonate from sodiomalonic ester and chloroacetone, but barbituric acid itself was alkylated readily in boiling aqueous solution.

Acetonylbarbituric acid forms flat, yellow crystals, m. p.  $238-240^{\circ}$  (decomp.); it liberates acetic acid from its salts. Halogenation yielded respectively acetonylbromobarbituric acid, white needles, decomp. about  $143^{\circ}$  without melting, and acetonylchlorobarbituric acid, white needles, which begin to decompose about  $175^{\circ}$  and melt about  $245^{\circ}$ . The following dialkylated acids were prepared by further treatment of acetonylbarbituric acid in the usual manner: diacetonylbarbituric acid, white needles, m. p.  $264-266^{\circ}$  (decomp.), acetonylallylbarbituric acid, large, white crystals, m. p.  $216-217^{\circ}$ , acetonylbenzylbarbituric acid, large, prismatic crystals, m. p.  $224-225^{\circ}$ ; acetonylethylbarbituric acid, flat, white crystals, m. p.  $238-239^{\circ}$ . F. A. M.

#### Velocity of Spontaneous Oxidation of Uric Acid in Alkaline

Solution. L. PIAUX (*Compt. rend.*, 1924, **178**, 637—640; cf. Biltz and Robl, A., 1920, i, 883, and More, this vol., i, 315).—An aqueous solution containing 5 mols. of potassium hydroxide to 1 mol. of uric acid rapidly absorbs oxygen; with a smaller porportion of base oxidation is less rapid. A considerable quantity of ammonia is formed. On acidifying, carbon dioxide is evolved, and addition of alcohol then causes the precipitation of potassium oxonate,  $C_4H_2O_4N_3K$ . The main reaction may be written thus:  $C_5H_4O_3N_4 + O_2 + H_2O = CO_2 + NH_3 + C_4H_3O_4N_3$ .

Since allantoin was not formed in these oxidation processes, the author examined the action of air (1) on an alkaline solution of potassium allantoate, and (2) on an alkaline solution of uric acid which had previously (by means of permanganate) been oxidised to the extent of 1 atom of oxygen. (Solution 2, according

to Biltz and others [*loc. cit.*] contains a substance which is oxidisable to an oxonate.) Neither (1) nor (2) absorbed oxygen.

E. E. T.

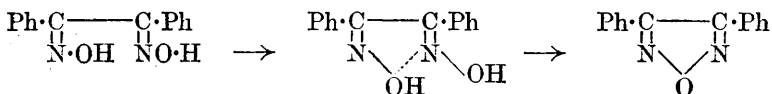
**Action of Catalysts on the Oxidation of Uric Acid. Iron and Manganese (Hydroxides).** L. PIAUX (*Compt. rend.*, 1924, 178, 782—785; cf. preceding abstract).—The aërial oxidation of uric acid (1 mol.) in potassium hydroxide (5 mols.) solution, is accelerated by traces of ferric hydroxide, potassium oxonate being formed. Manganese oxide hydrates (obtained by using manganese lactate) accelerate the initial aërial oxidation but diminish the amount of oxonate formed, none of the latter being obtained when 1 mol. of lactate is originally taken per 5.6 mols. of uric acid. Allantoin takes its place, and is formed from the intermediate compound described by Biltz and Behrend (cf. A., 1921, i, 893).

E. E. T.

**Ethylated Uric Acids.** H. BILTZ and K. SEDLATSCHKE (*Ber.*, 1924, 57, [B], 175—182).—The action of ethyl bromide on dipotassium urate in the presence of carbon tetrachloride at 110° leads to the production of moderate yields (12—13%) of 3 : 7 : 9-triethyluric acid, colourless aggregates of needles, m. p. 204°; the product is probably identical with the triethyluric acid obtained by Drygin in 1864 by the action of ethyl iodide on lead urate. The constitution of the acid is deduced from its oxidative degradation to *diethylalloxantin*,  $C_{12}H_{14}O_8N_4 \cdot H_2O$ , large, transparent crystals, m. p. 209°, and *1-ethylalloxan*,  $C_6H_6O_4N_2 \cdot H_2O$ , slender needles, m. p. 103° (decomp.); the latter substance is transformed by hydroxylamine hydrochloride into the previously described 1-ethylvioluric acid. Two of the ethyl groups of the triethyluric acid must therefore be present in the glyoxalone ring, that is, in positions 7 and 9, whilst the third must occupy position 3, since the alkylated compound is prepared from the solid potassium salt. As recorded by Drygin, when 3 : 7 : 9-triethyluric acid is warmed with concentrated hydrochloric acid, an ethyl group is eliminated as ethyl chloride and 3 : 7-diethyluric acid, slender, rhombic leaflets, m. p. 350—355°, is almost quantitatively produced; the same change occurs under the conditions of Zeisel's alkoxy determination. The presence of an ethyl group in position 3 is proved by oxidation of the acid to diethylalloxantin and ethylalloxan, m. p. 103°, whilst the second ethyl group necessarily occupies position 7, since fission of the acid with concentrated hydrochloric acid at 170° leads to the production of ethylglycine hydrochloride, which is identified by transforming it into 1-ethylhydantoin. 3 : 7 : 9-Triethyluric acid is readily converted by diazomethane in ethereal solution in the presence of a little water into 1-methyl-3 : 7 : 9-triethyluric acid, long, colourless needles, m. p. 104°. 1 : 3 : 7 : 9-Tetraethyluric acid, aggregates of slender needles, m. p. 82°, is prepared similarly with the aid of diazoethane. Treatment of the tetra-alkyl compounds with concentrated hydrochloric acid leads to the production of 1-methyl-3 : 7-diethyluric acid, feathery aggregates of needles, m. p.

257—258°, and 1 : 3 : 7-triethyluric acid, colourless needles, m. p. 218—219°. H. W.

**The Beckmann Transformation. II.** J. MEISENHEIMER and W. LAMPARTER (*Ber.*, 1924, **57**, [B], 276—282).—Reasons have previously been advanced (Meisenheimer, A., 1922, i, 152) in favour of a redistribution of formulæ among the benzildioximes whereby the  $\alpha$ -dioxime receives the *anti*-, the  $\beta$ -dioxime the *syn*-, and the  $\gamma$ -dioxime retains the *amphi*-configuration. The tendency of the dioximes to lose water has been examined by heating in evacuated tubes at 155°; under these conditions, the  $\alpha$ -dioxime is volatilised most slowly and with partial isomerisation to the  $\beta$ -dioxime; the latter sublimes more readily without undergoing decomposition, whereas only the  $\gamma$ -dioxime loses water and forms an anhydride; transformation into the  $\beta$ -dioxime accompanies the latter action and the formation of the anhydride ceases as soon as the isomerisation is complete. The behaviour of the oximes themselves is in harmony with that of their acetates, since the derivatives of the  $\alpha$ - and  $\beta$ -forms are hydrolysed by cold sodium hydroxide solution to the corresponding oximes, whereas the diacetate of the  $\gamma$ -variety yields the anhydride. The behaviour of the dibenzoates exactly resembles that of the diacetates. The observations necessitate a new conception of the mechanism of anhydride formation, that represented in the following scheme being suggested :



*Dibenzoyl- $\alpha$ -benzildioxime*, prepared from the  $\alpha$ -dioxime and benzoyl chloride in the presence of pyridine, crystallises in colourless needles, m. p. 220°; *dibenzoyl- $\beta$ -benzildioxime*, m. p. 157—158°, and *dibenzoyl- $\gamma$ -benzildioxime*, m. p. 135°, are described. *Benzoyl- $\alpha$ -benzilmonoxime*, m. p. 96°, is obtained from the  $\alpha$ -oxime and benzoic anhydride at 60—70°; it is reduced by zinc dust and glacial acetic acid to deoxybenzoin and, in this respect, it resembles the  $\alpha$ -oxime. It is therefore regarded as a simple derivative of the latter and not as *ON*-dibenzoylisobenzamide,  $\text{OBz} \cdot \text{CPh} \cdot \text{NBz}$  (cf. Werner and Piguet, A., 1905, i, 66; Meisenheimer, *loc. cit.*). *Acetyl- $\alpha$ -benzilmonoxime*, m. p. 67—68°, can be prepared from the  $\alpha$ -monoxime and acetyl chloride in pyridine solution.

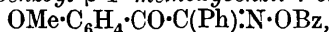
The conversion of diacetyl- $\beta$ -benzildioxime, m. p. 124—125°, when heated above its melting point into a product, m. p. 148°, is accompanied by very slight loss in weight. When hydrolysed by sodium hydroxide, the latter substance gives mainly  $\beta$ -benzildioxime mixed with traces of the anhydride; it is therefore regarded as a dimorphous form of the ordinary diacetyl- $\beta$ -benzildioxime containing small quantities of diacetyl- $\gamma$ -benzildioxime.

$\delta$ -Benzildioxime (cf. Atack and Whinyates, T., 1921, **119**, 1184) is shown (cf. Brady and Dunn, this vol., i, 292) to be a mixture of much  $\alpha$ - with little  $\beta$ -dioxime. H. W.

**The Beckmann Transformation. III.** J. MEISENHEIMER and H. LANGE (*Ber.*, 1924, **57**, [B], 282—289).—A continuation of previous work (Meisenheimer, A., 1922, i, 152).

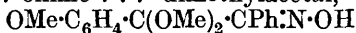
3 : 5-Diphenyl-4-p-anisylisooxazole,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{CPh} \cdot \text{O} \\ \text{CPh} \cdot \text{N} \end{smallmatrix}$ , m. p. 189°

(cf. Meisenheimer and Weibezahn, A., 1922, i, 176), prepared by the action of boiling sodium hydroxide solution on  $\alpha$ -nitro-4-methoxystilbene, is converted by ozone in the presence of carbon tetrachloride into *benzoyl- $\beta$ -4'-methoxybenzil-7-oxime*,



colourless, prismatic plates, m. p. 95.5—96.5°, the configuration of which is thus established. This compound is also produced by the benzoylation of the 4'-methoxybenzil-7-oxime obtained by Meisenheimer and Jochelson (A., 1907, i, 858) from  $\alpha$ -nitro-*p*-methoxystilbene; on hydrolysis, it gives the  $\beta$ -oxime and benzoic acid. The oxime is therefore the  $\beta$ -compound. This conclusion is confirmed by the observation that the oxime is converted by phosphorus pentachloride in the presence of ether into *anisoylformanilide*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO} \cdot \text{NH} \cdot \text{Ph}$ , slender, yellow needles, m. p. 106—107° (the synthesis of which from anisoylformic acid is described). *Acetyl- $\beta$ -4'-methoxybenzil-7-oxime*, obtained from the  $\beta$ -oxime and boiling acetic anhydride, forms coarse crystals, m. p. 85—86°.

*$\alpha$ -4'-Methoxybenzil-7-oxime*, slender, colourless needles, m. p. 87.5—89°, is prepared by the action of amyl nitrite and sodium ethoxide on *p*-methoxydeoxybenzoin or (better) by treatment of 4'-methoxybenzil-7-oxime-7 : 7'-dimethylacetal,

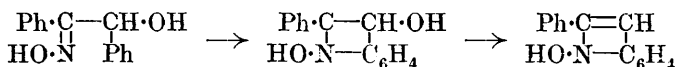


(cf. Meisenheimer and Jochelson, *loc. cit.*), with boiling glacial acetic acid. *Acetyl- $\alpha$ -4'-methoxybenzil-7-oxime*, prepared from the oxime and boiling acetic anhydride, forms coarse, colourless crystals, m. p. 133—134°. *Benzoyl- $\alpha$ -4'-methoxybenzil-7-oxime*, obtained by benzoylation of the parent substance in the presence of pyridine or from the  $\alpha$ -oxime and benzoic anhydride at 40—50°, crystallises in slender, colourless needles, m. p. 137.5—138.5°; it is converted by aqueous-alcoholic sodium hydroxide solution into benzonitrile and benzoic and anisic acids.  *$\alpha$ -4'-Methoxybenzil-7-oxime methyl ether*, colourless, transparent plates, m. p. 62—63°, is isomerised to the methyl ether of the  $\beta$ -oxime by protracted treatment with hot, concentrated hydrochloric acid.

The view of Meisenheimer and Heim (A., 1907, i, 858) that 4'-methoxybenzil-7-oxime-7' : 7'-dimethylacetal belongs to the  $\alpha$ -series is confirmed by the observations that its methyl ether and *benzoyl* derivative (colourless needles or prisms, m. p. 127—128° dependent on the rate of heating) are converted by glacial acetic acid into the  $\alpha$ -oxime or its derivatives, and that the oxime, when dissolved in glacial acetic acid and acetic anhydride, is converted by hydrogen chloride into benzonitrile and anisic acid. H. W.

**The Beckmann Transformation. IV.** J. MEISENHEIMER and H. MEIS (*Ber.*, 1924, **57**, [B], 289—297).—In connexion with

the new conception of the course of the Beckmann transformation (cf. Meisenheimer, A., 1922, i, 152), the behaviour of a number of ortho-substituted benzophenoneoximes has been examined. Although not conclusive in any case, the results generally favour the authors' views. The only case recorded in the literature in which the stereochemical configuration of an oxime is definitely established and harmonises with the older conception of the Beckmann transformation is that of benzoin- $\alpha$ -oxime, which, according to Fischer and Hütz (A., 1895, i, 371), is converted by concentrated sulphuric acid into a derivative of indole, whereas the  $\beta$ -oxime does not behave in this manner. Doubts as to the constitution of the product have been expressed by Fischer (A., 1896, i, 696), but the definite proof that it is not 2-phenylindoxyl is afforded by the synthesis of the latter (Kalb and Bayer, A., 1912, i, 727) and its non-identity with the product obtained by Fischer and Hütz. Loss of water from benzoin- $\alpha$ -oxime must therefore occur in accordance with the scheme :



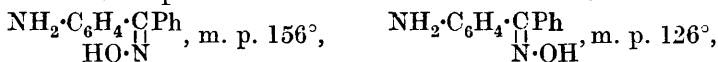
which necessitates a transposition of the configurations assigned previously to the  $\alpha$ - and  $\beta$ -oximes. The modified conception of the course of the reaction explains the inability of deoxybenzoinoxime or phenylacetaldoxime to give a derivative of indole and the conversion of methylbenzoinoxime and benzoinoxime into the same product. The observation that acetyl- $\beta$ -benzoinoxime can be oxidised to acetyl- $\beta$ -benziloxime establishes the relationship between the benzoin- and benzil-oximes, which are thereby brought into complete harmony with one another.

*o*-Benzoylbenzoic acid is converted by hydroxylamine into an oxime-anhydride,  $\begin{array}{c} \text{CPh} = \text{N} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \cdot \text{CO} \end{array} \text{O}$ , m. p. 163—164°, which is unaffected by the customary reagents of the Beckmann change but is converted by concentrated sulphuric acid into phthalanil, whereby the oximino oxygen atom changes place with the oppositely situated phenyl radical. *o*-Chloro- and *o*-bromo-benzophenone-oximes lose halogen acid when treated with concentrated sodium hydroxide solution and yield the compound  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CPh} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \right\rangle \text{N}$ , thus

rendering the configuration  $\begin{array}{c} \text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{Ph} \\ \parallel \\ \text{HO} \cdot \text{N} \end{array}$  probable. When treated with ether and phosphorus pentachloride they are converted into *o*-chloro- and *o*-bromo-benzanilide; benzoic *o*-chloro(*o*-bromo)-anilide is not produced, as would be expected from an oxime of the proposed configuration in accordance with the older view of the Beckmann transformation. For analogous reasons, the *syn*-configuration is assigned to the only known form of *o*-hydroxybenzophenoneoxime; it is converted by phosphorus pentachloride into salicylanilide accompanied by small amounts of anhydrobenzoyl-

*o*-aminophenol,  $\text{C}_6\text{H}_4\langle\text{O}\rangle\text{CPh}$ , which can be derived only from the stereoisomeric oxime.

*o*-Aminobenzophenoneoxime exists in two stereoisomeric forms,



the configurations of which are deduced from their behaviour when diazotised. The oxime of higher melting point is transformed by phosphorus pentachloride into the anilide of anthranilic acid, whereas crystalline products are not isolated from the isomeride of lower melting point.

2 : 4-Dimethylbenzophenone-2'-carboxylic acid gives only a single *oxime-anhydride*,  $\text{CO}\cdot\text{C}_6\text{H}_4\langle\text{O}\rangle\text{C}\cdot\text{C}_6\text{H}_3\text{Me}_2$ , cubic crystals, m. p.

133—134°, which is transformed by concentrated sulphuric acid into 1 : 2 : 4-xylydine and phthalic acid. *Methyl 2 : 4-dimethylbenzophenone-2'-carboxylate*, coarse, colourless crystals, m. p. 69—70°, b. p. 209—210°/10 mm., could not be caused to react with hydroxylamine.

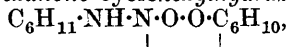
Mandelanilide is transformed by concentrated sulphuric acid at the ordinary temperature into *phenyloxindole*,  $\text{C}_6\text{H}_4\langle\text{N}\rangle\text{CHPh}\cdot\text{C}\cdot\text{OH}$ , colourless, cubic crystals, m. p. 185—187°, but the yields are poor in consequence of simultaneous sulphonation. Mandel-*p*-toluidide, on the other hand, is converted quantitatively into *5-methyl-3-phenyloxindole*, m. p. 211°. H. W.

***p*-Nitrobenzeneazopyrogallol (Chrome Brown P.A.).** P. JUILLARD (*Mon. Sci.*, 1924, **14**, 25—27).—An account of work already published (A., 1923, i, 1139). E. H. R.

**Symmetrical Dicyclohexylhydrazine and Related Compounds.** H. H. HARKINS and H. L. LOCHTE (*J. Amer. Chem. Soc.*, 1924, **46**, 450—455).—The authors have investigated the reduction of *cyclohexylideneazine* by Skita's method. In no experiment did they obtain the unsymmetrical *dicyclohexylhydrazine* described by Kijner and Beloff (A., 1911, i, 678).

*s*-Dicyclohexylhydrazine (*hydrazocyclohexane*) (*hydrochloride*, white needles, m. p. 271° [corr.]) is very unstable in air, and has m. p. 6—10°; b. p. 260—270°/740 mm.;  $d_4^{20}$  0.9384;  $n_D^{20}$  1.4888. The crystalline *oxalate* and unstable *nitroso* derivative are also described.

*Azocyclohexane*,  $\text{C}_6\text{H}_{11}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_{11}$ , from *dicyclohexylhydrazine* by oxidation with bromine water, forms straw-coloured needles, m. p. 34.5°. By hydrolysis of the azo compound with hydrochloric acid, *cyclohexylhydrazine* (Kijner, *loc. cit.*) is obtained; the thioureide has m. p. 148°, instead of 143° (Kijner); the *benzylidene* compound  $(\text{C}_6\text{H}_{11}\cdot\text{N}\cdot\text{N}\cdot\text{CHPh})_2\text{CHPh}$ , colourless needles, has m. p. 183° (corr.). *cycloHexanone cyclohexylhydrazone peroxide*,



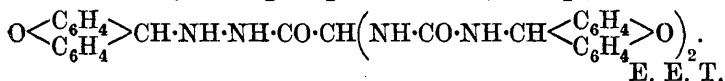
is formed by the interaction of equivalent amounts of *cyclohexyl*-

hydrazine and cyclohexanone. It crystallises in fine, white needles, m. p. 76° (decomp.), or when slowly heated, 74°. In contact with air it changes into an oil and a crystalline substance, m. p. 136—137°, neither of which has been identified. Attempts to obtain the free cyclohexanone cyclohexylhydrazone in the solid form failed.

Attempts to reduce dicyclohexyl nitrosoamine to as.-dicyclohexylhydrazine by Fischer's method were unsuccessful. A. B. S.

**Action of Hydrazine on Hydantoin and Allantoin.** R. FOSSE, P. HAGÈNE, and R. DUBOIS (*Compt. rend.*, 1924, **178**, 578—581).—Hydrazine hydrate converts hydantoin, at the ordinary temperature, into hydantoylhydrazide (A., 1923, i, 938). Hydantoylhydrazide affords sparingly soluble crystalline precipitates with aqueous solutions of benzaldehyde and anisaldehyde. *Benzylidenehydantoylhydrazide*,  $\text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , has m. p. 206—209° (decomp. and varying with rate of heating); *p*-methoxybenzylidenehydantoylhydrazide becomes coloured at 215—220° and melts at 220—227°, the temperatures varying with rate of heating.

Allantoin is converted by hydrazine into the monohydrate of allantoylhydrazide,  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2\cdot\text{H}_2\text{O}$ . The anhydrous hydrazide has m. p. 185° (decomp.). Allantoylhydrazide (1 mol.) condenses with xanthhydrol (3 mols.) to give a substance (annexed formula), having m. p. 223—225° (decomp.).



**Additive Products of the Phosphineimines.** M. MASRIERA (*Anal. Fís. Quím.*, 1924, **22**, 25—48; cf. this vol., i, 234).—A continuation of earlier work on the additive compounds derived from phosphineimines. Acetylphenylchloroamide gives with triphenylphosphine an additive compound, probably  $\text{Cl}\cdot\text{PPh}_3\cdot\text{NPhAc}$ , which is thought to be isomeric with the unstable compound formed from triphenylphosphinephenylimine and acetyl chloride. It is stable in air and forms white tablets having m. p. 109°. Triphenylphosphine and *p*-toluenesulphonophenylchloroamide gives a compound identical with that obtained from toluene-*p*-sulphonyl chloride and triphenylphosphinephenylimine. 2:4-Dichlorophenyl azide (obtained by the action of sodium nitrite and hydrochloric acid on 2:4-dichlorophenylhydrazine hydrochloride, white needles, m. p. 205—208° [decomp.]), forms yellow needles, m. p. 51°, and is explosive when dry. With triphenylphosphine in ethereal solution it affords triphenylphosphine-2:4-dichlorophenylimine,  $\text{PPh}_3\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Cl}_2$ , white tablets, m. p. 161°. The last substance is not basic and does not give an additive compound with toluene-*p*-sulphonyl chloride. Triphenylphosphine and *p*-toluenesulphone-2:4-dichlorophenylchloroamide give an unstable additive compound. Various methods for the *N*-chlorination of anilides are studied. G. W. R.

**Intensely Coloured Sodium Triphenylboryl, a remarkable Analogue of Sodium Triphenylmethyl.** E. KRAUSE (*Ber.*, 1924, **57**, [B], 216—217).—A preliminary communication. Ethereal



solutions of boron triphenyl (Krause and Nitsche, A., 1922, i, 694) become intensely coloured in the presence of sodium wire and ultimately deposit orange-yellow, prismatic crystals. The coloured solutions are immediately decolorised by oxygen. H. W.

**Organo-chromium Compounds. IV. Chromium Tetraphenyl Hydroxide.** F. HEIN and O. SCHWARTZKOPFF (*Ber.*, 1924, 57, [B], 8—14; cf. A., 1921, i, 826; 1922, i, 76, 77).—*Chromium tetraphenyl hydroxide*,  $\text{CrPh}_4 \cdot \text{OH} \cdot 3\text{H}_2\text{O}$ , is prepared by the action of silver oxide on chromium tetraphenyl iodide dissolved in moist chloroform or methyl alcohol, or by the electrolysis of a solution of the iodide in alcohol with a platinum or mercury cathode and rotating silver anode. It crystallises in orange leaflets, m. p. 104—105°, and resembles closely the corresponding pentaphenyl derivative. Measurements of its electrolytic conductivity in aqueous solution show that it is comparable with the alkali hydroxides in strength, whilst comparative experiments in methyl-alcoholic solution show it to be a stronger base than chromium pentaphenyl hydroxide. The base is converted into the corresponding iodide, bromide, and chloride, and into chromium tetraphenylchromitetrathiocyanatodiammine,  $\text{Ph}_4\text{Cr}[\text{Cr}(\text{CNS})_4(\text{NH}_3)_2]$ , which are identical with the compounds obtained previously (with elimination of a phenyl group) from chromium pentaphenyl hydroxide (cf. A., 1922, i, 76). *Chromium tetraphenyl hydrogen carbonate*,  $\text{CrPh}_4 \cdot \text{HCO}_3 \cdot 2\text{H}_2\text{O}$ , forms orange crystals, m. p. 110—111°. *Chromium tetraphenyl dianthranilate*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{CrH} \cdot \text{Ph}_4$ , orange needles, m. p. 145—146°, and the salt,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{CrHPh}_4 \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , m. p. 130°, are also described. H. W.

**Structure of Proteins.** E. ABDERHALDEN and W. STIX (*Z. physiol. Chem.*, 1923, 132, 238—250).—With the view of differentiating between dipeptides and the corresponding diketopiperazines the formyl and acetyl derivatives of these compounds have been investigated. *Diformylglycine anhydride* crystallises in rosettes, m. p. 112° (not sharp). A formyl derivative of leucylglycine anhydride could not be prepared. Diacetylglycine anhydride was obtained crystalline (cf. Franchimont and Friedmann, A., 1908, i, 509), also *diacetylglucylalanine anhydride* (m. p. 47°, not sharp) but the *acetyl* derivative of *leucylglycine anhydride* could be obtained only as a syrup. *Diacetyl-leucylglycine* was obtained as a yellow powder (m. p. 95°) by the action of acetyl chloride on the dipeptide. An attempt to prepare bisulphite derivatives of glycine anhydride and silk peptone was unsuccessful. By the reduction of glycine anhydride, alanylglycine anhydride, and leucylglycine anhydride with metallic sodium in ethyl or amyl alcohol, small yields of the corresponding piperazines were obtained. *Dibenzoylmethylpiperazine*,  $\text{C}_5\text{H}_{10}\text{N}_2\text{Bz}_2$  (crystallising in small plates), and *methylpiperazine dihydrochloride* were prepared from methylpiperazine obtained by reduction of alanylglycine anhydride. The

reduction of diacetylglycine anhydride, diacetylglycylalanine anhydride, and diacetyl-*dl*-leucylglycine anhydride yielded piperazines, whilst from *dl*-leucylglycine and glycyl-*d*-alanine subjected to the same reaction the unchanged compounds were obtained. On applying the method to silk peptone, a mixture of piperazines was obtained yielding crystalline picrates and platinum salts, but these were not further characterised. It is hoped to extend the method to decide whether or not diketopiperazines are present as such in the protein molecule. J. P.

**Effect of Ultra-violet Rays on Protein Solutions.** R. MOND (*Pflüger's Archiv*, 1923, **200**, 374—378; from *Chem. Zentr.*, 1924, i, 69; cf. A., 1923, i, 868).—Solutions of crystalline egg-albumin or serum-albumin having  $p_H$  greater than 4.6 are rendered more acid by ultra-violet radiation, whilst solutions with  $p_H$  less than 4.3 are rendered more alkaline. The acidity of suspensions of lecithin is appreciably increased. Sera subjected to radiation have no hæmolytic effect and no effect on an isolated frog's heart. It is supposed that radiation causes the development in sera of substances which exert a dilatory effect on the vascular system. G. W. R.

**New Sulphur-containing Amino-acid Isolated from the Hydrolytic Products of Protein. II. Sulphur Excretion after Ingestion.** J. H. MUELLER (*J. Biol. Chem.*, 1923, **58**, 373—375).—When the amino-acid  $C_5H_{11}O_2NS$  (cf. A., 1923, i, 869) is ingested by man, the sulphur which it contains is excreted in the urine in the form of inorganic sulphate. This is further evidence in favour of the view that the compound is a primary cleavage product of proteins. E. S.

**Lysolecithins and Lysocephalins. II. Isolation and Properties of Lysolecithins and Lysocephalins.** P. A. LEVENE, I. P. ROLF, and H. S. SIMMS (*J. Biol. Chem.*, 1924, **58**, 859—871; cf. A., 1923, i, 650).—The mixture of lysocephalin and lysolecithin, resulting from the action of cobra venom on egg yolk, has been separated by fractional crystallisation from chloroform and ether after precipitation with cadmium chloride. Lysocephalin has m. p.  $198^\circ$  (decomp.) and  $[\alpha]_D^{25} + 2.0^\circ$  in glacial acetic acid; lysolecithin, which is much more soluble in solvents, softens at about  $100^\circ$ , decomposes at  $263^\circ$ , and has  $[\alpha]_D^{20} - 2.6^\circ$  in chloroform, and  $[\alpha]_D^{25} + 0.8^\circ$  in glacial acetic acid. Hydrolysis yielded palmitic and stearic acids, whereas lysocephalin only yielded stearic acid. Dissociation constants were found, for lysolecithin  $K_1 = 0.18$ ,  $K_2 = 1.3 \times 10^{-12}$ , and the isoelectric range  $p_H 2.75$ — $9.90$ ; for lysocephalin  $K_1 = 3 \times 10^{-4}$ ,  $K_2 = 3.4 \times 10^{-10}$  and isoelectric range  $p_H 5.5$ — $7.5$ . The question as to which of these constants is the acid and which the basic one is discussed. The hæmolytic activity of lysolecithin was found to be three times that of lysocephalin. G. M. B.

**The Carbohydrate Group of Thymonucleic Acid.** H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1924, **132**, 297—300).—Thymonucleic acid on being hydrolysed and steam distilled yields a distillate which gives a red fuchsin-sulphite reaction, a green

coloration with pine shavings, a red coloration with aniline acetate, and with orcinol-hydrochloric acid an intense reddish-violet product soluble in amyl alcohol. The ethereal extract of the hydrolysate gives the same reactions. The reactions formerly regarded as being those of a glucal-like residue are therefore ascribed to a volatile, ether-soluble substance which is regarded as furfuraldehyde. No definite conclusions are drawn as to the nature of the sugar residue responsible for the furfuraldehyde reactions.

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J. P.

## Biochemistry.

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**Carbon Dioxide Absorption Curve of Human Blood. IV. Relation of the Hæmoglobin Content of Blood to the Form of the Carbon Dioxide Absorption Curve. V. The Construction of the  $\text{CO}_2$  Absorption Curve from One Observed Point. VI. The Relationship of the  $\text{CO}_2$  of Blood to that of Plasma.** J. P. PETERS, H. A. BULGER, and A. J. EISENMAN (*J. Biol. Chem.*, 1924, **58**, 747—768, 769—771, 773—791).—IV. From a number of determinations of the carbon dioxide content of blood and its “true” plasma at various values of  $P_{\text{CO}_2}$  (*ibid.*, 1923, **55**, 687, 709), the relation of the hæmoglobin content of human blood to the slope of the absorption curve has been studied. The assumption (Van Slyke, Hastings, and Neill, A., 1923, i, 163) that values of individual buffers occurring in a complex system such as blood, when measured by the ratio  $\Delta[\text{MHCO}_3]/\Delta P_{\text{H}}$  (Van Slyke, A., 1922, i, 893), can be considered as simple additive functions is shown to be unwarranted. Under the restricted conditions of the experiments recorded, the simple difference in the values of blood carbon dioxide content at  $P_{\text{CO}_2}$  60 and 30 mm. (written  $\Delta[\text{CO}_2]_{60-30}$ ) is a satisfactory and practical measure of buffer. From the scanty data available it seems possible that the buffer values of individual constituents, or at least the two main phases of the blood, when estimated as  $\Delta[\text{CO}_2]_{60-30}$ , may be considered as simple additive functions.

V. The determinants of the slope of the carbon dioxide absorption curve, other than the hæmoglobin concentration, have not yet been completely ascertained, but a method of calculation is now given which allows for this factor. In the relation  $\Delta[\text{CO}_2]_{60-30} = 0.334 \times (\text{oxygen capacity}) + 6.3$ , cell volume may be substituted for oxygen capacity by means of the further equation:  $(\text{oxygen capacity}) = 0.464 (\text{cell volume})$  where both are expressed in vols. %. By the use of these relations, together with the graphic logarithmic method previously described (A., 1923, i, 1249), it is possible to construct the absorption curve from any single point. The average deviation of  $\Delta[\text{CO}_2]_{60-30}$  from the mean in the experiments recorded is 0.5 vol. %.

VI. Determinations are recorded of oxygen capacity ( $h$ ), cell volume, and carbon dioxide content of whole blood  $[\text{CO}_2]_b$ , and of

the carbon dioxide content  $[\text{CO}_2]_p$  of the plasma at  $P_{\text{CO}_2}=40$  mm. on a number of specimens of blood, and on others at  $P_{\text{CO}_2}=30$  and 60 mm. The relation  $[\text{CO}_2]_p=[\text{CO}_2]_b+(0.0159[\text{CO}_2]_b-0.281)h$  is found to hold when  $P_{\text{CO}_2}=40$  mm. and allows of the calculation of the carbon dioxide content of plasma from that of whole blood. For tensions other than 40 mm., a slightly modified relation is used.

G. M. B.

**Rates of Reduction and Oxidation of Blood.** A. E. KOEHLER (*J. Biol. Chem.*, 1924, **58**, 813—830).—The rate of oxidation and reduction of blood was followed by comparison with fully oxygenated blood in a colorimeter so designed as to allow of rotation of the specimen in a stream of gas. The velocity of the reactions was found to be largely affected by the oxygen tension. An increase of  $p_{\text{H}}$  increases the rate of oxidation and depresses the rate of reduction, whilst a decrease of  $p_{\text{H}}$  has the opposite effects. The influence of carbon dioxide or lactic acid on the velocities is in accordance with the changes of  $p_{\text{H}}$  produced, there being no specific action of carbon dioxide. Certain ions such as  $\text{Na}^+$  modify the oxidation and reduction curves considerably.

G. M. B.

**Cholesterol and Bicarbonate Content of Blood in Experimental Kidney Diseases.** A. STASIEK (*Biochem. Z.*, 1924, **144**, 477—481).—Hypercholesterinæmia can be produced in dogs by inducing kidney disease by such drugs as cantharidine, uranium nitrate, and mercuric chloride. As the animals were fed during the experimental period on diets free from fat and cholesterol it may be assumed that the hypercholesterinæmia is of endogenous origin. Acidosis is not responsible for this metabolic derangement, since the bicarbonate content of the blood remains normal until after the manifestation of the hypercholesterinæmia. It is suggested that this condition is produced, not only because of the damage done to the cells of the kidney by the above agents, but also by the effect of these agents on the lipoids in other parts of the body.

S. S. Z.

**Amino-acid Content of the Blood in Normal and Pathological Conditions.** C. H. GREENE, K. SANDIFORD, and H. ROSS (*J. Biol. Chem.*, 1924, **58**, 845—857).—The amino-nitrogen content of blood as determined by the Folin method (which was found to be trustworthy in presence of an excess of urea) in cases of twenty different pathological conditions was similar to that in the blood of normal persons, namely, between 4.8 and 7.8 mg. per 100 c.c., with an average of 6.3 mg. The level of amino-nitrogen may be increased by flooding the organism with amino-acids during digestion or from the rapid autolysis of body-tissue, but otherwise deviation beyond the limits mentioned is rare.

G. M. B.

**Effect of Adrenaline on the Composition of Blood under Normal Conditions in Fasting, and in Avitaminosis.** D. ALPERN and J. A. COLLAZO (*Z. ges. exp. Med.*, 1923, **35**, 288—295; from *Chem. Zentr.*, 1924, i, 67—68).—Residual nitrogen, urea, sugar, and amino-acids in the blood of fasting dogs were found to be scarcely above normal. Values appreciably above the normal

were obtained with a diet poor in vitamins. The total ethereal extract of blood was depressed in fasting, but increased by a diet low in vitamins. Adrenaline hyperglycemia was less marked with low-vitamin diet than in fasting. This was the case even with a triple dose of adrenaline. In the case of fasting and normally-fed animals, the administration of adrenaline resulted in a decrease in the total ether extract and the total ethyl alcohol extract of the blood. With a diet poor in vitamins, on the other hand, increases in these values were observed. The adrenaline effect is related to the diminished power of oxidation and assimilation in the body-cells in avitaminosis.

G. W. R.

**Formation of Methæmoglobin.** W. LIPSCHITZ and J. WEBER (*Z. physiol. Chem.*, 1924, **132**, 251—274).—The influence of various aromatic and other compounds in converting the blood pigment into methæmoglobin has been investigated.  $\beta$ -Phenylhydroxylamine, hydrazobenzene, and arsenic hydride form methæmoglobin only in the presence of oxygen and have no action on reduced hæmoglobin. Dimethylaminophenyl ether, azo- and azoxy-benzene, and *p*-hydroxyazobenzene are without effect on hæmoglobin. Benzoquinone and its oximes are decreasingly active in forming methæmoglobin in the order given, but quinonechlorimine is five times as active as quinone. Hæmoglobin at 20° brings about a catalytic decomposition of hydroxylamine into nitrogen and ammonia which reaches a maximum when the reactants are present in the proportion 2 mols. of hydroxylamine : 1 mol. of hæmoglobin. Methæmoglobin catalyses the same reaction. Whilst hydroxylamine and  $\alpha$ -methylhydroxylamine convert both oxyhæmoglobin and reduced hæmoglobin into methæmoglobin,  $\beta$ -phenylhydroxylamine acts on oxyhæmoglobin only, and when present in excess converts methæmoglobin into reduced hæmoglobin. By treating reduced hæmoglobin with arsenic hydride followed by a little oxygen a pigment is obtained with a band at 608—625  $\mu\mu$ , which on further treatment with oxygen yields methæmoglobin. This is in agreement with the "nitrobenzenehæmoglobin" described by Filehne (*Arch. exper. Path.*, 1878, **9**, 329), and the latter supposed pigment is therefore regarded as unspecific.

J. P.

**Formation of Porphyrin from Blood Pigment. I. Spectroscopic Properties of Porphyrin Esters.** O. SCHUMM (*Z. physiol. Chem.*, 1924, **132**, 34—61).—By treatment of hæmoglobin free from oxygen, from blood corpuscles, with 25% hydrochloric acid, a porphyrin is formed. The same porphyrin is formed along with hæmatin if fuming hydrochloric acid is used. If, however, the hæmoglobin is treated with 1.3—2.6% of alcoholic hydrogen chloride, in the presence or in the absence of air, no formation of porphyrin occurs. A porphyrin, obtained from hæmatin by treatment with hydrazine hydrate, possesses properties and spectrum similar to those of the porphyrin obtained from hæmoglobin by the action of hydrochloric acid, but it has not been proved that they are identical. The spectroscopic properties of the methyl esters of urinoporphyrin

(Fischer), cotporphyrin, and of Nenki's hæmatoporphyrin are described.

W. O. K.

**Blood Pigment of *Arenicola*.** J. BARCROFT and H. BARCROFT (*Proc. Roy. Soc.*, 1924, **B**, 96, 28—42).—The blood pigment of *Arenicola* differs from human hæmoglobin in the following facts: (1) the  $\alpha$ -absorption bands of the oxy and carboxy compounds are displaced towards the violet end of the spectrum; (2) its affinity for oxygen is much greater, so that gaseous exchange can take place at pressures of oxygen between 2 and 3 mm.; (3) carbon monoxide has only 70 times the affinity for *Arenicola* hæmoglobin that oxygen has (as compared with 250 times for human hæmoglobin). The function of the pigment is probably to act as a reserve store of oxygen for those periods during which the animal has not access to sea-water.

C. R. H.

**Inorganic Bases and Phosphates in Relation to the Protein of Blood and other Body Fluids in Bright's Disease and in Heart Failure.** H. A. SALVESEN and G. C. LINDER (*J. Biol. Chem.*, 1923, **58**, 617—634).—Determinations have been made of the content of certain inorganic constituents (bases and phosphates) and of proteins in the blood plasma of patients suffering from Bright's disease. In the absence of uræmia, the content of calcium and of protein was found to run parallel. In uræmic cases, however, this parallelism was absent, a marked fall in the calcium content occurring with a protein content only slightly below normal; this effect is attributed to a great retention of phosphates in these cases.

From analyses of blood plasma and other body fluids in cases of heart failure, it appears that 55—70% of the serum calcium is diffusible. The non-diffusible calcium is probably bound to proteins.

E. S.

**Action of Peptone and of Nucleic Acids on the Coagulability of the Blood.** J. W. PICKERING and J. A. HEWITT (*Proc. Roy. Soc.*, 1924, **B**, 96, 77—94).—Intravascular injection of Witte's peptone inhibits coagulation of the blood in tortoises which have been deprived of hepatic activity, and, to a variable extent, in rats and dogs. Addition of peptone to shed blood delays its coagulation if the blood has not been in contact with damaged tissue. Such blood contains fibrinogen, and will clot on dilution with water or on prolonged exposure to air. Similar results are obtained with nucleic acids derived from thymus and yeast. In all cases the anti-coagulant effect is antagonised by the presence of increased amounts of carbon dioxide in the circulating blood; animals can be immunised against the nucleic acid effect by serial intravascular injections of protein-free nucleic acid preparations.

C. R. H.

**Equilibria involving Calcium, Hydrogen, Carbonate, Bicarbonate, and Phosphate Ions.** I. N. KUGELMASS and A. T. SHOHL.—(See ii, 235.)

**Physico-chemical Basis of Vital Permeability. IV.** R. BRINKMAN and A. VON SZENT-GYÖRGI.—(See ii, 235.)

**Relation between Calcium and Protein of Serum in Tetany due to Parathyroidectomy.** H. A. SALVESEN and G. C. LINDER (*J. Biol. Chem.*, 1923, **58**, 635—639).—The decrease in serum calcium in parathyroidectomised dogs is not accompanied by a decrease in plasma protein. Apparently, a parallelism between the decrease in calcium and protein (cf. preceding abstract) indicates a decrease in protein-bound calcium and does not lead to tetany, whereas a decrease in calcium without a corresponding decrease in protein (as in parathyroidectomy) indicates, primarily, a decrease in ionised calcium, which leads to tetany. E. S.

**Mechanism of Syphilitic Serological Reactions. The Protein Fractions of Human Blood Serum.** R. STERN (*Biochem. Z.*, 1924, **144**, 115—137).—A study has been made of the protein fractions of syphilitic and non-syphilitic sera. The so-called euglobulin fraction, comprising a small part of the water-insoluble globulin, has no significance for the typical serological reactions in syphilitic conditions. This is called "Labileglobulin." The separation from sera of a true euglobulin is described and this on peptisation in "Normosal" (Sächsischen Serumwerke) gives positive or negative Wassermann and Sachs-Georgi reactions according to the reaction of the original serum. The residual serum after removal of the euglobulin gives uniformly negative results, whether separated into its fractions or otherwise. The electrical charge of the euglobulin responsible for the specific reactions bears no relation to the positive or negative nature of the tests. Tannin solutions may convert negative into positive sera, and may themselves react positive to the Wassermann and Sachs-Georgi tests. It is tentatively suggested that the specific action of the euglobulin is due to dehydration in accord with the action of tannin in sensitising dyestuff sols. J. P.

**Physiology of Digestion. I. The Diastatic Power of the Mixed Saliva of Man, the Horse, Ox, Pig, and Dog, with Observations on the Complex Nature of Salivary Diastase. II. Fluctuations in the Diastatic Power of Mixed Saliva.** C. SCHWARZ and K. STEINMETZER (*Fermentforsch.*, 1924, **7**, 229—253).—I. For man the mean diastatic power (D) found was 1600, for the pig only 14. The saliva of the other animals contained no amylase. Amylase exists in the human salivary glands as an inactive proferment which becomes active upon secretion under the influence of the salts (possibly sodium chloride) of the saliva. II. The diastatic power of human saliva becomes constant in the fasting state. R. K. C.

**Physiology of Digestion. X. The Effect of Kristallose, Saccharin, and Parasaccharin on Salivary Diastase.** C. SCHWARZ and E. BUCHLMAN (*Fermentforsch.*, 1924, **7**, 282—300). **XI. The Effect of Kristallose, Saccharin, and Parasaccharin on Peptic and Tryptic Digestion.** C. SCHWARZ and V. ZELLINGER (*ibid.*, 301—306).—X. These substances have no effect on salivary diastase in concentrations up to 1%. Earlier results



to the contrary are due to failure to control the  $p_H$  of the tests. XI. In concentrations such as might be taken by man, these are without effect on protein digestion by pepsin or trypsin. ("Kristallose" is the sodium salt of saccharin.) R. K. C.

**Physiology of Digestion. VIII. Digestion in the Crop of the Fowl.** C. SCHWARZ and H. TELLER (*Fermentforsch.*, 1924, 7, 254—269).—The secretion of the crop is a yellow, viscid fluid generally acid to litmus but devoid of amylolytic or proteolytic activity. Lactic acid is generally to be found in the crop contents, but free hydrochloric acid is absent. Food remains many hours in the crop whilst it undergoes swelling (and some auto-fermentation) preparatory to digestion elsewhere. No absorption of water, salt, or dextrose by the mucous membrane of the crop was detected. R. K. C.

**Absorption of Lecithin.** F. EICHHOLTZ (*Biochem. Z.*, 1924, 144, 66—69).—Lecithin (Witte) fed to young dogs produced an increase in the alcohol-ether-soluble organic phosphorus compounds of the blood, but had no effect on the total fat. It is concluded that lecithin is assimilated as such and that its fatty acid residue is not built up into neutral fats. J. P.

**Digestion Experiments with the Raw White of Egg. II. The Digestibility of Unbeaten in Comparison with Beaten Whites.** M. S. ROSE and G. MACLEOD (*J. Biol. Chem.*, 1923, 58, 369—371; cf. *ibid.*, 1922, 50, 83).—In general, the digestion of beaten egg whites is somewhat more complete than that of unbeaten. The average coefficient of digestibility obtained for raw white of egg is 83%, and for cooked white of egg 86%. E. S.

**Effect of Reaction Changes upon Human Carbohydrate and Oxygen Metabolism.** J. B. S. HALDANE, V. B. WIGGLESWORTH, and C. E. WOODROW (*Proc. Roy. Soc.*, 1924, B, 96, 15—28).—In the alkalosis produced by forced breathing or by ingestion of sodium bicarbonate the preliminary activation of glucose, which is necessary before it can be metabolised, is inhibited, with resulting acetoneuria, and hyperglycæmia and glycosuria after less than half the normally tolerated dose of glucose.

The acidosis caused by breathing carbon dioxide has no effect on carbohydrate metabolism; after ingestion of ammonium chloride there is observed a lowering of sugar tolerance in the post-acidotic stage which is probably due to a failure of the glycogenic function of the liver.

Ingestion of sodium hydrogen carbonate causes an increase in the consumption of oxygen, the reverse effect being produced by ammonium chloride. C. R. H.

**Clinical Calorimetry. XXXIV. Ketosis and the Respiratory Exchange in Diabetes.** H. B. RICHARDSON and W. S. LADD (*J. Biol. Chem.*, 1924, 58, 931—968).—The fatty acid : glucose ratio, calculated from the data obtained by the calorimetric method previously described (Richardson and Mason, *ibid.*, 1923, 57, 587),

was found to be parallel to the excretion of acetone compounds. The threshold of ketosis was found at a ratio of about 1.5 to 1, which corresponds with the presence, during oxidation, of 1 mol. of keto-acid for every mol. of glucose. This parallelism is evidence that the respiratory quotient in diabetes is a true measure of oxidation. Diabetic patients were often able to take diets containing a larger proportion of ketogenic substances than is called for by the above-mentioned molecular ratio, which indicates that the proportions of foodstuffs oxidised were not the same as those ingested.

The fall of ketosis observed in diabetic patients, when fasting, is accounted for by the simultaneous drop in the fatty acid : glucose ratio calculated from the calorimetric data. It was due primarily to a decrease in the total metabolism with a consequent diminution in the metabolism of fat and protein.

During fasting there was little or no increase in the total quantity of glucose oxidised when this was computed as being derived from protein and the glycerol of the fat, as well as from the carbohydrate, undergoing metabolism. Fasting reduces the blood-sugar chiefly by depleting the endogenous sources of glucose. There is often an increase in the oxidation of glucose during the subsequent period of restricted diet, but this is not necessarily due to the fast.

G. M. B.

**Acetonæmia, especially in Avitaminosis.** M. HÄNDEL (*Biochem. Z.*, 1924, **144**, 258—264).—Using a micro method based on that of Bang, the acetone content of the blood of normal, starving, phloridzinised, depancreatized, and avitaminosed dogs, and of normal ox and human blood, has been determined. Avitaminosis leads to no increase in the acetone compounds of dog's blood. Normal human blood contains only traces of free acetone, 2 to 4 mg.% as acetoacetic acid, and 3 to 5 mg.% as  $\beta$ -hydroxybutyric acid. Acetonæmia is most marked in depancreatized dogs and in dogs which have been simultaneously starved and phloridzinised. J. P.

**Carbohydrate Metabolism. XXI. The Relation of Sugar Excretion to Renal Integrity.** F. P. UNDERHILL and G. WILENS (*J. Biol. Chem.*, 1923, **58**, 153—162).—Following experimental tartrate nephritis, the renal threshold for dextrose appears to be alternately raised and lowered. An injection of dextrose increases the hyperglycæmia.

E. S.

**Physiological Behaviour of Glucosan.** J. KERB. **Glucosan.** J. KERB and E. KERB-ETZDORF (*Biochem. Z.*, 1924, **144**, 60—63).—Arising from Grafe's treatment of diabetes with caramel (*Deutsch. Arch. f. klin. Med.*, 1914, **116**, 437) the physiological action of  $\alpha$ -glucosan, *l*-glucosan, and *lævulosan* is under investigation. The administration of  $\alpha$ -glucosan to diabetics and to depancreatized dogs does not produce a rise in blood-sugar. In one case of severe diabetes a slight decrease lasting for one hour was observed. J. P.

**Some Changes in the Composition of Blood due to the Injection of Insulin.** A. P. BRIGGS, I. KOECHIG, E. A. DOISY, and C. J. WEBER (*J. Biol. Chem.*, 1924, **58**, 721—729).—A series of

analyses of the blood of dogs after injection of insulin, show that the concentrations of glucose, inorganic phosphate, and potassium in the blood are thereby decreased. A parallel increase observed in the concentration of lactic acid present, is believed to be due to the influence of insulin on the reversible reaction :  $\text{glucose} \rightleftharpoons \text{lactic acid}$ .  
G. M. B.

**Insulin and Phloridzin Diabetes.** T. P. NASH, jun. (*J. Biol. Chem.*, 1923, **58**, 453—462).—The results reported are of a preliminary nature and appear to indicate that the administration of insulin to a phloridzinised dog does not cause a utilisation of sugar. E. S.

**Influence of Insulin on Phloridzin Diabetes.** M. RINGER (*J. Biol. Chem.*, 1923, **58**, 483—501).—Injection of insulin into completely phloridzinised dogs causes the oxidation of dextrose. At the same time, deposition of dextrose as glycogen takes place, the protein metabolism and the heat production are reduced, and the excretion of ketonic substances ceases. These results indicate that the effect of phloridzin is due to a transitory injury to the pancreas. It is suggested that, using phloridzinised dogs, insulin might be assayed in terms of the utilisation of dextrose. The maximum utilisation (oxidation) obtained in the present experiments was 0.95 g. of dextrose per unit of insulin.  
E. S.

**Effect of Alcoholic Pancreas Extract (Insulin) on the Behaviour of the Kidneys towards Dextrose.** S. VAN CREVELD and E. VAN DAM (*Nederl. Tijdschr. Geneeskunde*, 1923, **67**, II, 1498—1510; from *Chem. Zentr.*, 1924, i, 215).—From experiments on the perfusion of frog kidneys with dextrose solutions after administration of insulin it is concluded that the specific substance of insulin has a direct effect on the kidneys.  
G. W. R.

**What Substance in the Carbohydrate Metabolism is acted on by Insulin?** E. TOENNIESSEN (*Z. physiol. Chem.*, 1924, **133**, 158—164).—The author maintains that insulin acts on the lactic acid formed in the metabolism of carbohydrates in the animal organism, since all the previous stages in this metabolic process proceed normally in the absence of the pancreas. He was able to demonstrate that on adding lactic acid to minced pancreas there is no increase in the formation of acetaldehyde, but in the presence of pancreas and minced muscle the amount of acetaldehyde formed was double that formed by the control organs alone. Acetaldehyde was also formed on introducing insulin into normal and more so into diabetic blood. It is supposed to be derived from lactic acid.  
S. S. Z.

**Comparative Study of the Blood-sugar Concentration in the Liver Vein, the Leg Artery, and the Leg Vein during Insulin Action.** C. F. CORI, G. T. CORI, and H. L. GOLTZ (*J. Pharm. Exp. Ther.*, 1923, **22**, 355—373).—Determinations of the blood-sugar show that in the rabbit, starved for twenty-four hours, the concentration in the liver vein is on the average 28 mg.% higher than in the neck vein, and 23 mg.% higher than in the

femoral artery, whilst that in the femoral vein is 8 mg. % higher than that in the femoral vein. Under the influence of insulin, the first two figures tend to decrease and the last one to increase, so that there would appear to be diminished output of sugar by the liver, and increased uptake by the muscles.

W. O. K.

**Physiological Action of Insulin.** U. SAMMARTINO and D. LIOTTA (*Arch. Farm. Sperim.*, 1924, **23**, 13—46).—The authors discuss the question of glycaemia in relation to the action of insulin. The blood-sugar content of fasting rabbits following the injection of a unit dose of insulin falls below 0.045 mg. %, and is accompanied by hypoglycaemic convulsions and death. Even after death has been prevented by intravenous injection of dextrose (1 g. per kg. body weight), hypoglycaemia persists for 3—5 days. After repeated unit doses, recovery through injection of sugar is no longer possible. Administration of sucrose, or of dextrose in amount less than 1 g. per kg. body weight, does not prevent death from hypoglycaemia. Insulin also produces a fall in glycaemia in hyperglycaemia produced by adrenaline or lesion of the fourth ventricle. Hypoglycaemic coma and death are not prevented by administration of vaso-constrictive substances, such as ergotine and pituitary extract. Injection of insulin produces a lowering of blood pressure which cannot be neutralised by intravenous injection of sugar.

G. W. R.

**Glucokinin. III. An Apparent Synthesis in the Normal Animal of a Hypoglycaemia-producing Principle. Animal Passage of the Principle.** J. B. COLLIP (*J. Biol. Chem.*, 1923, **58**, 163—208).—The marked hypoglycaemia and other symptoms which are produced in normal rabbits by the injection of glucokinin (A., 1923, i, 1247) have also been observed after injection of guanidine sulphate or of overdoses of insulin, and after prolonged fasting; hypoglycaemia also occasionally occurs spontaneously, in which case *Coccidia oviforme* have been found in the liver. Transitory relief of the symptoms may be effected by injection of dextrose, but the death of the animal ultimately results. When defibrinated blood or serum from such hypoglycaemic rabbits is injected into normal rabbits, similar symptoms occur, animal passage (rabbit) of the hypoglycaemia-producing principle apparently being capable of indefinite extension. The principle is thermostable, undergoes dialysis, and is precipitated from blood by ammonium sulphate, but not by tungstic acid.

E. S.

**Aqueous Extracts of Pancreas. II. Physical and Chemical Behaviour of Insulin.** H. A. PIPER, R. S. ALLEN, and J. R. MURLIN (*J. Biol. Chem.*, 1923, **58**, 321—336).—Observations which have been made during the preparation of insulin lead to the conclusion that insulin is not a protein; it appears, however, to exist in the pancreas in combination with protein. The purest preparations of insulin are fairly stable and may be stored for 4 months without loss of potency; solutions may be heated at 80° for half an hour without marked destruction. Insulin

does not diffuse readily through parchment membranes; it is adsorbed by charcoal from acid but not from neutral solution.

E. S.

**Aqueous Extracts of Pancreas. III. Some Precipitation Reactions of Insulin.** C. P. KIMBALL and J. R. MURLIN (*J. Biol. Chem.*, 1923, **58**, 337—346).—In developing a method for the preparation of insulin from aqueous extracts of pancreas a large number of both organic and inorganic precipitants have been tested, but the majority have been rejected owing to the difficulty of removing them from the precipitate. Among the more successful precipitants are amyl alcohol and sodium chloride. The former is used in conjunction with ethyl alcohol. Four to five volumes of ethyl alcohol are added to the aqueous extract; the addition of amyl alcohol then causes the insulin to separate as a solid layer between the aqueous and the alcoholic layers. Acetone also precipitates the insulin but it has the disadvantage that it precipitates at the same time a substance, to which the name *glucagon* is given, which produces a distinct hyperglycæmic effect in animals; it may be removed from the precipitated insulin by extraction with 95% alcohol. Saturation of an aqueous extract with sodium chloride causes complete precipitation of the insulin. Sodium chloride has the advantage over ammonium sulphate that traces of it are not harmful to the organism, whereas the ammonium sulphate, if not completely removed from the precipitate, may cause a hyperglycæmic reaction.

E. S.

**Action of Ammonium Hydroxide and other Alkaline Compounds on Insulin.** E. J. WITZEMANN and L. LIVSHIS (*J. Biol. Chem.*, 1923, **58**, 463—474).—Treatment of insulin with 0.5 or 0.7*N*-ammonia or with 0.1*N*-sodium or potassium hydroxide for some days causes complete inactivation. When ammonia has been employed, the activity may be quickly restored by acidification with hydrochloric acid; inactivation by sodium or potassium hydroxide, however, is irreversible. Sodium carbonate and hydrogen carbonate and disodium hydrogen phosphate have scarcely any action on the activity of insulin. When insulin is treated with mixed alkalis the inactivation may be either accelerated or retarded according to the mixture employed. The effect of ammonia is regarded as indicating a tautomeric change in the molecule.

E. S.

**Chemical Reactions of the Substance containing Insulin.** H. A. SHONLE and J. H. WALDO (*J. Biol. Chem.*, 1924, **58**, 731—736).—A detailed chemical examination of an insulin preparation from the pancreas of hogs. Precipitation and other methods of purification failed to separate a physiologically active substance of constant ultimate composition. The preparation appeared to be a complex mixture of proteoses, and the active principle itself may either be a proteose or be intimately associated with a proteose fraction.

G. M. B.

**Adrenaline Secretion in Adrenaline Glycæmia.** P. TRENDELLENBURG (*Pflüger's Archiv*, 1923, 201, 39—55; from *Chem. Zentr.*, 1924, i, 212).—Decomposition of glycogen results from the administration of smaller amounts of adrenaline than has been previously supposed. Blood-sugar in rabbits was increased by continuous administration of 0.00006—0.0001 mg. of adrenaline per kg. live weight per minute. Glycosuria does not appear unless larger doses are given. The secretion of adrenaline by the suprarenal bodies after the production of adrenaline hyperglycæmia was found to be more than 0.0005 mg. per kg. live weight per minute, a rate of production sufficient to cause glycosuria within a short time. There is probably a direct nervous stimulation of the liver cells in addition to the chemical effect. G. W. R.

**Carbohydrate Metabolism of *Ascaris Megalocephala*.** A. FISCHER (*Biochem. Z.*, 1924, 144, 224—228).—In view of the fact that the acid formation in autolysis of *Ascaris megalcephala* is accounted for by the breakdown of glycogen to lactic acid and carbon dioxide, doubt is expressed regarding the conclusions of Weinland (*Z. Biol.*, 42, 43), who regarded the acidity as being due to valeric acid, and the carbohydrate metabolism of these worms as being abnormal. J. P.

**Fat Metabolism in Avitaminosis. V. Distribution of Fats and Lipoids in the Liver after Phosphorus Poisoning in Normal, Starving, and Avitaminosed Animals.** K. ASADA (*Biochem. Z.*, 1924, 144, 203—211).—A histological study of the distribution of neutral fat in the livers of normal, starved, and avitaminosed rats confirms the author's earlier observations (A., 1924, i, 122, 245), but as regards lipoids, the microscopical appearance of the phosphorus-poisoned avitaminosed liver is the same as that of the poisoned normal liver despite the increased cholesterol content of the former as revealed by chemical methods. The conclusions of Salvioli and Sacchetto (*Frankf. Z. Path.*, 1922, 28) regarding the effect of phosphorus poisoning on the fat and lipid content of the livers of normal and starving dogs are based on too short periods of starvation. J. P.

**Comparative Metabolism of certain Aromatic Acids. V. Fate of some Ring Substitution Products of Phenylacetic Acid in the Organisms of the Dog, Rabbit, and Man.** L. R. CERECEDO and C. P. SHERWIN (*J. Biol. Chem.*, 1923, 58, 215—224).—When fed to human beings, dogs, or rabbits, *o*-nitrophenylacetic acid, *o*-aminophenylacetic acid, *o*-hydroxyphenylacetic acid, *o*-chlorophenylacetic acid, and 2 : 4-dinitrophenylacetic acid were excreted unchanged with the following exceptions: *o*-aminophenylacetic acid, which was excreted by rabbits in an acetylated form, and *o*-chlorophenylacetic acid, which was conjugated with glycine both in man and in the dog and excreted as *o*-chlorophenaceturic acid. All the above acids were less toxic than phenylacetic acid. The results show that *o*-compounds are not readily oxidised in the organism and that they are not necessarily more toxic than the *m*- and *p*-isomerides.

*o*-Chlorophenaceturic acid, m. p. 135°, has been synthesised from glycine and *o*-chlorophenylacetyl chloride, b. p. 119—121°/12 mm. The latter substance was obtained by the action of phosphorus pentachloride on *o*-chlorophenylacetic acid. E. S.

**Detection of Pyruvic Acid in Muscle and Liver.** L. J. SIMON and E. AUBEL (*Compt. rend.*, 1924, 178, 657—659; cf. A., 1923, i, 875).—Pyruvic acid is not destroyed under aseptic conditions by macerated liver or fresh muscle. If injected as the sodium salt *in vivo* into the liver, it disappears, but not rapidly. Alanine, dextrose, and sodium lactate under similar conditions are not converted into detectable quantities of pyruvic acid. The latter, however, may possibly be produced in very small quantities, or undergo immediate conversion into other substances. E. E. T.

**Specific Dynamic Action of Proteins.** P. LIEBESNY (*Biochem. Z.*, 1924, 144, 308—350).—The specific dynamic action of proteins, following the ingestion of 200 g. of flesh and 100 g. of bread, reveals itself in an increase of 20—40% above the oxygen consumption shown in the resting and fasting condition, the maximum increase occurring in from 1 to 2½ hours after the meal. For any one individual, the specific dynamic action is constant under like conditions over a period of some months. It is diminished or entirely lacking in cases of affection of the hypophysis and in conditions involving disturbance of the autonomic nervous system. Administration of preparations of the anterior lobe of the pituitary gland produces an increase in the specific dynamic action. J. P.

**Adsorption of Amino-acids by Animal Tissues.** W. MOELLER (*Biochem. Z.*, 1924, 144, 152—158).—Hide powder adsorbs tyrosine from aqueous solution to the extent of 45% in 10 days. Importance is attached to the part played by such adsorption phenomena in the biosynthesis and hydrolysis of proteins. J. P.

**Arginine Metabolism.** K. FELIX and K. MORINAKA (*Z. physiol. Chem.*, 1924, 132, 152—166).—*dl*-Arginine, when passed through the liver of a cat, is hydrolysed fairly completely into ornithine and urea, both isomerides being attacked. Arginine, absorbed through the intestinal wall and then allowed to pass through the liver, is similarly hydrolysed by the liver. On the other hand, arginine in clupeon, which is built up of 2 mols. of arginine and 1 mol. of a monoamino-acid, is not hydrolysed by the liver. It would appear, therefore, that arginine, after absorption from the intestine, escapes complete destruction by the liver by being at least partly combined in the form of a polypeptide. W. O. K.

**Animal Calorimetry. XXIII. Influence of the Metabolism of the Nucleic Acids on Heat Production.** M. RINGER and D. RAPPORT (*J. Biol. Chem.*, 1923, 58, 475—482).—It is concluded from experiments on dogs that nucleic acids exert no specific dynamic effect. E. S.

**Metabolism of l-Pyrrolidonecarboxylic Acid and its Stability to Acids and Alkalis.** R. M. BETHKE and H. STEENBOCK (*J. Biol. Chem.*, 1923, **58**, 105—115).—When fed in large amounts to pigs maintained on a starch diet, pyrrolidonecarboxylic acid is partly metabolised and partly excreted unchanged. No increase occurs in the amino-nitrogen content of the urine, thus indicating that the hydrolysis of the acid is not sufficiently rapid to lead to the production of glutamic acid in amounts greater than those which the organism can deaminate. The acidity and alkalinity of the alimentary canal are insufficient to account for the hydrolysis.  
E. S.

**Effects of Iodides on Nitrogen Metabolism.** G. P. GRABFIELD, B. J. ALPERS, and A. M. PRENTISS (*J. Pharm. Exp. Ther.*, 1924, **22**, 393—400).—Administration of sodium or potassium iodides to man increases the output of nitrogen in the urine; the latter salt also increases the non-protein nitrogen of the blood.  
W. O. K.

**Effect of Reaction Changes on Human Inorganic Metabolism.** J. B. S. HALDANE, V. B. WIGGLESWORTH, and C. E. WOODROW (*Proc. Roy. Soc.*, 1924, **B**, **96**, 1—14).—The alkalosis of forced breathing produces a fall in the inorganic phosphate of the blood accompanied by a fall in the excretion in the urine; the reverse effects are observed in the acidosis caused by the breathing of carbon dioxide. The ingestion of sodium bicarbonate produces no effect. In the acidosis following ingestion of ammonium chloride there is a heavy excretion of phosphate in the urine which falls off with the exhaustion of the available store of phosphate in the body, the immediate cause of the falling off being the low concentration of phosphate in the blood. Ammonium chloride acidosis also causes the body to lose large amounts of water, sodium, and potassium.  
C. R. H.

**Acid-Base Metabolism. I. Determination of Base Balance.** A. T. SHOHL and A. SATO (*J. Biol. Chem.*, 1923, **58**, 235—255).—Analyses have been made of the food, urine, and faeces of four male infants less than 1 year old. For purposes of calculating the acid-base balance, only sodium, potassium, calcium, magnesium, sulphates, phosphates, and chlorides are considered. Sulphur and phosphorus contained in the food are regarded as acidic constituents to the extent that they are oxidised in the organism to sulphates and phosphates. The results show that there is a normal positive base balance equivalent to 10 c.c.  $\pm$  2 c.c. of 0.1N base per kg. per day. This balance is lowered by the addition of hydrochloric acid to the diet and raised by the addition of sodium hydrogen carbonate. The acid added to the food is excreted in the urine; the base, however, is excreted partly in the urine and partly in the faeces.  
E. S.

**Acid-Base Metabolism. II. Mineral Metabolism.** A. T. SHOHL and A. SATO (*J. Biol. Chem.*, 1923, **58**, 257—266).—Hydrochloric acid increases the excretion of ash, nitrogen, calcium, sodium, phosphorus, and chlorine in the urine of infants, and of ash,



nitrogen, calcium, magnesium, and chlorine in the fæces, and decreases that of phosphorus in the fæces; the excretion of potassium, magnesium, and sulphur in the urine and of sodium and potassium in the fæces is unaffected. The net result is a decreased retention of ash, nitrogen, calcium, magnesium, sodium, potassium, phosphorus, sulphur, and chlorine. Sodium hydrogen carbonate increases the excretion of ash, nitrogen, sodium, potassium, sulphur, and chlorine in the urine, and of ash, nitrogen, calcium, sodium, potassium, phosphorus, sulphur, and chlorine in the fæces; it decreases the calcium, magnesium, and phosphorus in the urine, and the magnesium in the fæces. In this case, the net result is an increased retention of magnesium and sodium and a decreased retention of ash, nitrogen, calcium, potassium, phosphorus, sulphur, and chlorine. E. S.

**Calcium Content of the Organs of Cats Treated with Calcium [Salts]. III and IV.** H. JUNGSMANN and M. SAMTER (*Biochem. Z.*, 1924, **144**, 265—269).—III. Determinations have been made of the distribution of calcium in the tissues of cats to which intravenous injections of calcium chloride and of calcium fructosephosphate had been given. After chloride administration the kidney showed a very high calcium content, and the lesser intestine, in contrast to that of normal animals, showed a uniform distribution of calcium along its entire length. Injection of calcium fructosephosphate, which has a more marked effect than has the chloride in increasing the calcium of the tissues generally, gave a notable increase in the calcium content of liver and kidney. IV. Intravenous injection of calcium chloride produces a greater increase in the calcium of the cat's kidney than does subcutaneous administration (cf. Heubner and Rona, A., 1923, i, 415). After intravenous injection of calcium fructosephosphate, the blood-serum and liver contain up to six times as much calcium as does the blood or liver of normal cats, or of cats given subcutaneous injections of calcium chloride. In acute calcium poisoning the calcium content of the skin may possibly be increased. Repeated injection of calcium acetate produces no alteration in the calcium content of the liver, heart, or other organs, nor does it affect the growth curves of the cats, as does subcutaneously administered calcium chloride (cf. Heubner and Rona, *loc. cit.*). J. P.

**Metabolism of Inorganic Salts. IV. The Content of Inorganic Salts in the Blood in Pregnancy, with Especial Reference to Calcium.** F. P. UNDERHILL and ALICE DIMICK (*J. Biol. Chem.*, 1923, **58**, 133—140).—In general, little change occurs in the inorganic constituents of the blood during pregnancy, although the calcium content (determined on whole blood) is somewhat higher for pregnant than for non-pregnant women. The calcium content does not vary in a regular manner with the course of pregnancy. These results give no support to the view that an increased calcium content of the blood is of significance in the induction of labour. E. S.

**Metabolism of Inorganic Salts. V. Inorganic Salt Metabolism in Cocaine Poisoning.** F. P. UNDERHILL and E. G. GROSS (*J. Biol. Chem.*, 1923, **58**, 141—146).—No change is produced in the inorganic constituents of the blood by cocaine poisoning. The relief afforded by the administration of calcium salts is due to their action as central nervous depressants. E. S.

**Absorption of Metallic Salts by Fish in their Natural Habitat. II. The Absorption of Nickel by *Fundulus Heteroclitus*.** A. THOMAS (*J. Biol. Chem.*, 1924, **58**, 671—674; cf. *ibid.*, 1912, **11**, 381).—Nickel salts are not toxic to the *Funduli* in sea-water, but are extremely so in fresh-water, death being preceded by signs of intoxication in the fish. A number of analyses are given showing the dependence of the nickel absorbed on the concentration of the solution and on the time of immersion.

G. M. B.

**Method of Determining the Biological Value of Protein.** H. H. MITCHELL (*J. Biol. Chem.*, 1924, **58**, 873—903).—Details of the experimental methods are given, by which trustworthy data are secured on the nitrogenous metabolism of rats. The “metabolic nitrogen” of the faeces is measured by the total excretion of faecal nitrogen on a nitrogen-free diet adjusted to have a “roughage” content approximately equal to that of the normal protein-containing diet. The excretion of nitrogen in the urine resulting from the catabolism of the tissues is not markedly depressed by protein feeding. The true basal catabolism of nitrogenous substances in the tissues is therefore measured by the total excretion of nitrogen in the urine in an adjacent period of feeding a nitrogen-free diet. This basal value is, however, subject to unexplained variations and must be redetermined at intervals in any long series of experiments.

The biological value of a protein is given by the percentage of the absorbed nitrogen (nitrogen intake—faecal nitrogen of dietary origin) that is not eliminated in the urine. This value for the protein of a food is practically a coefficient of digestibility applied to the total protein present, and by means of it a “net protein value” of the food may be calculated.

G. M. B.

**Biological Value of Proteins at Different Levels of Intake.** H. H. MITCHELL (*J. Biol. Chem.*, 1924, **58**, 905—922).—The biological values of the proteins (total nitrogen) of milk, maize, oats, rice, yeast, potatoes, navy beans, and the packing house by-product “tankage,” have been determined by a modified Thomas method (preceding abstract). In the case of maize, milk, oats, and potatoes, experiments were made with rations containing 5 and 10% of protein, and, except for potatoes, the biological values were smaller at the higher level; the reasons for this are discussed.

G. M. B.

**Supplementary Relations among Proteins.** H. H. MITCHELL (*J. Biol. Chem.*, 1924, **58**, 923—929).—If the biological value of the proteins in a mixture of two foods is found to be higher than that

calculated from the values for each food used separately, assuming the effect to be directly additive, this shows the existence of a supplementary relation between the proteins of the two foods in question. A considerable supplementary relation has been shown to exist between the proteins of maize and of milk, and between those of maize and of "tankage." No such relation could be detected between gelatin and the proteins of the oat kernel. G. M. B.

**Vitamins. I. Antineuritic Vitamins.** G. GAGLIO (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 479—482).—Many different substances are able to exert antineuritic properties, some of them removing all, and others only certain, of the symptoms of experimental polyneuritis in pigeons. Of all the materials which have been investigated, rabbits' urine produces the most complete and permanent antineuritic effects. Investigations are necessary to ascertain the action of different mixtures of the chemical compounds known to occur in urine or blood plasma when administered to pigeons in conjunction with polished rice. The known facts warrant the statement that the conception of a single specific antineuritic principle is not justifiable. T. H. P.

**Presence of Vitamin-A in Commercial Lecithin.** F. EICHHOLTZ (*Biochem. Z.*, 1924, **144**, 70—71).—From feeding experiments on white mice the presence of vitamin-A in lecithin (Witte) is inferred. J. P.

**Effect of Diet on the Content of Vitamin-B in the Liver.** T. B. OSBORNE and L. B. MENDEL (*J. Biol. Chem.*, 1923, **58**, 363—367).—When rats are maintained on a diet free from vitamin-B, the normal store of this factor in the liver is to a large extent depleted. E. S.

**Fat-soluble Vitamins. XV. Calcium and Phosphorus Relations to Growth and Composition of Blood and Bone with Varying Vitamin Intake.** R. M. BETHKE, H. STEENBOCK, and M. T. NELSON (*J. Biol. Chem.*, 1923, **58**, 71—103).—Normal calcification takes place in the bones of rats maintained on a diet otherwise deficient in fat-soluble vitamins when 20 c.c. of skimmed milk or 1 c.c. of whole milk per rat per day is added to the diet; with smaller additions, the calcification is poor.

The femurs and humeri of normal rats yield 45% of ash at the age of 24 days, 59% at 66 days, and 66% at maturity. The blood phosphates and calcium are slightly higher in young than in old animals.

A quantitative relation appears to exist between vitamin and calcium whereby poor assimilation of the latter due to deficiency of the former in the diet may be counteracted by increases in the calcium content of the diet. When, owing to lack of vitamin or of calcium salts, normal growth does not occur, there is a tendency for the calcium content of the blood and the ash content of the bones to suffer a diminution. Absence of fat-soluble vitamins from the diet depresses the calcium content of the blood, the depression being

increased by the addition of phosphates to the diet; radiation with ultra-violet light for 10 minutes per day increases both the calcium and phosphorus content of the blood. E. S.

**Influence of Diet on Teeth and Bones.** G. TOVERUD (*J. Biol. Chem.*, 1923, **58**, 583—600).—When guinea pigs are maintained on a diet deficient in antiscorbutic vitamin, both histological and chemical changes occur in the front teeth. The total ash and calcium content decrease whilst the magnesium content increases. White rats fed on a diet poor in calcium show a low calcium and a high magnesium retention and fail to breed normally. Their bones are low in total ash, calcium, and phosphorus, whilst the composition of their teeth is abnormal, the molars being low in total ash, slightly low in calcium and phosphorus, and slightly high in magnesium, and the front teeth low in all respects. Changes in the diet can thus produce chemical changes in a formed tooth. E. S.

**Effect of Hæmatoporphyrin on the Deposition of Calcium in the Bones of Rachitic Rats.** E. C. VAN LEERSUM (*J. Biol. Chem.*, 1924, **58**, 831—844).—Injection of hæmatoporphyrin causes a great increase in sensitiveness of the subject to rays of light lying within the visible part of the spectrum. The effect of such injections was therefore studied on rats in which, by a restricted diet, signs of rickets had been produced. X-Ray- and photomicrographs are given showing that under this treatment deposition of calcium was proceeding and the effects were similar to those of cod-liver oil or irradiation treatment. Direct proof of the influence of light has not yet been obtained. G. M. B.

**Dietary Requirements for Reproduction. I. Nutritive Value of Milk Proteins from the Point of View of Reproduction. II. Existence of a Specific Vitamin for Reproduction.** B. SURE (*J. Biol. Chem.*, 1924, **58**, 681—692, 693—709).—Rats fed on a complete artificial diet, with milk protein as a source of nitrogen, were found either to be sterile or to be unable to rear their young. Cod-liver oil was substituted for butter fat as a source of vitamin-A; vitamin-B, the antirachitic factor, and the necessary salts and iodine were provided. The further addition of casein, arachin, or edestin with 0.4% of cystine and in other experiments of lysine, proline, tyrosine, and tryptophane still failed to secure normal reproduction.

From these experiments and those of Evans and Bishop (*J. Metabol. Research*, 1922, **1**, 319, 335; 1923, **3**, 201, 233) it is concluded that there exists another hitherto unrecognised vitamin which is essential for reproduction. This factor has been found by breeding experiments to be present in Georgia velvet bean pod meal, polished rice, yellow corn, and rolled oats.

Accepting Macdonald's opinion that the "vitamin-D" of Funk and Dubin (*A.*, 1922, **i**, 203) is wrongly classified as a vitamin, the term "*D*" is proposed for the antirachitic factor of McCollum and others (*J. Biol. Chem.*, 1922, **53**, 293), and the term "*E*" is adopted for the new vitamin which affects reproduction. G. M. B.

**Chemical Changes in the Lipoids of Kidneys with Degenerated Cells.** P. SCHNAPP (*Z. physiol. Chem.*, 1924, **133**, 62—79).—By clamping the vascular system of the kidney degeneration is induced in the cells of this organ. The ethereal extract of such degenerated kidneys showed a lower total lipid content, a lower acidity (Spaltungszahl), and a lower iodine value than the normal kidney. On the other hand, the unsaponifiable and the saponifiable (Restzahl) residue showed an increase above the normal. S. S. Z.

**R. Engeland and W. Biehler's Article "Some Compounds Extracted from Human Skeletal Muscle"** (A., 1923, i, 72). J. A. SMORODINCEV (*Z. physiol. Chem.*, 1924, **132**, 328).—Attention is directed to the investigations by the author on the extractives of human and mammalian skeletal muscle (*Z. physiol. Chem.*, 1913, **87**, 12; 1914, **92**, 214; 1922, **123**, 116). J. P.

**Saccharophosphatase in Human Organs.** E. FORRAI (*Biochem. Z.*, 1924, **144**, 149—151; cf. A., 1922, i, 960; 1924, i, 120).—Saccharophosphatase is present in normal human pancreas and suprarenal bodies, but is absent from normal kidneys, testes, heart muscle, thyroids, skeletal muscle, and blood-serum. In cancerous conditions, it is found in certain organs (notably the liver) from which it is normally absent. J. P.

**State of Combination of Nucleic Acids in Cell Nuclei.** H. STEUDEL and T. TAKAHATA (*Z. physiol. Chem.*, 1924, **133**, 165—172).—The nucleic acid of yeast-cells is present in a free state and not in combination with protein. Nucleic acid was obtained from yeast by extraction with sodium chloride and precipitation with hydrochloric acid by Clarke and Schryver's method. S. S. Z.

**Biological Significance of Nucleic Acid Compounds.** E. HAMMARSTEN (*Biochem. Z.*, 1924, **144**, 383—465).—An important paper, in which the conductivity, hydrogen-ion concentration, osmotic pressure, and viscosity of thymus nucleic acid and its salts have been studied and discussed.

Thymonucleic acid is a strong polyphosphoric acid in which each of the four phosphorus atoms is associated with one dissociable hydrogen atom. Fresh thymonucleic acid dissolves to a concentration of about  $3 \times 10^{-3}M$ , yielding a turbid solution. It is supposed that the suspended particles causing the turbidity are due to the undissociated acid. From dialysis experiments carried out on the quadrivalent sodium salt of thymonucleic acid it is found that the salt possesses an apparent degree of dissociation of 0.25. The sodium salt of thymonucleic acid shows an osmotic pressure corresponding with that of the undissociated salt. On the other hand, when the acid is in combination with trimethyl-, triethyl-, or tripropyl-amine or with tetramethylammonium hydroxide, the osmotic pressure increases with the increase in volume of the cation. The sodium salt manifests the Donnan equilibrium in neutral solution. The relative viscosity of the sodium salt is very high, and it combines in dilute solutions with about 400 times its volume of water. Various agencies which lower the viscosity of its solution bring about an only

partly reversible gel formation, which is most probably due to a phase reversal. The relative viscosity of the sodium salt is reduced by kations even in concentrations of less than  $10^{-3}N$ . The valency of the kations is of importance. Strong acids reduce the relative viscosity of sodium thymonucleate; the maximum reduction is reached when two of the sodium atoms are replaced by hydrogen. The viscosity of protein-nucleic acid salts is raised by the addition of sodium chloride, probably because of the formation of the tetrasodium salt by double decomposition. The ampholyte salts of thymonucleic acid are hydrolysed during dialysis if the ampholyte is diffusible. Salts of thymonucleic acid and proteins with an isoelectric point of  $p_H$  4.7 exist as precipitates in equilibrium with the protein in hydrogen-ion concentrations approximating to the isoelectric point. When an excess of the sodium salt of thymonucleic acid is added, the protein salts dissolve in water at lower hydrogen-ion concentrations than  $3-3.5 \times 10^{-3}$ . Protein and thymonucleic acid combine in varying proportions. Proteins with an isoelectric point of  $p_H$  4.7 combine with thymonucleic acid during the first two stages of dissociation of the acid more readily than during the later stages of dissociation. Double decomposition takes place when the neutral salts of thymonucleic acid and diaminoacids are dialysed in the presence even of small quantities of sodium chloride with the formation of the sodium salt of the nucleic acid and the chloride of the diamino-acid. Histone compounds of thymonucleic acid are soluble in water when at least two of the sodium atoms of the salt and an equivalent of histone are in combination with 1 mol. of nucleic acid. The bearing of the above experimental observations on the biology of the cell is fully discussed, particularly with regard to the importance of the Donnan effect. S. S. Z.

**Carbohydrate Group of Thymonucleic Acid.** H. STEUDEL and E. PEISER.—(See i, 438.)

**Distribution of Pentose Compounds in the Pancreatic Tissues of the Ling Cod (*Ophiodon elongatus*, Girard).** C. BERKELEY (*J. Biol. Chem.*, 1923, **58**, 611—616).—Considerably more pentose is present in the islet than in the zymogenous tissue of the pancreas of the ling cod. It is suggested that it is produced from dextrose which has been activated by insulin.  
E. S.

**Nitrogenous Extractives from the Spleen.** S. DEMIANOWSKI (*Z. physiol. Chem.*, 1924, **132**, 109—153).—In spite of careful investigation of the phosphotungstic acid precipitate from the extract of the spleen of the freshly-killed ox, the presence of carnitine, methylguanidine, or of carnosine could not be detected. Tryptophan, approximately 0.0056% of the fresh horse spleen pulp, is extracted by water at 55—60°. Tryptophan is also extracted under similar conditions from the fresh spleens of oxen. Organic compounds other than tryptophan such as arginine, carnosine, tyrosine, or cystine are precipitated by Hopkins' reagent.  
W. O. K.

**Hydrogen-ion Concentrations within the Alimentary Tract of Insects.** W. J. CROZIER (*J. Gen. Physiol.*, 1924, 6, 289—293).—Larvæ of dipterous insects (*Psychoda* and *Chironomus*) were kept in solutions containing an indicator (bromophenol blue, phenol red, or neutral red), and then removed and dissected. The colours of the fluid in the various sections of the intestinal canal indicated that the  $p_H$  was approximately as follows: in the œsophagus, 7.1; the cardiac chamber, 6.2; the mesenteron, 7.5; and the hind-gut, 6.4. W. O. K.

**Behaviour of Calcium, Potassium, Chlorine, and Phosphorus in Milk and the Technique of Ultrafiltration.** C. WHA (*Biochem. Z.*, 1924, 144, 278—284).—Fifty % of the calcium of cow's milk is present in a colloidal non-diffusible form (cf. Rona and Michaelis, *ibid.*, 1909, 21, 114), but in the process of souring all the calcium becomes ionised and diffusible. Of the phosphorus in milk 60% is in a colloidal state, whilst all the potassium and chlorine present is diffusible (cf. György, this vol., i, 120). A vacuum dialyser of collodion is described. J. P.

**Influence of Phosphate and Bicarbonate on the Dissociation of Calcium Compounds in the Cerebro-spinal Fluid.** H. BEHRENDT (*Biochem. Z.*, 1924, 144, 72—80).—Using the method of Brinkman and van Dam, 20% of the total calcium (5 mg.%) of the cerebro-spinal fluid of children is found in the ionised condition at  $p_H$  7.6—7.7. Sodium hydrogen carbonate and sodium hydrogen phosphate solutions of the same  $p_H$  as the fluid markedly lower the calcium-ion concentration, the phosphate exerting an effect more than twice that of the carbonate. J. P.

**Ferments in the Amniotic Fluid.** K. MAEDA (*Biochem. Z.*, 1924, 144, 1—8).—The reaction of the amniotic fluid varies between  $p_H$  7.5 and 7.7. Diastase is present in the fluid in greater amount than in the blood from which it is derived. Lipase is sometimes present and originates from the foetal intestine. Pepsin, rennin, and thrombin (fibrin ferment) occur only in traces. Trypsin is absent. J. P.

**Urinary Excretion of Organic Acid and its Variation with Diet.** L. McLAUGHLIN and K. BLUNT (*J. Biol. Chem.*, 1923, 58, 267—284).—Determinations have been made by Van Slyke and Palmer's method (A., 1920, ii, 131) of the organic acid content of the urine of eight normal women. Under normal conditions, values (uncorrected for creatinine) equivalent to 6.8—10 c.c. of 0.1*N*-acid per kg. per day, which are similar to those obtained by Van Slyke and Palmer (A., 1920, i, 459) for men, were obtained. The amount excreted per hour by day (*i.e.*, during activity) was much greater than that by night. During fasting, the hourly excretion was equivalent to 15—24 c.c. of 0.1*N*-acid. This was markedly increased by diets rich in fruit or protein, but was only slightly affected by diets poor in these substances. One-third to one-half of the acids titrated by the above method consists of uric

acid, creatinine, creatine, and amino-acids. Diets which increase the organic acid excretion also increase that of uric acid. E. S.

**Creatinine Excretion of Women.** L. McLAUGHLIN and K. BLUNT (*J. Biol. Chem.*, 1923, 58, 285—290).—Determinations of the creatinine coefficients of eight normal women gave values (6.3—9.6 mg. of creatinine nitrogen per kg. per day) similar to those obtained by others for men. The higher values were obtained in the case of women who were below normal weight. There was no regular difference between the amounts excreted by day and those excreted by night. Creatine was almost invariably present in the day urine of one healthy woman. E. S.

**Excretion of Ammonia and Nitrogen.** R. S. HUBBARD (*J. Biol. Chem.*, 1924, 58, 711—719).—As the experiments of Marshall and Crane (A., 1923, i, 628) led to different conclusions from those drawn by Hubbard and Munford (A., 1923, i, 169) by a statistical examination of the results of analyses of human urine, a more extended series of figures has been obtained and examined as before. The results in general confirm the conclusions of Hubbard and Munford as to the excretion of ammonia by normal human subjects. G. M. B.

**Effect of Injections of Sodium Phosphates and Sodium Hippurate upon the Excretion of Acid and Ammonia by the Kidney.** B. M. HENDRIX and J. P. SANDERS (*J. Biol. Chem.*, 1923, 58, 503—513).—Injections of disodium hydrogen phosphate or of sodium hippurate in fasting dogs cause an increase in the titratable acidity and in the ammonia content of the urine, the sum of these increases being practically equivalent to the salts injected. The results obtained support the view of Nash and Benedict (A., 1922, i, 191) that a portion of the urinary ammonia is formed in the kidney, but it is suggested that part may have its origin in the intestine. The kidney can probably retain sodium from sodium salts of acids as strong as hippuric acid, but is unable to do so in the case of much stronger acids. E. S.

**Spontaneous Crystallisation of Uric Acid from Urine.** L.-C. MAILLARD (*Bull. Soc. Chim. biol.*, 1923, 5, 930—934).—It has been thought by some authors that uric acid is soluble in urine because it exists therein as a complex compound. The present author refers to an observation of his that uric acid crystallises spontaneously from urines which are markedly acid and show a high formol titration figure. He suggests that this may indicate that the compound mentioned above may be of the nature of an amino-acid complex. C. R. H.

**Natural Porphyrins. V. Coproporphyrin in the Urine and Serum in Normal and Pathological Conditions.** H. FISCHER and W. ZERWECK (*Z. physiol. Chem.*, 1924, 132, 12—33).—Urine (1000 parts) is made acid with acetic acid (3 parts) and extracted with ether (1000 parts). The ether is washed with water (20 parts) and extracted with 25% hydrochloric acid (3 parts)



and the solution observed spectroscopically. Coproporphyrin, if present, shows bands with centres at  $\lambda\lambda$  ca. 592, 548, and 491. To the acid solution, ether, sodium acetate, and sodium hydroxide solution are added so that the mixture is still acid with acetic acid. The ethereal solution is then washed, and if coproporphyrin is present, it shows bands at  $\lambda\lambda$  ca. 624, 567, 528. The coproporphyrin may be again extracted with acid and observed. Coproporphyrin has been found in the urine of normal individuals independently of whether their food has contained flesh or blood (cf. Schumm, A., 1923, i, 631, who found porphyrin present in normal subjects only after flesh or blood was consumed). From the united ethereal extracts, a solution containing cotporphyrin methyl ester, identified spectroscopically, was prepared. Coproporphyrin has been identified in the urine of guinea-pigs, in normal human serum, and in the serum of the horse, ox, and fowl. Investigations of the porphyrin in blood and urine in certain pathological conditions in man, as pernicious anæmia, hæmolytic icterus, and urobilinuria, are described.

W. O. K.

**Hæmatoporphyrin Congenita. IV. The Identification of Natural Porphyrins in Serous Fluids and in Organs.** O. SCHUMM (*Z. physiol. Chem.*, 1924, **132**, 62—71).—By means of spectroscopic observations, the presence of urinoporphyrin and of cotporphyrin has been detected in the pleural exudate from a patient suffering from hæmatoporphyrin congenita. Details are given of the methods to be followed in examining such fluids or organs for the presence of porphyrins.

W. O. K.

**Hæmatoporphyrin of Human Fæces.** A. PAPENDIECK (*Z. physiol. Chem.*, 1924, **133**, 97—99).—Polemical.

S. S. Z.

**Ether Extract of Fæces.** A. D. HOLMES and R. H. KERR (*J. Biol. Chem.*, 1923, **58**, 377—381).—Experiments made in connexion with the digestibility of edible fats indicate that the amount of unutilised fat excreted in the fæces in the form of soaps is insignificant. Further, the ethereal extract of the fæces appears to be of a uniform composition independent of the particular fat ingested.

E. S.

**Decolorisation of Ethereal Extracts.** J. MARKOFF (*Compt. rend. Soc. Biol.*, 1923, **89**, 113—115; from *Chem. Zentr.*, 1924, i, 80).—Directions are given for the use of phosphotungstic acid for decolorising ethereal extract of fæces. Preliminary removal of the ether by distillation is necessary.

G. W. R.

**Adsorption and the Distribution of Drugs in the Organism.** III. E. KEESER (*Biochem. Z.*, 1924, **144**, 536—544).—There is no parallelism between the adsorption capacity of charcoal for alkaloids and iodine *in vitro* and its detoxicating effect in the intestinal tract of the dog. The method by which a charcoal is prepared and not its origin is the determining factor of its adsorptive capacity. Strychnine nitrate is adsorbed more readily than morphine hydrochloride. In the presence of sodium bi-

carbonate, morphine hydrochloride and strychnine nitrate are adsorbed to a higher extent by charcoal. The electric charge changes in blood charcoal (Kahlbaum) at  $p_H$  3.5, in beech charcoal (Kahlbaum) at  $p_H$  6.6, in "carbovent" at  $p_H$  3.9. There is no change in the electric charge in bone charcoal (Kahlbaum), beech charcoal (Merck), and lime tree charcoal (Kahlbaum) at the investigated range of hydrogen-ion concentration. S. S. Z.

**Action of Different Substances, particularly the so-called Heart Remedies, on Disturbances of the Rhythm of the Heart.** W. SIMON (*Arch. Pharm. Exp. Ther.*, 1924, **100**, 307—315).—Only caffeine, calcium salts, human serum, and especially adrenaline, out of a large number of substances investigated, were able to relieve the disturbance of the rhythm of an isolated frog's heart, caused by cocaine or strychnine. W. O. K.

**Physico-chemical Technique for Detection of Polonium injected into Organs.** (MME.) J. S. LATTÈS and A. LACASSAGNE (*Compt. rend.*, 1924, **178**, 630—632; cf. this vol., i, 347).—The organ into which polonium has been injected is treated with potassium chlorate and hydrochloric acid until destroyed (fats, unaffected by this reagent, may then be separated mechanically); the solution obtained is boiled in presence of silver foil, and the polonium deposited on the latter determined by measuring its activity. This method is much more sensitive than the auto-histo-radiographic method, but obviously gives only the mean polonium content of an organ and not the distribution of that element. E. E. T.

**Influence of "Alkaloids" on Permeability.** W. HEUBNER (*Biochem. Z.*, 1924, **144**, 351—352).—The suggestion is made that the observations of Brinkmann and Szent-György (A., 1923, i, 974) on the action of morphine and codeine salts on the permeability of a collodion membrane to hæmoglobin, may have had their origin in the action of the anion; the work of Rhode (A., 1922, i, 1088) on the action of morphine chloride and codeine phosphate on hæmolytic is cited in this connexion. J. P.

**Vasodilatation by Amino-acids in Isolated Dog Kidneys.** H. FREDERICQ and L. BROUHA (*Compt. rend. Soc. Biol.*, 1923, **89**, 665—667; from *Chem. Zentr.*, 1924, i, 213).—Glycine, *l*-leucine, *d*-alanine, and *dl*-valine exert a vasodilatory effect in isolated dog kidneys, which is demonstrated by the increased flow of liquid from the renal vein and the ureter. The action of *dl*-phenylalanine is less definite. G. W. R.

**Effect of Amino-acids on Exchanges in Isolated Organs.** H. FREDERICQ and L. MÉLON (*Compt. rend. Soc. Biol.*, 1923, **89**, 668—669; from *Chem. Zentr.*, 1924, i, 213; cf. preceding abstract).—Isolated dog kidneys were perfused with Locke solutions containing 0.5% of different amino-acids. The first result was the production of an acid reaction, an effect not observed with Locke solution alone. *d*-Alanine and *l*-leucine cause an increase in

nitrogen titratable by formaldehyde in the liquid. Other compounds have no effect or depress the amount of nitrogen titratable by formaldehyde. G. W. R.

**Detection of Toluene in Organs and its Distribution in the Organism.** S. KURODA (*Biochem. Z.*, 1924, **144**, 287—293).—The toluene is distilled from a suspension of the organ in water and collected in carbon tetrachloride. It is nitrated, dissolved in water, made alkaline with sodium hydroxide, extracted with ether, and finally weighed. After toluene poisoning, the central nervous system of dogs and guinea pigs contains more toluene than the other organs, with the exception of the spleen, and the leucocytes of the blood are diminished. J. P.

**Effect of Chloroform and Phosphorus Poisoning on Carbohydrate Tolerance.** M. BODANSKY (*J. Biol. Chem.*, 1923, **58**, 515—522).—Experiments on dogs indicate that the lævulose tolerance test described in this paper is of great value in measuring the degree of liver injury during chloroform and phosphorus poisoning. Dextrose and galactose are not suitable for this purpose. E. S.

**Action of Hydrazine and some of its Derivatives in producing Liver Injury as measured by the Effect on Lævulose Tolerance.** M. BODANSKY (*J. Biol. Chem.*, 1924, **58**, 799—811).—The degree of liver injury produced in dogs by hydrazine and a number of derivatives have been determined by the lævulose tolerance test previously described (cf. preceding abstract), and the results confirmed by *post-mortem* examination. Hydrazine, phenylhydrazine, *s*-diisopropylhydrazine, and  $\beta\beta$ -azopropane ( $\text{CHMe}_2\text{N:N}\cdot\text{CHMe}_2$ ) are highly injurious to the liver, whereas methylphenylhydrazine, diphenylhydrazine, acetylphenylhydrazine, and *p*-hydrazinobenzoic acid have much less effect. G. M. B.

**Influence of Hydrazine on Blood Concentration and Blood-sugar Content.** F. P. UNDERHILL and S. KARELITZ, jun. (*J. Biol. Chem.*, 1923, **58**, 147—151).—The hypoglycæmia produced in dogs by the subcutaneous injection of hydrazine hydrate (cf. A., 1914, i, 632; 1915, i, 1037) is preceded by a transitory condition of hyperglycæmia; no sugar, however, appears in the urine. Hydrazine poisoning also causes a marked increase in blood concentration, which is ascribed both to the loss of fluid and to the inability of the animal to retain food or water; this effect probably contributes largely to the fatal results. There is no direct relationship between the degree of blood concentration and the extent of hypoglycæmia. E. S.

**Specificity of the Intracellular Hydrogenases in Frog's Muscle.** M. E. COLLETT (*J. Biol. Chem.*, 1924, **58**, 793—797).—The influence of certain protoplasmic poisons on the oxidation of citric and succinic acids by washed frog's muscle in presence of methylene-blue has been examined. The action is more readily inhibited by phenol and chloral hydrate in the case of the oxidation

of citric acid than in that of succinic acid : this order is reversed with poisons such as tellurites, selenites, selenates, and arsenates. The conclusion is drawn that there are two enzymes specific for the oxidation of citric and succinic acids, respectively.

G. M. B.

**Fungal Product,  $C_6H_6O_4$ , and its Behaviour on Hydration.** N. WIJCKMAN (*Z. physiol. Chem.*, 1924, **132**, 104—108).—When *Aspergillus* spp. are grown on a medium containing sucrose in quartz or paraffined glass flasks and the acidity of the medium is kept within certain limits, there regularly separate from the culture liquid crystals of a substance, which after sublimation under a low pressure melts at  $154^\circ$  and possess the formula  $C_6H_6O_4$  [copper salt,  $(C_6H_5O_4)_2Cu, H_2O$ ; acetyl compound,  $C_6H_4O_2(OAc)_2$ ]. On treatment with hydrogen in presence of a catalyst, a compound, m. p.  $80-90^\circ$ , b. p. ca.  $200^\circ/1$  mm., is obtained, which appears to be hydroglucal, although this has not been proved conclusively.

W. O. K.

**Simultaneity of Two Contradictory Toxic Effects (Immunity and Anaphylaxis) on the Same Cell.** C. RICHET, (MLLE.) E. BACHRACH, and H. CARDOT (*Compt. rend.*, 1924, **178**, 535—537).—The lactic acid bacillus, if cultivated in presence of copper sulphate (or of mercuric chloride) and potassium arsenate together, acquires simultaneously sensitivity towards the former and immunity towards the latter.

E. E. T.

**Diphtheria Toxin and Anatoxin. Flocculating Power and Immunising Properties.** G. RAMON (*Ann. Inst. Pasteur*, 1924, **38**, 1—10).—Antidiphtheria serum produces a flocculation when added to diphtheria toxin. The amount of antitoxin required to cause flocculation measures the toxicity of the toxin. When diphtheria toxin, to which formalin (3 or 4 parts per 1000) had been added to prevent bacterial contamination, was kept at  $40-42^\circ$ , it lost its toxicity, but retained its property of being flocculated by antitoxin. The anatoxin so produced retains also the immunising power, *in vivo*, of the original toxin, and its strength may be estimated by finding the amount of antitoxin required to cause flocculation, as this has been found experimentally to be proportional to its immunising effect.

W. O. K.

**Antiseptic Value of Hexamethylenetetramine *in vitro*.** A. DUTHOIT (*Compt. rend. Soc. Biol.*, 1923, **89**, 656—658; from *Chem. Zentr.*, 1924, i, 71).—With 2% hexamethylenetetramine in Ringer solution, paratyphoid and typhoid bacilli are completely killed in 4—7 days. *Bacillus coli* and pneumobacilli are not completely killed, even after 10 days. The antiseptic effect of hexamethylenetetramine does not reside in the formaldehyde group.

G. W. R.

**Antiseptic Effect of Hexamethylenetetramine.** A. DUTHOIT (*Compt. rend. Soc. Biol.*, 1923, **89**, 658—660; from *Chem. Zentr.*, 1924, i, 71; cf. preceding abstract).—Data are given for the bacteri-

cidal effect of the gall of dogs on different species of bacteria with and without preliminary injection of hexamethylenetetramine. It is found that hexamethylenetetramine is less effective as an anti-septic *in vivo* than *in vitro*.  
G. W. R.

**Effects of Electrolysis on Animal Tissue Enzymes. Abundance of Silicic Acid in the Ash.** F. MAIGNON (*Compt. rend.*, 1924, **178**, 654—657).—The enzymes from all body-tissues examined contained silica and calcium. Some tissue enzymes also contained characteristic quantities of phosphorus, arsenic, magnesium, and iron. Electrolysis of the enzyme preparations in aqueous solutions gave a coagulum at both anode and cathode with concomitant loss of therapeutic properties (cf. this vol., i, 350).

E. E. T.

**Rapid Analysis of Sugars. Purification and Concentration of Enzyme Solutions.** F. W. REYNOLDS (*Ind. Eng. Chem.*, 1924, **16**, 169—172).—Yeast extracts may be freed from colour and substances causing turbidity by dialysing or by washing on an ultra-filter and subsequently acidifying with acetic acid, whereby the substances causing turbidity are flocculated and can be removed by filtration through paper. Highly active preparations of invertase and melibiase may be obtained by concentrating crude or purified yeast extracts by ultra-filtration. A simple ultra-filter with a collodion membrane is described and illustrated. The impurities, especially those which are optically active, are largely eliminated and not concentrated with the enzyme. The activity of enzymes prepared by these means was about eight times that of the ordinary yeast extracts, and was such that sucrose solutions could be completely hydrolysed with their aid in 15 minutes at the ordinary temperature. Ultra-filtration should be useful as a means of concentrating other enzymes for use as analytical reagents and also in the study of the enzyme action of plant and fruit juices.

H. C. R.

**Purification of Toxins, Ferments, and other active Biological Organic Colloids.** L. MICHAELIS and H. DAVIDSOHN (*Biochem. Z.*, 1924, **144**, 294—297).—Details are given of the patented process (1912) used for purifying toxins, ferments, etc., by precipitation at the isoelectric point or at a definite hydrogen-ion concentration.

J. P.

**Mechanism of Alcoholic Fermentation. III.** A. LEBEDEV (*Z. physiol. Chem.*, 1924, **132**, 275—296).—Yeast incubated with sucrose in the presence of sodium sulphite and sodium or potassium dihydrogen phosphate, yields compounds the osazones of which (m. p. 202—209°) are free from phosphorus, but in the presence of these phosphates alone the osazones obtained (m. p. 143—152°) are those of phosphate esters differing from hexose biphosphate, whilst the presence of disodium or dipotassium hydrogen phosphates may or may not lead to the formation of a phosphate ester, the results varying with different yeast preparations. Whilst the analyses of the various phosphate esters has not yet been com-

pleted, it is apparent that it is possible to control, not only the amount, but also the nature of the hexose phosphate formed during yeast fermentation. The author supposes yeast fermentation to proceed in acid solution as follows: hexose  $\rightarrow$  two trioses  $\rightarrow$  glyceric acid  $\rightarrow$  pyruvic acid  $\rightarrow$  acetaldehyde  $\rightarrow$  alcohol  $\rightarrow$  carbon dioxide, whilst in neutral or alkaline solutions glycerol is formed along with glyceric acid and acetic acid accompanies alcohol. The formation of the four known hexose phosphates (including the new osazone-forming monophosphate described by the author) is correlated with the preliminary formation of glyceraldehyde, dihydroxyacetone, and the two corresponding monophosphates of these compounds. In accord with the author's views the presence of nine individual enzymes in the zymase complex is postulated. J. P.

**Influence of Amines on Fermentation. II.** J. ORIENT (*Biochem. Z.*, 1924, **144**, 353—360).—The effect of various alkylamines and their salts, glucosamine and its hydrochloride, diamines, and indole derivatives on yeast fermentation has been investigated. In general the salts of amines and diamines increase, whilst the free bases diminish fermentation. Indole has a slight inhibiting action, whilst scatole has the reverse effect (cf. A., 1923, i, 171). J. P.

**Action of Drugs containing Hydroxymethylanthraquinones on Fermentation.** J. ORIENT (*Biochem. Z.*, 1924, **144**, 361—365).—The action of various pharmacological preparations of *Rheum*, *Aloe*, *Senna*, *Cascara*, *Frangula*, *Cassia*, *Jalappa*, and *Colocynthis* on yeast fermentation has been investigated. In general fermentative action is increased, more especially by the rhubarb group rich in hydroxytrimethylanthraquinone. J. P.

**Fermentation with Non-ferments.** W. BIEDERMANN (*Z. angew. Chem.*, 1924, **37**, 71—73).—If a solution containing diastase (e.g., saliva or a solution of saliva albumose) is heated, a turbidity appears at 70—80°, owing to partial coagulation of the "zymogen," and the diastatic power is considerably diminished; it does not, however, disappear even by heating the solution to boiling, and may be considerable in the presence of oxygen. This regeneration by means of air is further enhanced by the presence of the above coagulate. A solution of saliva ash, or even simple salt solutions (particularly sodium chloride), can produce a slow degradation of amylose to sugar, although here again thorough aëration is necessary. The activity of the salts is increased, not only by the specific protein, but also by the inactive degradation products, the presence of amino-acids (e.g., glycine, leucine) being found advantageous. It appears that the organic ferment, and not the inorganic substance, should be regarded as the activator. Treatment of fibrin with steam yields solutions which, after addition of sodium chloride or a suitable phosphate mixture, are capable of fermenting amylose, if an adequate supply of air is maintained. By employing very dilute ferment solutions amylose can be converted into dextrin alone, without a simultaneous production of sugar. It may,

finally, be said that, below a certain dilution, small quantities of saliva diastase have exactly the same action as the "complementary" inorganic salts alone, provided the latter are in a corresponding concentration. W. T. K. B.

**Comparison of the Action of Acids and Enzymes in Hydrolytic Phenomena.** H. COLIN and A. CHAUDUN (*J. Chim. physique*, 1923, 20, 471—483).—The hydrolysis of sucrose by diastase is considered theoretically and it is shown that the velocity of the reaction does not increase with the concentration of the sucrose ( $a$ ) nor with the concentration of the diastase ( $n$ ), but rather with the ratio of these concentrations,  $a/n$ . The condition under which the reaction follows Wilhelmy's law is that  $a/n$  shall be less than a value  $a'/n'$  which is characteristic of the solution of diastase employed. When  $a/n < a'/n'$  then the amount of sucrose transformed each instant can be calculated by Wilhelmy's formula  $x = a(1 - e^{-kt})$ , which means that under these conditions the rates of hydrolysis by acids and diastase are identical. When  $a/n > a'/n'$  the initial velocity  $v = f(an)$  is independent of  $a$  and proportional to  $n$ . These facts indicate that the enzyme forms a complex with the sugar, which then decomposes with a finite velocity in keeping with the law of mass action. The above statements apply exactly to the action of emulsin on glycosides. The velocity of inversion by diastase decreases with increasing viscosity of the solution, but in the case of hydrolysis with acids the viscosity appears to have no influence on the velocity of the change. J. F. S.

**Inactivation of Invertase in Fresh Yeast by Silver Nitrate.** H. VON EULER and E. WALLIS (*Z. physiol. Chem.*, 1924, 132, 167—180).—The invertase of yeast-cells is inactivated by silver nitrate as the latter is taken up from the solution by the cells. It may regain its activity by self-regenerative processes or by treatment with hydrogen sulphide. The phenomenon is therefore parallel to the inactivation of yeast enzymes in solution (Euler and Myrbäck, A., 1922, i, 959). Yeast inactivated by silver nitrate and regenerated by treatment with hydrogen sulphide shows, after incubation, an increased activity. Owing to these protective mechanisms the invertase of the living yeast-cell is two hundred times more resistant to the toxic action of silver than is the same amount of the enzyme in solution. Zymase is much more susceptible to inactivation by silver than is invertase. J. P.

**Invertase. III.** H. VON EULER and K. JOSEPHSON (*Ber.*, 1924, 57, [B], 299—302; cf. A., 1923, i, 721).—The maximum purification of invertase preparations by the author's methods appears to be reached when the value  $If^0$  attains about 250.

Determinations of the molecular weight of invertase by measurements of diffusion indicate that the "active group" is contained in or associated with a complex of molecular weight about 20,000.

Specimens of invertase have been obtained in which the ash does not exceed 0.13%; the higher ash content of previous preparations is therefore due to impurities. The acidic and basic dissociation

constants have been determined provisionally to be  $K_a=10^{-7}$  and  $K_b=10^{-11}$ , respectively. The isoelectric point of invertase at  $20^\circ$  is calculated to be at  $p_H$  5.

H. W.

**Affinity of Invertase for Different Sugars.** H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **132**, 301—327).—At  $p_H$  4.5 invertase of bottom yeasts has a marked affinity for both  $\alpha$ - and  $\beta$ -dextrose, the affinity being slightly greater in the latter case than in the former. The affinity for l  vulose is of the same order as for dextrose. In contrast to the findings of Kuhn (*Z. physiol. Chem.*, 1923, **127**, 234; **129**, 57), no general support is forthcoming for the view that separate "gluco-" and "fructo-" invertases exists. The affinity of invertase for other hexoses and pentoses depends on the presence of a free reducing group (aldehydic or ketonic) and on the configuration of the remainder of the molecule, which may be considerably modified without entirely abolishing the affinity. In general, the  $\beta$ -forms of the hexoses and pentoses show a greater affinity than the  $\alpha$ -forms except in the cases of dextrose and xylose, where both stereoisomerides react practically alike. A relation appears to exist between the configuration of the sugar molecule and the relative affinity of invertase for its  $\alpha$ - and  $\beta$ -forms; thus the pairs dextrose-xylose and galactose-arabinose give parallel results. The affinity of invertase for the disaccharides has also been studied but no very definite conclusions are drawn.

J. P.

**Uniformity in Invertase Action.** J. M. NELSON and F. HOLLANDER (*J. Biol. Chem.*, 1923, **58**, 291—304).—The abnormality observed with certain invertase preparations (A., 1922, i, 388) has been shown to be due to inactivation. Thus, when the abnormal preparations were incubated at  $25^\circ$  with a citrate buffer mixture at  $p_H$  4.5 (the acidity at which the abnormality was observed) some loss of activity occurred, whilst this was not the case with normal preparations. Further, addition of sodium chloride or of boiled normal invertase prevented inactivation in the case of the preparation which was rendered normal by this treatment, but did not do so with the second abnormal preparation, which could not be rendered normal in this way. At  $25^\circ$  the point of maximum stability of one abnormal and two normal invertase preparations was found to lie, not at the acidity for maximum activity ( $p_H$  4.5; cf. Euler and Laurin, A., 1920, i, 506), but on the alkaline side of this (about  $p_H$  5.8).

E. S.

**Enzyme Adsorption.** I. H. KRAUT and E. WENZEL. **A Contribution to the Knowledge of "Invertin" of Willst  tter and his Collaborators** (*Z. physiol. Chem.*, 1924, **133**, 1—21).—The adsorption curve obtained by adsorbing the invertase of autolysed yeast juice with aluminium hydroxide deviates from the normal adsorption isotherm. The author argues that this is due to the interference of impurities adsorbed from the juice. Any change in the initial activity of an impure juice yields a different adsorption curve. In certain cases, it is even possible for aluminium hydroxide



to adsorb more of the enzyme out of dilute impure solutions than out of similar solutions of higher concentration. The adsorption value rises with the purity of an invertase preparation. S. S. Z.

**Influence of Alkaloids of the Atropine, Cocaine, and Morphine Groups on Yeast Invertase.** P. RONA, C. VAN EWYK, and M. TENNENBAUM (*Biochem. Z.*, 1924, **144**, 490—519).—A series of alkaloids of the above groups have been found to possess an inhibiting influence on the action of yeast invertase. Although the intensity of the inhibition varies with the various alkaloids, the general inactivating influence proceeds logarithmically according to the concentration of the alkaloid present. The inhibition is reversible, and is influenced by the hydrogen-ion concentration of the medium. No connexion exists between the optical configuration and the inhibitory power of *dl*-atropine and *l*-hyoscyamine; *l*-cocaine and *dψ*-cocaine; and *l*-ecgonine and *d*-ecgonine. In none of these three cases was there any difference between the inhibitory power of the isomers. Tropine inhibits much less markedly than atropine, whilst tropic acid does not inhibit at all; nor does an equimolecular mixture of tropine and tropic acid have a greater inhibiting effect than tropine alone. *d*- and *l*-Ecgonine do not inhibit, but, on the other hand, the chemically-related cocaine does. The substitution of the hydrogen of morphine by the methyl group (codeine) produced no apparent change in inhibitory power, but substitution by ethoxyl (dionine) produced a small though definite change. S. S. Z.

**Heat and Radiation Inactivation of Malt Amylase.** H. LÜERS and P. LORINSER (*Biochem. Z.*, 1924, **144**, 212—218).—The zone of maximal thermostability of malt amylase is displaced towards higher  $p_H$  values by increased concentration of an acetate buffer. Gelatin, egg-albumin, and gum arabic protect the amylase from heat inactivation especially between  $p_H$  6.0 and 7.0, and produce a flattening of the zone of maximum stability. Maltose has a similar protective influence and a direct proportionality exists between  $\log C_{\text{maltose}}$  and the coefficient of inactivation. The inactivation of amylase by ultra-violet radiation follows neither the mono- or bi-molecular equation, nor the Schütz law. The effect of alterations in the hydrogen-ion concentration is much less marked in this case than in that of heat-inactivation. The temperature coefficient for ultra-violet inactivation is  $k^{30}/k^{20}$  1.30, and physico-chemically the two methods of inactivation are dissimilar. J. P.

**Ferments and Light. IV. Diastase. III.** L. PINCUSSEN and F. DI RENZO (*Biochem. Z.*, 1924, **144**, 366—371; cf. A., 1924, i, 107).—The inactivation by ultra-violet light of 0.1% of malt diastase acting on 1% starch solution at varying  $p_H$  proceeds as a unimolecular reaction, whilst in the presence of 0.5% of starch only the later stages correspond with the unimolecular equation. The departure from the simple equation is still more marked in the presence of 0.25% of starch. A 0.2% solution of the enzyme gives complex results in the presence of 1.0, 0.5, and 0.25% starch solutions. J. P.

**Ferments and Light. V. Diastase. IV. L. PINCUSSEN** (*Biochem. Z.*, 1924, **144**, 372—378).—Sodium chloride protects both the diastase and maltase in malt diastase from inactivation by exposure to sunlight. *M/6*-Phosphate solution protects malt diastase and the maltase of "pancreatin Rhenania" from inactivation by ultra-violet light, whilst more dilute phosphate solutions are less effective. Similar results are given by acetate solutions of the same  $p_H$ . In the presence of a phosphate buffer, with or without the addition of sodium chloride, the protective action is at a maximum at  $p_H$  6.64. Ammonium, potassium, and lithium chlorides, potassium bromide, and sodium fluoride protect taka-diastase from ultra-violet light to varying degrees, an effect which is more marked in dilute solutions of these salts than in more concentrated solutions. Potassium and sodium nitrates and nitrites give similar results but do not show the same varying effects at different temperatures. J. P.

**Purification of Ferments by Electro-dialysis and Electro-osmosis. I. Malt Diastase. R. FRICKE and P. KAJA** (*Ber.*, 1924, **57**, [B], 310—313).—Electro-dialysis of solutions of malt diastase is effected in a cell divided into three compartments by collodion membranes. The central compartment contains the solution of malt diastase, whilst the outer compartments contain distilled water and the iron gauze cathode and carbon anode, respectively. The voltage used is 220 or 22. As soon as the current has attained a strength of 0.0045—0.006 amp. per sq. cm. the solution in the outer cells is replaced by distilled water and the process is repeated until the current strength remains practically constant at its initial value after recharging the anode and cathode cells. The dry matter concentration of the solution of malt diastase is very considerably lowered, whilst the activity of the enzyme towards starch is increased 2.1 to 2.5 times. After concentration by cautious freezing, the diastase solution gives slight protein but marked carbohydrate reactions. The ash is diminished from 5% to 1%, the nitrogen content from 6.14% to 3.51%.

Electro-osmosis is conducted in a five-compartment cell in which the extreme compartments which contain the electrodes are separated from the intermediate compartments by collodion membranes impermeable to diastase. The barrier between the intermediate and central cells is of collodion permeable to diastase. The central compartment contains the malt diastase solution, the others contain water. The pressure used is 22 volts. After electro-osmosis during 5 days, 39% of the malt diastase remains in the central compartment and shows a diminution in activity from 2.4 to 0.8, 32% has passed towards the anode and is inactive towards starch, 16% has passed towards the cathode and has increased in activity from 2.4 to 4.6, whilst 13% remains in the membranes. The highly active malt diastase gives a marked positive reaction for carbohydrates; it contains carbon 56.4%, hydrogen 7.9%, and nitrogen 3.28%. H. W.

**Non-homogeneity and other Properties of Malt Diastase.**

R. FRICKE and P. KAJA (*Ber.*, 1924, **57**, [B], 313—316).—A comparison of the starch-liquefying and saccharifying powers of Merck's "diastase absolut" with those of preparations purified by the authors' methods (preceding abstract) shows these properties to be affected to the same degree with respect to soluble starch; the purified product, however, appears to be relatively deficient in starch-liquefying power towards potato starch, thus supporting von Euler's hypothesis ("Chemie der Enzyme," II, 1922, 116) that at least two components are present in malt diastase. The previous conclusion that the presence of proteins in crude malt diastase is not essential to its diastatic properties is strengthened by the observation that the ferment is not affected by prolonged treatment with trypsin. Uranyl acetate is harmless as long as proteins are present with which it forms a precipitate, but after this point is passed, it acts as a vigorous poison. H. W.

**Amylolytic and Glycolytic Enzymes of the Pancreas and the Salivary Glands.**

C. SERONO and A. CRUTO (*Rass. Clin. Terap. Sci. aff.*, 1923, **22**, 139—142; from *Chem. Zentr.*, 1924, i, 62).—A glycerol extract of pancreas, an aqueous extract of dried sterilised pancreas powder, or salivary diastase, does not form maltose or dextrose from starch solution, but only isomaltose. The amount of isomaltose formed depends on the concentration of starch. The amylolytic enzyme from pancreas, after separation from lipolytic and proteolytic enzymes, is unstable, but can be stabilised by the addition of plant colloids to the solution. The presence of colloidal material increases the stability to heat of the pancreatic and salivary enzymes. The glycolytic enzyme obtained from the pancreas (Serono and Cruto, *Arch. Farm. Sperim.*, 1913, **14**, 501) is held to be an inner enzyme liberated by maceration, and may be obtained from other tissues in the same way. Only small quantities of ethyl alcohol and carbon dioxide are obtained by its action. It is concluded that no enzyme capable of synthesising sugar occurs in the pancreas. Glycogen is probably formed from isomaltose and not from the polymerisation of dextrose. Liver glycogen is only slightly attacked by pancreatic extract under aseptic conditions. G. W. R.

**Presence of Inulase in Takadiastase.**

Y. TAKAHASHI (*Biochem. Z.*, 1924, **144**, 199—202).—Takadiastase contains an inulase capable of hydrolysing inulin to lævulose. J. P.

**Inulin and Inulase. IV.**

H. PRINGSHEIM and G. KOHN (*Z. physiol. Chem.*, 1924, **133**, 80—96).—When inulin is heated in glycerol it is "dissociated" into polymers which consist of 8—10 monoses. Such "dissociated" inulin gradually acquires the properties of "associated" inulin when in solution and eventually separates out as such. The most favourable reaction for the action of inulase on inulin is  $p_H$  3.8, and the hydrolysis proceeds according to the formula of a unimolecular reaction.

Press juices of inulase obtained from older moulds (*Aspergillus niger*) were more active than those derived from younger moulds. The reaction constants have been worked out for inulins of various degrees of purity and for "dissociated" inulin (obtained by heating inulin in glycerol). Invertase hydrolyses inulin and "dissociated" inulin at a hydrogen-ion concentration of the order of that of gastric juice. *Aspergillus niger* contains an invertase as well as an inulase. S. S. Z.

**Polysaccharides. XXII. Lichenase and Reserve Cellulose (Lichenin).** P. KARRER, M. STAUB, A. WEINHAGEN, and B. JOOS (*Helv. Chim. Acta*, 1924, 7, 144—154).—Lichenin, which has already been recognised as a form of cellulose (A., 1923, i, 1182), is now identified with so-called reserve cellulose. It follows that the enzyme lichenase is closely related to cytase. Since the latter, however, contains enzymes which attack not only reserve celluloses but mannan and galactan, the term lichenase is retained for the enzyme obtained from the snail, *Helix pomatia*. The crude snail extract contains, besides lichenase, a variety of other enzymes, including invertase, lipase, diastase, inulase, maltase, and a cellobiase. The lichenase can be purified from the accompanying enzymes by dialysing, since all of them, with the exception of cellobiase, are unstable in water and quickly disappear. Some of the lichenase is lost during the purification, since it can diffuse through a membrane. The lichenase is best isolated by precipitation from the dialysed solution with acetone. The enzyme rapidly loses its activity if heated above 36°. The most active lichenase preparations are those which have not passed through a drying stage. Basic aluminium sulphate adsorbs lichenase almost completely from neutral solution; the enzyme can be brought into solution again by potassium dihydrogen phosphate and the solution so obtained can be purified by dialysis. Aluminium hydroxide also adsorbs the enzyme completely, but recovery is not so good as from the basic sulphate. The activity of lichenase solutions is not affected by sodium chloride, albumin, or soap, but is lowered by all sugars. The work of Pringsheim and Seifert (A., 1923, i, 998) indicates the presence of lichenase in barley, and it appears to be present in many other plants. Plant lichenase is, however, difficult to separate from accompanying enzymes. E. H. R.

**Polysaccharides. XXIII. Separation of Lichenase into Constituent Enzymes.** P. KARRER, M. STAUB, and B. JOOS (*Helv. Chim. Acta*, 1924, 7, 154—159).—When a snail lichenase preparation is preserved, its activity gradually diminishes in the course of about 14 days by some 30%, and then remains constant for a long period. The change is shown to be due to the disappearance of cellobiase, a constituent enzyme. Whereas fresh lichenase decomposes lichenin or cellobiose completely to dextrose, lichenase which has been preserved only carries the decomposition of lichenin to an intermediate stage, probably to cellobiose.

E. H. R.

**Serum Lipase.** G. FANCONI (*Fermentforsch.*, 1924, 7, 307—348).—Some hydrolysis of fats and cholesterol esters is shown to occur in human serum. Since the tributyrinase of serum (the so-called serum lipase) can be extracted in part by fats and lipoids, and since in lipæmic serum the lipolytic activity is less than in that from the fasting animal, it is argued that the tributyrinase is probably identical with the fat-splitting agent of the serum. The view that serum lipase and complement are closely related is not supported by the fact that quinine and atoxyl inhibit the lipolytic activity but not the complement function of serum. The variations in the lipolytic activity of serum in physiological and pathological conditions are described. R. K. C.

**Action of Arsenic and Antimony Compounds on the Fermentative Functions of the Organism. II. Action of certain Arsenic and Antimony Preparations on Pepsin.** J. A. SMORODINCEV and N. P. RIABOUSHINSKY (*Biochem. Z.*, 1924, 144, 26—30).—Sodium and potassium arsenites and arsenates, and potassium antimonyl tartrate retard the action of pepsin on casein, the last-mentioned in  $N/50$ , the others in  $N/40$  solutions. Lower concentrations of these salts from  $N/80$  to  $N/10240$  have no influence on the activity of pepsin. In contrast to ptyalin (A., 1923, i, 1246), pepsin is not so susceptible to antimony as to arsenic, and is more stable to both types of compound than is the former enzyme. Hydrochloric acid ( $N/40$  to  $N/1600$ ) and tartaric acid ( $N/10$  to  $N/1280$ ) have no influence on the action of pepsin. J. P.

**Adsorption of Trypsin by Filter-paper.** TSOU-HIA HSÜ (*Biochem. Z.*, 1924, 144, 303—307).—Trypsin (Merck) is adsorbed from solution by various makes of filter-paper (Schleicher and Schüll, Dreverhoff). The adsorbed enzyme may be partly recovered by washing with dilute sodium hydroxide and with phosphate solutions of  $p_H$  6.6 to 7.6. Washing with acid, sodium carbonate, and ammonia is ineffective. Variations in temperature have little or no effect on the extent of the adsorption. J. P.

**Influence of Colloids on Enzymes. III. I. HAGIHARA** (*Biochem. Z.*, 1924, 144, 482—489).—Cholesterol has no influence on the action of trypsin at the hydrogen-ion concentration range  $p_H$  5.3— $p_H$  10.6. Lecithin, on the other hand, stimulates the action of the enzyme in proportion to the quantity present. This stimulation occurs only in alkaline solutions, being entirely absent at or below  $p_H$  6.8; it reaches its maximum at  $p_H$  7.6 and falls in more alkaline solutions. S. S. Z.

**Kinetics of Trypsin Digestion. I. Experimental Evidence Concerning the Existence of an Intermediate Compound.** J. H. NORTHROP (*J. Gen. Physiol.*, 1924, 6, 239—243).—If, as has been suggested, a compound is formed between trypsin and its substrate, the presence of gelatin should decrease the rate of hydrolysis of casein, but this was found not to be the case. This result cannot be explained on the hypothesis that different enzymes

in the trypsin act on the two proteins, since the presence of casein, or of gelatin, inhibits the heat-inactivation of the gelatin-hydrolysing power, or of the casein-hydrolysing power, respectively, of the trypsin used (Fairchild's).  
W. O. K.

**Test for Diffusible Ions. I. Ionic Nature of Trypsin.**

J. H. NORTHRUP (*J. Gen. Physiol.*, 1924, **6**, 337—347).—The ratio of the concentrations of trypsin inside and outside the particles of gelatin suspended in water, is equal to the ratio of the hydrogen-ion concentrations on the two sides between the limits of  $p_H$  2 to 10.2. Above  $p_H$  10.2 the trypsin is distributed in the same ratio as the chlorine ion. Trypsin would therefore appear to be a diffusible amphoterie electrolyte, with isoelectric point at  $p_H$  10.2, giving positive univalent ions below this value and negative univalent ions above it, and to be distributed on the two sides of the surface of the gelatin particles in accordance with the Donnan equilibrium. It would seem to be a strong base below  $p_H$  10.2, as no evidence was obtained of undissociated trypsin. With increasing salt content, the same relations in the concentrations hold. The ratios of the concentrations of trypsin, and of hydrogen- and chlorine-ions all change in accordance with the Donnan equilibrium.  
W. O. K.

**[Pancreatic Enzymes. V. R. WILLSTÄTTER and collaborators.] Enterokinase and the Tryptic Action of the Pancreas.**

E. WALDSCHMITZ-LEITZ (*Z. physiol. Chem.*, 1924, **132**, 181—237).—A detailed investigation of the influence of enterokinase on the tryptic hydrolysis of gelatin in which the tryptic activity was determined by a method based on that of Willstätter and Waldschmitz-Leitz (cf. A., 1922, ii, 169). The activation of trypsinogen by the kinase is, in its initial stages, proportional to the time and reaches a constant value, less than the maximum possible degree of activation, in from 30 to 60 minutes according to the amount of kinase present. The speed of activation is greatest in neutral solutions. For any given preparation there is a direct proportionality between the amount of kinase necessary for the final degree of activation attained, and the amount of the enzyme activated. Glycerol and ethylene glycol and substances of autolytic origin have an inhibiting effect on the activation. The preparation of purified enterokinase free from proteolytic enzymes is described. Such preparations are highly specific and have no influence on pancreatic lipase or diastase. The author interprets his results as pointing to a simple activation of trypsinogen by the kinase, and as opposing the view that the process is an enzymic one. Using alumina as adsorbent, it is possible to separate the enzyme and its activator and so convert an active trypsin preparation into an inactive trypsinogen, which may then be subsequently reactivated. The trypsinogen of fresh or dried pancreas becomes "spontaneously" activated on keeping, especially in acid solution. This is regarded not as an autolytic change of the inactive enzyme, but as analogous to the activation by enterokinase, since, like the latter, the substance responsible for the

phenomenon may be adsorbed by alumina and so separated from an active trypsin which is thus reconverted to trypsinogen. The possible identity of this "spontaneous" activator with enterokinase is discussed in relation to the secretion of active pancreatic juice under the influence of pilocarpine and peptone. It is concluded that the activation of trypsinogen by enterokinase is a specific reaction conditioned in part by adsorption, but chiefly by the mutual influence of enzyme and activator on the affinities of specific groups, which is likened to the effect of hydrogen-ion concentration.

J. P.

**Arginase in Bacteria.** S. HINO (*Z. physiol. Chem.*, 1924, **133**, 100—115).—Living *Bacillus pyocyaneus* and *B. fluorescens*, as well as their acetone preparations, act on *D*-arginine. Filtrates from their cultures were inactive. The arginase is more active in the living organisms. The presence of urease in the above organisms has also been established. *Staphylococci*, *B. prodigiosus*, *B. coli*, *B. paratyphosus*, *B. typhosus*, *B. dysenteriae* (Shiga), and *Streptococci* do not contain arginase.

S. S. Z.

**Preparation of Dried Urease and Determination of Urea in Normal and Pathological Urines.** G. REVOLTELLA (*Biochem. Z.*, 1924, **144**, 229—257).—Improvements are given in the method already described by the author (*ibid.*, 1922, **134**, 336) for preparing dried urease from soya beans. A correction factor of 5.3% must be added to the urea determined by means of urease prepared by the author's old method in view of the incomplete nature of the conversion of urea to ammonium carbonate. Two improved methods for determining urea are described. In the direct method, 5 c.c. of urine and 2 drops of 0.3% methyl-orange are placed in each of two 50-c.c. graduated flasks, and 0.05*N*-sulphuric acid is added until the colour is light orange; 0.25—1.0 g. of urease (according to the activity of the preparation) is added, the solutions are diluted to 50 c.c. with distilled water, and the flasks are stoppered and placed in a water-bath for 1 hour at 45—50°. Ten c.c. of solution from one flask are titrated against 0.05*N*-sulphuric acid to a light orange and the number of c.c. of acid required multiplied by 0.15525 gives the corrected urea content in grams per 100 c.c. The second flask serves as a control on the completion of the fermentation. An improved direct aspiration method for determining the preformed ammonia and urea in urine or in any body fluid is also given, for details of which the original must be consulted. The influence of various normal and pathological constituents of urine, such as uric acid, proteins, amino-acids, dextrose, sodium chloride, and ammonium carbonate, and of varying conditions of temperature, hydrogen-ion concentration, and light, on the urease method of determining urea has been studied. It is concluded that urease methods provide, when properly controlled, the most convenient and most accurate means of determining urea.

J. P.

**Auxoureases.** F. DI RENZO (*Biochem. Z.*, 1924, **144**, 298—302).—Preliminary heating of a solution of urease for periods

varying from 10 to 30 minutes increases the activity of the enzyme, the maximum effect being attained with temperatures of 60–70° using 0.3% solutions of urease. The phenomenon is regarded as being similar to the activating effect of “auxo” bodies such as potassium cyanide and glycine on urease. J. P.

**Sulphatase. IV. Enzymic Fission of  $\beta$ -Naphthyl Hydrogen Sulphate.** J. NOGUCHI (*Biochem. Z.*, 1924, **144**, 138–140).— $\beta$ -Naphthyl potassium sulphate was prepared by treating  $\beta$ -naphthol in the presence of pyridine with chlorosulphonic acid dissolved in chloroform, followed by removal of the solvents and neutralisation with potassium hydroxide. The potassium salt, obtained as fine white plates, gave no precipitate in aqueous solution with barium chloride. On incubation with sulphatase (A., 1923, i, 1148; 1924, i, 107), it is hydrolysed to  $\beta$ -naphthol and potassium sulphate. J. P.

**Acid Production by *Bac. Granulobacter*.** H. B. SPEAKMAN. —(See i, 371.)

**Isoelectric Points for the Mycelium of Fungi.** W. J. ROBBINS (*J. Gen. Physiol.*, 1924, **6**, 259–271; cf. *Amer. J. Bot.*, 1923, **10**, 412).—Mycelia of *Rhizopus nigricans* and of *Fusarium lycopersici* behaved towards acid and basic dyes similarly to amphoteric colloids with isoelectric points  $p_H$  5.0 and 5.5 respectively. The amount of growth of *Rhizopus nigricans* on potato-dextrose agar and also the dry matter produced when grown on potato-dextrose broth, when plotted against the  $p_H$  of the medium, show a double maximum with an intervening minimum at initial  $p_H$  5.2. W. O. K.

**Assimilation of Aldehydes by Plants. II. Polymerisation of Formaldehyde by *Phaseolus multiflorus* and *Pelargonium* with the Formation of Higher Aldehydes.** T. SABALITSCHKA and H. RIESENBERG (*Biochem. Z.*, 1924, **144**, 545–550).—The above plants assimilate formaldehyde in the dark with the formation of sugar and starch. S. S. Z.

**Assimilation of Aldehydes by Plants. III. Does the Presence of Formaldehyde interfere with the Determination of Sugar and Starch in the Experimental Plants of T. Sabalitschka?** T. SABALITSCHKA and H. RIESENBERG (*Biochem. Z.*, 1924, **144**, 551–555).—It does not. S. S. Z.

**Respiratory Quotient of Roots and its Variation with the Development of the Plant.** R. CERIGHELLI (*Compt. rend.*, 1924, **178**, 645–647).—The respiratory quotient for the detached roots of various plants has been determined at different periods of growth. It was always found to be less than unity at the beginning of growth, and with annuals poor in reserve materials (wheat, maize, etc.), it remains so throughout the whole of the growth period. These two facts are the reverse of those observed in the case of the leaves.

As previously found, the respiratory quotient often falls at the time of flowering or of fruit-bearing, or at some time after this. The root in this case behaves analogously to the leaves.



Annuals possessing plentiful reserve materials (radish, lupin, etc.) and most perennials (iris, rhubarb, etc.) give a respiratory quotient greater than unity, except at the beginning of the growth period.  
E. E. T.

**Effect of Phosphates on [Plant] Respiration.** C. J. LYON (*J. Gen. Physiol.*, 1924, 6, 299—306).—The effect of increasing the phosphate content of the medium upon which *Elodea canadensis* is growing is to increase within about 30 minutes the rate of respiration as measured by the production of carbon dioxide. This effect increases with the concentration of phosphate-ion up to a concentration of 0.1M, beyond which it remains constant. When plotted against time it is found that for any given phosphate concentration the rate of respiration rises to a maximum, falls, rises to a second higher maximum, and again falls. The death of the plant occurs during the fall from the first maximum, the subsequent respiration being a *post-mortem* phenomenon. To investigate the anaërobic respiration wheat seedlings were used, and a similar increase in the production of carbon dioxide in the presence of phosphate was observed.  
W. O. K.

**Development of Pentosans in Barley during Germination.** M. H. VAN LAER and A. MASSCHELEIN (*Bull. Soc. chim. Belg.*, 1923, 32, 402—404).—During the germination process a distinct increase in the quantity of pentosans occurs in barley, especially in the embryo and the radicles. The endosperm also shows an appreciable increase. On steeping in water the total pentosan loss is about 4%; this takes place almost entirely from the chaff. Malting also results in the formation of pentosans, but in this case the distribution is not similar, the increase being considerable in the endosperm, whilst it is very small in the radicles.  
H. J. E.

**Absorption of Carbon by the Roots of Plants.** J. F. BREAZEALE (*J. Agric. Res.*, 1923, 26, 303—311).—Wheat seedlings were grown in a number of different culture solutions, and the plant ashes examined. Carbonates were found in the ash of plants grown in solutions containing sodium or ammonium nitrate, or the carbonates of calcium, sodium, or potassium. The carbonate ion was absorbed by the roots of the plants, but free carbon dioxide could not be taken up in the absence of soluble bases; the rate of absorption of bases depended largely on the absorption of an acid radical. It is suggested that such salts as sodium nitrate influence carbonate absorption as a result of the more rapid removal of the nitrate ion and the subsequent formation of sodium carbonate from atmospheric carbon dioxide. Evidence is advanced that the so-called "lime-loving" plants are in reality those requiring considerable amounts of carbonate. The plant root may maintain equilibrium in its tissues or in the nutrient solution by the intake of carbonate ions or by the excretion of free carbon dioxide.  
A. G. P.

**The Form of Nitrogen most Favourable for Higher Plants.**

G. TRUFFAUT and N. BEZSSONOFF (*Compt. rend.*, 1924, **178**, 723—725).—An investigation of the effect of various nitrogenous fertilisers on the growth of several common crops in pots and in the field. It is concluded that mixtures containing nitrogen in the form of carbamide are more effective than nitrates, ammonium salts, or even carbamide alone. In acid soils, carbamide-sodium nitrate mixtures, in alkaline soils, carbamide-ammonium sulphate mixtures, appeared to give the best result. In some cases mixtures of this type have enabled the authors to reduce the percentage of nitrogen in the fertiliser from 3% to 2% and yet to obtain an increased yield.  
E. E. T.

**Influence of a Deficiency of Potash on the Development of Barley Manured with different Amounts of Sodium Nitrate.**

H. WEISSMANN (*Z. Pflanz. Düng.*, 1924, **A**, **3**, 21—24).—Barley was grown in sand cultures, with a potash-free nutrient solution, to which increasing amounts of sodium nitrate were added. The dry-weight of the crop decreased with increasing amounts of sodium nitrate, only those plants having the smallest amount of sodium nitrate in the nutrient reaching the grain stage. The other plants died prematurely. The total intake of potassium by the plants decreased with larger doses of sodium nitrate, but the nitrogen- and sodium-intake increased with the proportion of sodium nitrate in the nutrient. The bearing of these results on the influence of potash-starvation on growth (cf. *ibid.*, 1923, **A**, **2**, 1) is discussed.  
A. G. P.

**Coexistence of Starch and Inulin in certain *Compositae*.**

L. DANIEL (*Compt. rend.*, 1924, **178**, 726—727).—Starch and inulin have been found to occur together in *Helianthus tuberosus* and *H. multiflorus* grafted on to the sunflower (annual). On one occasion they were both found in an artichoke graft. They were also found in ungrafted plants, e.g., *Jurinea alata* and various species of *Centaurea*.  
E. E. T.

**State of Tannins in the Vegetable Cell.**

MICHEL-DURAND (*Compt. rend.*, 1924, **178**, 586—589).—Young oak or chestnut plants, on being extracted with acetone, yield, in general, less tannin than when extracted with boiling water. It is concluded that the tannin is present, in the cell, in more or less intimate combination with mucilaginous substances.  
E. E. T.

**Protopectin and some other Constituents of Lemon Peel.**

R. SUCHARIPA (*J. Amer. Chem. Soc.*, 1924, **46**, 145—156).—The author distinguishes between "free pectin," the soluble jelly-making portion of fruits etc.; "protopectin," the water-insoluble pectin occurring in the cell wall closest to the cellulose layer; and "pectic acid," the ultimate product of hydrolysis of pectic substances.

Protopectin was prepared from the white pericarp of *Citrus limonum*. It gave pectin and cellulose on hydrolysis besides a small amount of impurities, including lignocelluloses that could not be removed previously. Pectins with different methoxly

contents have been prepared from the same source. It has been shown that the cell-wall of the parenchymatous tissue of *Citrus* contains "free" cellulose, which dissolves readily in Schweitzer's reagent, and also cellulose combined with pectin, which becomes soluble only after hydrolysis. An hypothesis is advanced as to the linking of the cellulose and pectin, based on the replacement of the cellulose in protopectin by methoxyl groups. The question of the transition of protopectin to pectin in the cell is discussed. F. A. M.

**Constitution of Derris Root.** I. S. TAKEI (*Rikwagaku Kenkyujo Iho*, 1923, 2, 485—496; cf. Kariyone and Atsumi, A., 1923, i, 477).—When extracted with hot ether, roots of *Derris elliptica*, Benth., grown in Singapore, gave colourless, hexagonal plates, m. p. 163°, which correspond with tubatoxin; the formula was found to be  $C_{19}H_{18}O_5$ , whilst former investigators gave  $C_{18}H_{18}O_5$ . Its methoxyl content corresponded with 1.5 methoxy groups in 1 mol.; it gave a phenylhydrazone, yellow needles, m. p. 243—245°. For the rabbit, the minimum lethal dose was 0.00125 g. per 100 g. of body-weight. When treated with concentrated sulphuric acid, it was changed into an *isomeride*, colourless needles, m. p. 177—178°, having no poisonous properties. The saponification of tubatoxin with 3% hot alcoholic potash gave a *phenolcarboxylic acid*,  $C_{10}H_{10}O_3$ , m. p. 128—129°, which absorbed bromine and gave a violet colour with ferric chloride. When the saponification was conducted in a current of hydrogen, an *isomeride*, colourless needles, m. p. 209—210°, was obtained which had no poisonous action. By fusion with potassium hydroxide, tubatoxin itself or the acids mentioned above gave another *phenolcarboxylic acid*,  $C_9H_9O_3$ , colourless needles, m. p. 182°. This acid sublimed at about 160°, and is probably a methylated benzoic acid. K. K.

**Chemical Analysis of *Jatropha stimulos*.** P. MENAUL (*J. Agric. Res.*, 1923, 26, 259—260).—The seeds of *Jatropha stimulos* resemble castor beans, and contain 61% of kernel. The expressed oil had the following characteristics:  $d^{15}_4$ , 0.9257;  $n^{15}_D$ , 1.4765; solidifies below  $-15^\circ$ ; iodine number, 124.65—129.47; saponification number, 186; volatile fatty acids, none; free fatty acids, trace; fatty acids, 95.6%; glycerol about 4.2%. The seeds also contain much protein, the analysis and nitrogen distribution of which has been studied. There is a high histidine content. A. G. P.

**Mono- and Di-methylolcarbamide. Their Effect on Plant Growth, and their Decomposition in the Soil.** E. BLANCK and F. GIESECKE (*Z. Pflanz. Düng.*, 1923, 2, 393—420).—When formaldehyde is added as a preservative to liquid manure (urine) containing carbamide, monomethylol carbamide,  $CO(NH_2)NH\cdot CH_2\cdot OH$ , and dimethylolcarbamide,  $CO(NH\cdot CH_2\cdot OH)_2$ , may be formed. Experiments are described on the effect of these compounds, and also of liquid manure-formaldehyde mixtures, on the growth of plants in sand and soil cultures. Both compounds at first depress the germination of oats and turnips. This effect is, however, followed

by stimulation. Monomethylolcarbamide is equally effective with ammonium sulphate as a source of nitrogen for oats and mustard. Dimethylolcarbamide is generally less satisfactory, and may in some cases be actually harmful. The experiments with liquid manure-formaldehyde mixtures show similar results, large amounts of formaldehyde being injurious. The nitrogen of these compounds is readily ammonified by soil organisms. It is concluded that whilst formaldehyde may be used as a preservative with liquid manure, excess should be avoided.

G. W. R.

#### **Nature of the Activity of the Colloidal Clay of Acid Soils.**

R. BRADFIELD (*J. Amer. Chem. Soc.*, 1923, **45**, 2669—2678).—In this investigation, standard solutions of sodium hydroxide and calcium hydroxide were titrated with the colloidal material from four acid soils and the end-points determined by both conductivity and hydrogen-ion concentration measurements (cf. *ibid.*, 1923, **45**, 1245). The end-points found by both methods were fairly definite, and the titration curves were of the type commonly obtained in the titration of a strong base by a weak acid. The same amounts of the colloidal acids were required to neutralise equivalent quantities of the two bases, and definite breaks were obtained in the conductivity curves, indicating the neutralisation of definite acids. The reaction between acid colloidal clays and strong bases appears to be an ordinary neutralisation. The results obtained tend to show that the colloidal material of an acid soil is itself an acid which ionises to produce a definite Sørensen value and which shows a definite titrable acidity on titration with strong bases. F. G. P.

#### **Soil Reaction in Relation to Calcium Adsorption.**

C. O. SWANSON (*J. Agric. Res.*, 1923, **26**, 83—121).—The adsorption of calcium and the alterations in soil reaction, following the addition of lime to a number of soils, are described. Potassium chloride was found to reduce the adsorption of calcium in soils unless relatively large amounts of calcium carbonate were present. Soil suspensions showed lower  $p_H$  values than filtered soil extracts. The adsorption of calcium by soils was more intimately connected with the clay content than with the original hydrogen-ion concentration of the soil. Fuller's earth had a greater hydrogen-ion concentration and a greater adsorptive power than any soil examined. Leaching with water did not affect the adsorptive power or  $p_H$  value of soils. The presence of calcium carbonate did not influence the calcium adsorption from calcium hydroxide. Dilute hydrochloric acid increased the hydrogen-ion concentration of soils to an extent proportional to the amount of acid. Small additions of oxalic acid to soil decreased the hydrogen-ion concentration and larger amounts increased this figure, but to a less extent than did equivalent quantities of hydrochloric acid. Acidity of mineral soils is attributed to the leaching out of bases leaving acid alumino-silicates, which readsorb soluble bases (particularly calcium), leaving an insufficient supply for the normal growth of plants. A new apparatus for determining hydrogen-ion concentrations of soils is described.

A. G. P.

**Partial Sterilisation of Soil by Antiseptics.** (MRS.) A. MATTHEWS (*J. Agric. Sci.*, 1924, **14**, 1—57).—An examination is recorded of the microflora in soils treated with a number of organic antiseptics. The normal effect of antiseptics—an initial decrease in bacterial numbers followed by a sudden rise, which was maintained for varying periods and finally tended to return towards normal—was observed. The antiseptics disappeared from the soil fairly quickly. Aération increased the rapidity of these changes. The extent of the increase in bacterial numbers varied according to the molecular weight and heat of combustion of the antiseptics used, and some correlation with the latter factor is indicated. Bacterial changes seemed in no way connected with protozoa and occurred in a normal manner even in protozoa-free soils. Increases in bacterial population are ascribed to the feeding effect of the antiseptics or the bacteria, and the improved fertility following partial sterilisation to the breaking down of soil organic matter by the increased number of organisms. The action of lime and of steaming in increasing the bacteria is assumed to result from improved conditions, due to the breaking down of plant residues, etc. Aliphatic compounds produce quicker but smaller changes than aromatic ones. Among aromatic compounds, the introduction of the  $-\text{CH}_3$  group into the benzene ring lessened the toxicity of the compound to soil organisms, whereas  $-\text{Cl}$  and  $-\text{NO}_2$  produced increased toxicity and stability in the soil. The toxic effects of a number of antiseptics on protozoa, eelworm, and fungi are recorded.

A. G. P.

**The Manurial Properties of Lead Nitrate.** R. A. BERRY (*J. Agric. Sci.*, 1924, **14**, 58—65).—A number of culture and field experiments are described in which lead nitrate was used as the source of nitrogen to plants, in comparison with sodium nitrate. Similar yields were obtained by both treatments. The lead salt tended to produce plants with wider leaf blade and of slightly darker colour. When used in commercial quantities, no lead was found in the plants produced, nor could any be leached from the soil. Except when high concentrations were used, lead was adsorbed and rendered non-toxic by the soil. It would appear probable that lead salts increased the rate of nitrification in soils.

A. G. P.

**Action of Sodium Nitrite in the Soil.** R. H. ROBINSON (*J. Agric. Res.*, 1923, **26**, 1—7).—Experiments are described demonstrating the unsuitability of sodium nitrite as a fertiliser, particularly on acid soils. In all soils examined, there was a steady loss of nitrogen from the nitrite, only a small proportion of which became oxidised to nitrate. This loss was much accelerated in acid soils. The addition of lime or calcium carbonate to such soils retarded the decomposition of nitrites, but no increased nitrate content could be observed.

A. G. P.

## Organic Chemistry.

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**Silver-sulphochromic Oxidation of Coal.** L. J. SIMON (*Compt. rend.*, 1924, **178**, 775—777).—When coal is heated with a mixture of silver dichromate and concentrated sulphuric acid at 100°, 4—5% of the carbon present remains unoxidised. Formation of gaseous oxidation products is more rapid at 50° than at 60°, at which temperature 28% of the coal remains unchanged, about 6.7% being rendered soluble. When powdered coke is oxidised by chromic acid, 54.2% is unaffected, as against 39% when silver dichromate is used. It is concluded from the results that coal contains two constituents intimately mixed. One is oxidised at low temperatures, the other, like coke, requiring a temperature of 100°.

E. E. T.

**Composition of Natural Gas Gasoline.** R. P. ANDERSON and A. M. ERSKINE (*J. Ind. Eng. Chem.*, 1924, **16**, 263—267).—Fractional distillation shows that the approximate composition of this gasoline is: propane and butanes, 20% (by volume); *iso*-pentane, 13%; *n*-pentane, 17%; *iso*hexane, 9%; *n*-hexane, 15%; *iso*heptane, 8%; *n*-heptane, 12%; octane, 4%, and absorption oil, 2%; the presence of traces of benzene and toluene is indicated.

C. I.

**Composition of Low-temperature Tar. IV.** F. SCHÜTZ, W. BUSCHMANN, and H. WISSENBACH (*Ber.*, 1924, **57**, [B], 421—423; cf. A., 1923, i, 1080).—An examination of the requisite C<sub>9</sub> to C<sub>12</sub> fraction of neutral oil from low-temperature coal-tar showed that 80—86% consists of unsaturated and aromatic hydrocarbons, whilst the remaining 14—20%, boiling from 30° to 220°, probably contains *n*-nonane, *n*-decane, *n*-undecane, and *n*-dodecane, as indicated by the boiling points of the fractions, although the densities are slightly too high. [Cf. B., 1924, 367.]

F. A. M.

**Action of Sodamide on True Acetylene Hydrocarbons.** BOURGUEL (*Compt. rend.*, 1924, **178**, 777—779; cf. A., 1923, i, 1176).—When chloro-compounds are treated, by the author's method, with sodamide, the acetylene hydrocarbon is never present as such at the end of the reaction, but as a sodamide or sodium derivative of the hydrocarbon. If pure pentinene, diluted with xylene, is added to a xylene suspension of sodamide heated at 120°, 1 mol. of ammonia is evolved per mol. of pentinene, with formation of a sodium derivative of the latter.

E. E. T.

**Chlorination of Butylene and the Properties of Dichlorobutane.** E. BRINER, J. HAUSSER, and E. DE LUSERNA (*Helv. Chim. Acta*, 1924, **7**, 374—376).—*n*-Butyl alcohol is readily

converted into butylene by passage over alumina at  $480^{\circ}$ . Butylene combines with chlorine, with evolution of heat, forming dichlorobutane, the molecular heat of reaction being 33.4 Cal. The reaction is not explosive. Dichlorobutane has b. p.  $114.6-114.8^{\circ}/730$  mm.;  $n_D^{20}$  1.4325;  $d_4^{20}$  1.144,  $d_4^{22.2}$  1.115,  $d_4^{99.5}$  1.032; ignition temperature,  $62^{\circ}$ . The viscosity coefficient is 0.0515 at  $0^{\circ}$ , 0.01073 at  $22.2^{\circ}$ , 0.00535 at  $99.5^{\circ}$ . It is a good solvent for oils and fats and is not poisonous.

E. H. R.

**Action of Ammonia on Organic Halogen Compounds at High Temperature.** J. HESLINGA (*Rec. trav. chim.*, 1924, **43**, 178—180).—The halogen in organic compounds containing chlorine or bromine is quantitatively converted into ammonium halide when the substance is heated to redness in a current of ammonia. Chloro derivatives of benzene, if substituted in the ring, are exceptions to the general rule. (Cf. this vol., ii, 55.) H. J. E.

**Near Ultra-red Absorption Spectra of some Organic Liquids.** J. W. ELLIS.—(See this vol., ii, 218.)

**Analogues of Citronellol Richer and Poorer in Carbon.** I. J. VON BRAUN and R. GOSSEL (*Ber.*, 1924, **57**, [B], 373—382).—The effect of the position of the double bond and of the number and position of the methyl groups on the odour of citronellol,  $\text{CMe}_2\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , has been examined. The conversion of the terminal group,  $\text{CMe}_2\cdot\text{C}-$ , into the complex,  $\text{CH}_2\cdot\text{C}-$ , causes a very marked alteration in odour which is less marked when the group is  $\text{CHMe}\cdot\text{C}-$ ; the introduction of further methyl radicals (in addition to the  $\gamma$ -methyl group) does not cause an appreciable change in odour, whence it is probable that the  $\gamma$ -methyl group is itself unimportant. The decisive factor appears to be the presence of the group  $\text{CMe}_2\cdot\text{C}-$ , or to a less extent of  $\text{CHMe}\cdot\text{C}-$ , at a definite distance from the primary alcoholic group. The alcohols described in the present communication are optically inactive, but the comparison of them with optically active citronellol is regarded as justifiable, since, in general, little difference in odour is observed between isomeric active and racemic substances.

$\Delta^8$ -Butenyl bromide reacts readily with an alcoholic solution of ethyl sodioacetoacetate to give a mixture of *ethyl butenylacetoacetate*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\cdot\text{CH}\cdot\text{CHMe})\cdot\text{CO}_2\text{Et}$ , a mobile liquid, b. p.  $112-114^{\circ}/11$  mm., and *ethyl dibutenylacetoacetate*, b. p.  $135-137^{\circ}/12$  mm. The former ester is hydrolysed by dilute, aqueous potassium hydroxide solution to  $\Delta^8$ -heptene- $\xi$ -one,  $\text{CHMe}\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{COMe}$ , b. p.  $152-155^{\circ}$ /atmospheric pressure,  $42-43^{\circ}/9$  mm.,  $d_4^{20}$  0.8446,  $n_D^{20}$  1.4292 (*semicarbazone*, lustrous leaflets, m. p.  $97^{\circ}$ ). *Ethyl methylbutenylacetoacetate*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CMe}(\text{CH}_2\cdot\text{CH}\cdot\text{CHMe})\cdot\text{CO}_2\text{Et}$ , b. p.  $120-122^{\circ}/20$  mm., is hydrolysed to  $\gamma$ -methyl- $\Delta^8$ -heptene- $\beta$ -one,  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{COMe}$ , b. p.  $62-64^{\circ}/20$  mm.,  $d_4^{18}$  0.8463,  $n_D^{18}$  1.4345, which resembles amyl acetate in odour.

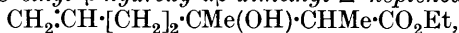
Ethyl  $\beta$ -methyl- $\Delta^8$ -heptadienoate, a colourless liquid, b. p.  $103-105^{\circ}/22$  mm., prepared by the action of potassium hydrogen

sulphate at  $150^{\circ}$  on ethyl  $\beta$ -hydroxy- $\beta$ -methyl- $\Delta^{\epsilon}$ -heptadienoate, is reduced by sodium and alcohol to  $\gamma$ -methyl- $\Delta^{\zeta}$ -heptenol,

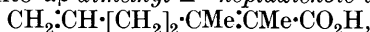


b. p.  $97-99^{\circ}/22$  mm.,  $d_4^{25}$  0.8562,  $n_D^{25}$  1.4470, which has no resemblance in odour to citronellol.

$\Delta^{\beta}$ -Hexene- $\zeta$ -one is transformed by zinc and ethyl  $\alpha$ -bromopropionate into ethyl  $\beta$ -hydroxy- $\alpha\beta$ -dimethyl- $\Delta^{\epsilon}$ -heptenoate,

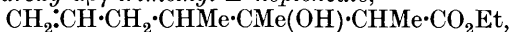


a somewhat viscous, colourless, odourless liquid, b. p.  $124-126^{\circ}/18$  mm., which is hydrolysed to the corresponding acid, a colourless, viscous liquid with a very unpleasant odour, b. p.  $175-176^{\circ}/18$  mm. The latter compound is converted by acetic anhydride and anhydrous sodium acetate into  $\alpha\beta$ -dimethyl- $\Delta^{\epsilon}$ -heptadienoic acid,

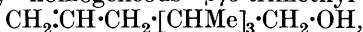


an unpleasant smelling liquid, b. p.  $145-146^{\circ}/18$  mm., from which ethyl  $\alpha\beta$ -dimethyl- $\Delta^{\epsilon}$ -heptadienoate, b. p.  $103-105^{\circ}/18$  mm., is prepared. The ester is reduced by sodium and alcohol to  $\beta\gamma$ -dimethyl- $\Delta^{\zeta}$ -heptenol,  $\text{CH}_2\text{:CH}\cdot[\text{CH}_2]_2\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$ , b. p.  $101-102^{\circ}/20$  mm.,  $d_4^{21}$  0.8741,  $n_D^{21}$  1.4570, the odour of which is quite distinct from that of citronellol.

Ethyl  $\beta$ -hydroxy- $\alpha\beta\gamma$ -trimethyl- $\Delta^{\epsilon}$ -heptenoate,



a viscous liquid with a very faint odour, b. p.  $123-125^{\circ}/17$  mm., is readily obtained from  $\gamma$ -methyl- $\Delta^{\epsilon}$ -heptene- $\beta$ -one, zinc, and ethyl  $\alpha$ -bromopropionate. Complete dehydration of this compound or of the corresponding hydroxy acid could not be accomplished. The incompletely homogeneous  $\beta\gamma\delta$ -trimethyl- $\Delta^{\zeta}$ -heptenol,



does not, however, resemble citronellol in odour.

Ethyl  $\beta$ -hydroxy- $\beta$ -methyl- $\Delta^{\epsilon}$ -octenate,



b. p.  $121-122^{\circ}/10$  mm., is hydrolysed to the corresponding acid, a viscous liquid, b. p.  $177-180^{\circ}/16$  mm., which is transformed by sodium acetate and acetic anhydride into  $\beta$ -methyl- $\Delta^{\epsilon}$ -octadienoic acid,  $\text{CHMe}\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , b. p.  $149-150^{\circ}/18$  mm., from which ethyl  $\beta$ -methyl- $\Delta^{\epsilon}$ -octadienoate, b. p.  $114-115^{\circ}/18$  mm., is obtained. The ester is readily reduced by sodium and alcohol to  $\gamma$ -methyl- $\Delta^{\zeta}$ -octenol (norcitronellol),

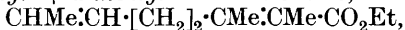


b. p.  $109-111^{\circ}/20$  mm.,  $d_4^{20}$  0.8674,  $n_D^{20}$  1.4560, which has a terpene-like odour with a faint resemblance to that of citronellol.  $\beta$ -Methyl- $\Delta^{\epsilon}$ -octenoic acid,  $\text{CHMe}\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , b. p.  $145-146^{\circ}/18$  mm., is obtained as by-product of the reduction; the corresponding ethyl ester has b. p.  $109-111^{\circ}/21$  mm.

Ethyl  $\beta$ -hydroxy- $\alpha\beta$ -dimethyl- $\Delta^{\epsilon}$ -octenoate,



b. p.  $139-142^{\circ}/20$  mm., is converted by potassium hydrogen sulphate into ethyl  $\alpha\beta$ -dimethyl- $\Delta^{\epsilon}$ -octadienoate,

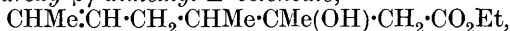


a liquid with a tolerably pleasant odour, b. p.  $115-116^{\circ}/19$  mm., and the corresponding acid, an unpleasant smelling liquid, b. p.



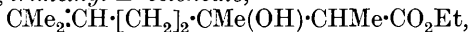
152—155°/20 mm. The ester is reduced by sodium and alcohol to  $\beta\gamma$ -dimethyl- $\Delta^5$ -octenol,  $\text{CHMe}\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot[\text{CHMe}]_2\cdot\text{CH}_2\cdot\text{OH}$ , b. p. 111—112°/21 mm.,  $d_4^{21}$  0.8775,  $n_D^{21}$  1.4670, which resembles the terpenes and citronellol in odour.

*Ethyl  $\beta$ -hydroxy- $\beta\gamma$ -dimethyl- $\Delta^5$ -octenoate,*

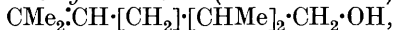


an odourless liquid, b. p. 137—139°/20 mm., is transformed successively into *ethyl  $\beta\gamma$ -dimethyl- $\Delta^5$ -octadienoate*, a very pleasant smelling liquid, b. p. 123—124°/20 mm., and  $\gamma\delta$ -dimethyl- $\Delta^5$ -octenol,  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot[\text{CHMe}]_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , b. p. 114—115°/17 mm.,  $d_4^{19}$  0.8775,  $n_D^{19}$  1.465, which is allied to citronellol in odour.

Methylheptenone, zinc, and ethyl  $\alpha$ -bromopropionate yield *ethyl  $\beta$ -hydroxy- $\alpha\beta\zeta$ -trimethyl- $\Delta^5$ -octenoate,*



a colourless, viscous liquid, b. p. 145°/16 mm., which is transformed by potassium hydrogen sulphate at 150° into *ethyl  $\alpha\beta\zeta$ -trimethyl- $\Delta^5$ -octadienoate*, b. p. 126—128°/20 mm. The latter ester is smoothly reduced to  $\beta\gamma\eta$ -trimethyl- $\Delta^5$ -octenol (*homocitronellol*),



a mobile liquid, b. p. 125—127°/20 mm.,  $d_4^{17}$  0.8860,  $n_D^{17}$  1.4725. The odour of the substance is more closely similar to that of citronellol than are those of the alcohols containing the terminal group,  $\text{CHMe}\cdot\text{C}-$ . When preserved, it exhibits the same change and refinement of odour which is characteristic of citronellol, and is possibly due to an establishment of an equilibrium between two forms containing the groups,  $\text{CMe}_2\cdot\text{C}-$  and  $\text{CH}_2\cdot\text{CMe}\cdot\text{C}-$ . H. W.

**Manufacture of Ether.** J. DESMAROUX (*Mém. Poudres*, 1923, 20, 335—390).—The system,  $\text{H}_2\text{SO}_4$ — $\text{EtOH}$ — $\text{H}_2\text{O}$ — $\text{Et}_2\text{O}$ — $\text{EtHSO}_4$ , is considered theoretically, and a diagram is evolved showing the interdependence of the concentrations of the various components. Phase-rule considerations show that the system has three degrees of freedom. The state of equilibrium, particularly with regard to ether, is practically independent both of the temperature and of the sulphuric acid concentration. The experimental results obtained are in excellent agreement with the formulæ  $Y=m(1-10^{-ht})$  and  $X=r(1-S\cdot 10^{kt})$  where  $Y$ =the percentage of alcohol converted into ether and  $X$ =the percentage of free acid in the mixture at the end of time  $t$ . Tables giving the values of the constants  $m$ ,  $h$ ,  $r$ ,  $k$ , and  $S$  for the various temperatures and concentrations of sulphuric acid and alcohol are appended. A comprehensive thermodynamic study of the conditions of the reaction enables results to be deduced which are in general agreement with practical experience of ether manufacture. A laboratory investigation of the nature of the vapour given off showed that with a fall in the acidity of the mixture the quantity of alcohol in equilibrium with it increases and the proportion of ether in the vapour falls. [Cf. *B.*, 1924, 313.] H. C. R.

**Termolecular Gas Reactions. I. Mechanism of the Formation of Acetic Acid from Acetaldehyde and Oxygen.** A. KISS and L. DEMÉNY (*Rec. trav. chim.*, 1924, 43, 221—248).—The reaction between pure acetaldehyde and pure oxygen was examined

by the method previously described (A., 1923, ii, 237), the theory developed by Trautz (A., 1918, ii, 151) being applied. If the formation of an intermediate compound,  $\text{CH}_3\cdot\text{CHO}\cdot\text{O}_2$ , is postulated:  $\text{CH}_3\cdot\text{CHO} + \text{O}_2 = \text{CH}_3\cdot\text{CHO}\cdot\text{O}_2$ ;  $\text{CH}_3\cdot\text{CHO}\cdot\text{O}_2 + \text{CH}_3\cdot\text{CHO} = 2\text{CH}_3\cdot\text{CO}_2\text{H}$ , the velocity constant passes through a maximum with lapse of time, which suggests catalytic action. The reaction was also studied in presence of water vapour. At  $20^\circ$ , a long period of induction (10 hours) set in; at  $60-80^\circ$ , the induction period was shorter than for the dry gases at the same temperatures. These results showed that the action was autocatalytic, the formation of the autocatalyst being accelerated by moisture. The experimental results did not indicate whether the catalysis was chemical or physical. The autocatalyst is probably acetic acid:  $\text{CH}_3\cdot\text{CHO} + \text{CH}_3\cdot\text{CO}_2\text{H} \rightleftharpoons \text{CH}_3\cdot\text{CHO}\cdot\text{CH}_3\cdot\text{CO}_2\text{H}$  (infinitely rapid);  $\text{CH}_3\cdot\text{CHO}\cdot\text{CH}_3\cdot\text{CO}_2\text{H} + \text{O}_2 = \text{CH}_3\cdot\text{CO}_2\text{H} + \text{CH}_3\cdot\text{CHO}\cdot\text{O}_2$  (measurable speed). The formation of this intermediate compound was shown to be a true gas reaction of the second order, catalysed by acetic acid but uninfluenced by water. With increasing oxygen pressure, the reaction is retarded; excess of aldehyde accelerates it, which seems to point to the complex  $\text{CH}_3\cdot\text{CHO}\cdot\text{CH}_3\cdot\text{CO}_2\text{H}$  as the catalyst. Indifferent gases (nitrogen, carbon dioxide) exerted no influence, neither, apparently, did the surface of the containing vessel. The reaction was not sensitive to light.

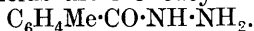
S. K. T.

**Ammonium Oleate.** M. MŁODZIEJEWSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 471—478).—Ammonium oleate when gently heated with alcohol dissolves, and on cooling crystallises in the form of plates possessing double refraction. When it is heated more strongly and then allowed to cool, a fine emulsion possessing double refraction is formed. This is followed by the appearance of fluid crystals in the form of "puppets" and sometimes also liquid spherulites and oily strips. On further cooling, the liquid crystals disappear; an emulsion is temporarily formed which is then followed by the appearance of the solid crystals. The same changes can be studied repeatedly on a single microscopic slide.

S. P. S.

**Simple and Mixed Acid Anhydrides.** W. AUTENRIETH and G. THOMÆ (*Ber.*, 1924, **57**, [B], 423—437; cf. A., 1901, i, 185).—It is shown that it is not possible to prepare mixed aliphatic-aromatic or aromatic-aromatic anhydrides either by the action of acetic anhydride on aromatic acids or by the action of the acid chloride on the sodium salt of another acid. The reaction given in Beilstein's "Handbuch" (3 *Aufl.*, **1**, 461):  $(\text{C}_2\text{H}_3\text{O})_2\text{O} + 2\text{C}_2\text{H}_5\cdot\text{OH} = 2\text{C}_2\text{H}_3\text{O}_2\cdot\text{C}_2\text{H}_5 + \text{H}_2\text{O}$ , is shown to be incorrect, as in all cases examined 1 mol. of anhydride yielded only 1 mol. of ester and 1 mol. of free acid.

Ammonia, phenylhydrazine, and aniline react with aromatic anhydrides to give 1 mol. of free acid and 1 mol. of the acid amide, anilide, or hydrazide. Hydrazine hydrate reacts with *p*-toluic anhydride to give *s*-di-*p*-toluoylhydrazine, whilst a 50% aqueous solution of the base yields the monoacyl derivative,



*p*-Bromobenzoic anhydride yields only *p*-bromobenzoylhydrazine, m. p. 167°. The following anhydrides were prepared by the action of acetic anhydride on the requisite acid: stearic anhydride, m. p. 70—71°; palmitic anhydride, m. p. 62—63°; phenylacetic anhydride, prisms, m. p. 71—72°; *o*-toluic anhydride, m. p. 38—39°; *m*-toluic anhydride, prisms, m. p. 70—71°; *p*-toluic anhydride, leaflets, m. p. 95°; *p*-bromobenzoic anhydride, white plates, m. p. 218°; *m*-nitrobenzoic anhydride, prisms, m. p. 159—160°; *p*-ethoxybenzoic anhydride, m. p. 108° (which yields with aniline *p*-ethoxybenzanilide, m. p. 169°). The following new compounds are also noted: *Phenyl phenylacetate* (from phenylacetic anhydride and phenol), prisms, m. p. 42°. *p*-Tolyl phenylacetate, prisms, m. p. 75—76°. *p*-Tolyl *p*-toluate (from *p*-toluic anhydride and *p*-cresol), plates, m. p. 91—92°. F. A. M.

**The Influence of Constitution on the Catalytic Hydrolysis of Esters by Acids.** G. BERGER (*Rec. trav. chim.*, 1924, **43**, 163—177).—The rate of hydrolysis of about twenty esters of monobasic fatty acids and of substituted acetic and benzoic acids was studied. The catalyst used was *N*/10-hydrochloric acid and the medium of hydrolysis a mixture of alcohol and water containing 42.34% of alcohol. Experiments were carried out at different temperatures owing to the variation in ease of hydrolysis shown by the esters, and in calculating the reaction-velocity the presence of ethyl alcohol as solvent was recognised as a factor in the case of ethyl esters. The author draws the conclusions that the acceleration of hydrolysis brought about by hydrogen ions decreases with the strength of the ester acid (cf. Olivier and Berger, A., 1923, ii, 144) and, in the case of esters with negative alcoholic groups, *i.e.*, where the alcoholic constituent possesses a somewhat acid character, the acceleration is small. In the case of methyl and ethyl esters of the same acid, the difference in reaction velocity is not constant but decreases with the acidity of the ester. The accelerated action in the case of an ester of the type  $R'\cdot CO_2R''$  is thus conditioned by both the  $R'$  and  $R''$  groups, and these groups appear to be of equal importance and strength in their influence on hydrolysis from both the qualitative and quantitative points of view. H. J. E.

**Monocarboxylic Acids derived from Sugars. II. Methylation of Tetramethyl-gluconic Acid.** J. PRYDE (*J. Chem. Soc.*, 1924, **125**, 520—522).—Tetramethyl-gluconolactone, treated with one molecular proportion of water, and then with methyl iodide and silver oxide at 40°, yields methyl tetramethyl-gluconate,  $OMe\cdot CH_2\cdot CH(OMe)\cdot CH(OH)\cdot [CH(OMe)]_2\cdot CO_2Me$ , a neutral, mobile oil,  $n_D^{20}$  1.4480. On subjecting this to five successive methylations, methyl pentamethyl-gluconate was obtained as a neutral, colourless, limpid, very mobile oil, b. p. 100°/1.0 mm.,  $n_D^{15}$  1.4412,  $[\alpha]_{5461}^{15} +42.7^\circ$  in alcohol, and  $+24.9^\circ$  in water, falling to  $+21.9^\circ$  in 4 months. F. G. W.

**Oils in the Chaulmoogra Group.** G. A. PERKINS and A. O. CRUZ (*Philippine J. Sci.*, 1923, **23**, 543—569).—The oils from the

seeds of the following species were examined : *Gynocardia odorata*, *Hydnocarpus alcalæ*, *H. anthelminthica*, *H. Hutchinsonii*, *H. subfalcata*, *H. venenata*, *H. Wightiana*, *H. Woodii*, *Pangium edule*, and *Taraktogenos Kurzii*. The data obtained show a close similarity between the true chaulmoogra oil (from *Taraktogenos Kurzii*) and all the *Hydnocarpus* oils investigated. The oil from *Hydnocarpus alcalæ* is distinguished by its very high content of chaulmoogric acid. It contains little or no hydnocarpic acid. The other *Hydnocarpus* oils, like chaulmoogra oil, may each be separated by the distillation of the ethyl esters into fractions, one of which contains the acids with 16 carbon atoms and the other those with 18 carbon atoms. The former fractions of each oil contain hydnocarpic acid and an unknown acid or acids which cannot be completely separated from the hydnocarpic acid by one recrystallisation from 80% alcohol. This unknown acid portion has a lower optical activity than hydnocarpic acid. The latter fractions (acids with 18 carbon atoms) contain chaulmoogric acid, which can be separated more readily than hydnocarpic acid. A more highly unsaturated portion is left in the case of many samples when the chaulmoogric acid is crystallised out. Previous results placing *Gynocardia odorata* outside the chaulmoogra group were confirmed. *Pangium edule* seeds appear to contain no chaulmoogric or hydnocarpic acids.

H. C. R.

**Compounds Developed in Rancid Fats, with Observations on the Mechanism of their Formation.** W. C. POWICK (*J. Agric. Res.*, 1923, **26**, 323—362).—A large number of possible products of rancidity in fats have been examined. It is suggested that nonaldehyde is in part responsible for the odour of rancid fats. The glyceryl radical and the unsaponifiable portion of fats appeared to have no part in the phenomena of rancidity, which may be reproduced by the oxidation of oleic acid. The colour developed in the Kreis test for rancidity was spectroscopically identical with that obtained by applying the test to a mixture of acetaldehyde and hydrogen peroxide, and the essential compound appeared to be epihydrin aldehyde. Whilst this compound did not occur in rancid fats, a derivative, probably the acetal, is suggested as being the parent substance which is decomposed on the addition of hydrochloric acid in the Kreis test. A number of substances give a red coloration with phloroglucinol-hydrochloric acid, and spectroscopic examination is necessary to obtain positive evidence of rancidity. A possible mechanism for the formation of epihydrin aldehyde or its parent substance from fats is described. A. G. P.

**Reactivity of Iodine towards Fats. III. Production of Acidity in the Reaction and the Mechanism of its Formation.** B. M. MARGOSCHES and W. HINNER (*Chem. Umschau*, 1924, **31**, 41—45).—Acids are produced in the reaction between fats or unsaturated fatty acids and iodine solutions, the quantity varying with the solvent used for the iodine. Brown iodine solutions obtained with aqueous solvents or solvents miscible with water, from which an amount of iodine is absorbed by the fat which

almost corresponds with its iodine value (Hübl), give a large amount of acid, corresponding with about half the iodine absorbed. Solutions of iodine in carbon tetrachloride, however, produce no acid in their action on fats, and other violet iodine solutions (in benzene, chlorinated ethylenes, and chloroform) give varying but comparatively small amounts of acid when they react on fats. In the action of aqueous and alcoholic iodine solutions on fats, an additive product of hypiodous acid and the unsaturated molecule is formed, and not a simple iodine additive product as commonly supposed. This view is supported by the qualitative and quantitative production of acid. The action is analogous to Wijs' explanation of the action of his iodine monochloride solution on unsaturated linkings. The iodine from violet iodine solutions is mainly absorbed by unsaturated fats as such, but the reaction does not by any means proceed to completion. In the case of brown iodine solutions, the active mass of the hydrogen iodide formed during the reaction, or added to the solution, opposes itself to the complete addition of hypiodous acid to the unsaturated linkings, and so reduces the absorption of iodine.

H. C. R.

**Oxidation of Lumbang and Linseed Oils and of the Principal Compounds in Lumbang Oil.** A. P. WEST and A. I. DE LEON (*Philippine J. Sci.*, 1924, **24**, 123—140).—When lumbang and linseed oils are blown under the same conditions at 75°, the percentage of apparent oxygen absorption, volatile products evolved, and total oxygen absorption in the early stages of oxidation are greater for lumbang than for linseed oil. As the oxidation process continues, the velocity of oxygen absorption increases more rapidly for linseed than for lumbang oil until after 100 hours the percentage of total oxygen absorption of linseed is greater than that of lumbang oil. Data giving the total percentage of oxygen absorption per hour during definite periods of time for these two oils indicate that for about the first 30 hours lumbang oil absorbs oxygen much more rapidly than does linseed oil. After 30 hours of oxidation, the rate of absorption of oxygen by lumbang oil gradually decreases, whilst the corresponding rate for linseed oil considerably increases. Both oils have about the same absorption velocity for oxygen for the period of oxidation extending from 30 to 40 hours. In the case of linseed oil, the velocity of oxygen absorption increases continually up to a period of 100 hours, beyond which the oxidation experiments were not continued. Both linseed and lumbang oils contain linolenic, linolic, and oleic glycerides, and also saturated glycerides. Linseed oil contains a much larger percentage of linolenic glycerides and of saturated glycerides than does lumbang oil. Possibly autocatalysts are formed in both these oils during oxidation and tend to accelerate the velocity of oxygen absorption, whilst the saturated glycerides present tend to retard the velocity of absorption. Constants of samples of lumbang and linseed oils blown for various periods of time at 75° were determined. Both oils gave very similar results. The surface tensions and refractive indices of both oils increased slightly on oxidation, whilst

the iodine values decreased considerably. Samples of lumbang oil oxidised for various periods of time were analysed. The percentage of oxidised glycerides increased, whilst the percentage of unoxidised unsaturated glycerides decreased. The linolenic glycerides of lumbang oil were oxidised more readily than the linolic and the linolic more readily than the oleic glycerides. H. C. R.

**Quantitative Reduction by Hydriodic Acid of Halogenated Malonyl Derivatives. III. Mechanism of the Reaction.**

R. W. WEST (*J. Chem. Soc.*, 1924, **125**, 710—721).—The reaction between  $\alpha$ -bromomalonyldimethylamide and hydriodic acid is bimolecular, and is probably indicated by the scheme  $\cdot\text{CO}\cdot\text{CHBr}\cdot \rightarrow \cdot\text{C}(\text{OH})\cdot\text{Br}\cdot \rightarrow \cdot\text{Cl}(\text{OH})\cdot\text{CHBr}\cdot \rightarrow \cdot\text{C}(\text{OH})\cdot\text{CH}\cdot + \text{IBr}$  (cf. Meyer, A., 1911, i, 350). The rate of reaction between hydriodic acid and  $\alpha\alpha'$ -dibromo-,  $\alpha\alpha'$ -chlorobromo-, and  $\alpha$ -bromo- $\alpha'$ -alkylmalondimethylamides is independent of the concentration of the potassium iodide, but varies with that of the acid present, indicating that the primary (slow) reaction is the hydrolysis  $\cdot\text{CXBr} + \text{H}_2\text{O} = \cdot\text{CXH} + \text{HOBr}$ , which is followed by the instantaneous reduction of the hypobromous acid. The rate of reduction of the  $\alpha$ -bromo- $\alpha'$ -alkylmalondimethylamides decreases in the order *isobutyl* (*methyl*), *n*-propyl, *isopropyl*, *n*-butyl, ethyl, which is identical with that for the rates of formation of the methylamides from the corresponding ethyl  $\alpha$ -alkylmalonates. The effect is to be ascribed to steric hindrance rather than to polarity. The following  $\alpha$ -alkylmalondimethylamides are obtained by heating the corresponding  $\alpha$ -alkylmalonic ethyl esters with alcoholic monomethylamine at 100—140°:  $\alpha$ -methyl-, colourless plates, m. p. 154°;  $\alpha$ -ethyl-, small needles, m. p. 176°;  $\alpha$ -*n*-propyl-, thin needles, m. p. 171°;  $\alpha$ -isopropyl-, colourless needles, m. p. 167°;  $\alpha$ -*n*-butyl-, colourless needles, m. p. 177°, and  $\alpha$ -isobutyl-malonodimethylamide, thin needles, m. p. 163°.  $\alpha$ -Bromo- $\alpha'$ -methylmalonodimethylamide, colourless needles, m. p. 114°, was prepared by brominating the above methyl derivative in chloroform, the following by brominating the corresponding  $\alpha$ -alkylmalonodimethylamides in glacial acetic acid, all as colourless needles:  $\alpha$ -bromo- $\alpha'$ -ethyl-, m. p. 136°;  $\alpha$ -bromo- $\alpha'$ -*n*-propyl-, m. p. 106°;  $\alpha$ -bromo- $\alpha'$ -isopropyl-, m. p. 101°;  $\alpha$ -bromo- $\alpha'$ -*n*-butyl-, m. p. 89°, and  $\alpha$ -bromo- $\alpha'$ -isobutyl-malonodimethylamide, m. p. 111°. F. G. W.

**Action of Diacetyltartaric Anhydride and Chlorofumaryl Chloride on Aromatic Amines and Hydrazines.** F. D.

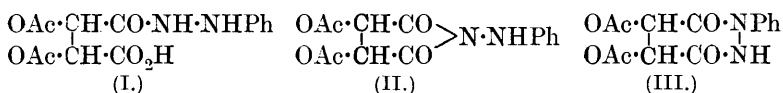
CHATTAWAY and G. D. PARKES (*J. Chem. Soc.*, 1924, **125**, 464—470).—Phenyliminosuccinanil (cf. T., 1923, **123**, 663) is obtained by the action of aniline on chlorofumaranilide at 150°. Chloromaleinanil,  $\begin{smallmatrix} \text{CCl}\cdot\text{CO} \\ | \\ \text{CH}\cdot\text{CO} \end{smallmatrix} > \text{NPh}$ , small, colourless needles, m. p. 170°, is formed

on heating the aniline salt of chloromaleic or chlorofumaric acid at 170—180°, and yields phenyliminosuccinanil on heating with aniline. Chloromalein-*p*-chloroanil, minute, glistening, irregular plates, m. p. 175°, and chloromalein-*p*-bromoanil, microcrystalline powder, m. p. 190°, are obtained similarly. Chlorofumarodiamide,

$\text{CONH}_2\cdot\text{CCl}\cdot\text{CH}\cdot\text{CONH}_2$ , needles, m. p.  $187^\circ$ , *chlorofumaro-dimethylamide*, minute, colourless needles, m. p.  $173^\circ$ ; *-di-p-chloroanilide*, clusters of pale yellow needles, m. p.  $223^\circ$ ; and *-di-p-bromoanilide*, minute, faintly yellow needles, m. p.  $236^\circ$ , are obtained by the action of chlorofumaryl chloride on ammonia and the corresponding amines, respectively. The *di-p-bromoanilide* is also obtained by the action of bromine in glacial acetic acid on chlorofumarodanilide.

Aqueous potassium hydroxide hydrolyses phenyliminosuccinanyl with formation of  $\beta$ -anilinoacrylic acid, whilst in alcohol the products are aniline, potassium oxalate, and potassium acetate.

*Phenylhydrazine diacetyltartrate*, a white, microcrystalline powder, melts partly at about  $70^\circ$  with loss of water and formation of *diacetyltartarophenylhydrazido-acid* (I), m. p.  $168^\circ$ , with formation of  $\alpha$ -*diacetyltartarophenylhydrazide* (II), small, faintly yellow needles,

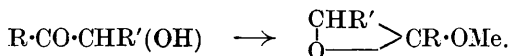


m. p.  $156^\circ$ , and this, on warming with sodium ethoxide in alcohol, is converted into  $\beta$ -*diacetyltartarophenylhydrazide* (III), minute, colourless, irregular plates, m. p.  $256^\circ$ . The action of excess of phenylhydrazine on diacetyltartaric anhydride, or on the above  $\alpha$ -hydrazide, affords tartarodiphenylhydrazide (T., 1903, **83**, 1349) and acetylphenylhydrazine. F. G. W.

**Formals of Primary Alcohols.** M. GHYSELS (*Bull. Soc. chim. Belg.*, 1924, **33**, 57—78).—Formals have been prepared by a direct distillation method from methyl, ethyl, *n*-propyl, *n*-butyl, isobutyl, and *n*-amyl alcohols. A non-volatile catalyst such as sulphuric acid or toluene-*p*-sulphonic acid is used which is eliminated immediately by the distillation. High yields of practically pure formals can be obtained in a single operation except in the cases of methylformal and ethylformal. Methylformal forms with the excess of alcohol an azeotropic mixture containing 92.15% of formal. Ethylformal gives a ternary azeotropic mixture with the excess of alcohol and the water produced in the reaction, from which it is separated by the addition of carbon disulphide; after separation of the aqueous layer and removal of the carbon disulphide, the ethylformal is obtained practically pure. *n*-Propylformal also yields a ternary azeotropic mixture with the excess of alcohol and water. All the formals prepared give binary azeotropic mixtures with water. The boiling points and approximate composition of these mixtures are given. R. B.

**Glucosidic Acetals derived from Simple  $\alpha$ - or  $\beta$ -Hydroxy-ketones and their Polymerisation.** M. BERGMANN and S. LUDEWIG (*Annalen*, 1924, **436**, 173—183; cf. Bergmann and Miekeley, A., 1921, i, 763; Fischer, A., 1895, i, 437).—The formation of glucosidic compounds from  $\alpha$ - or  $\beta$ -hydroxy-aldehydes or -ketones has not previously been observed. The authors have shown that

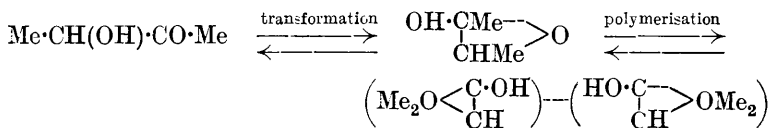
simple  $\alpha$ -hydroxyketones, such as acetol, acetoin, and benzoylcarbinol, yield glucosidic *cycloacetals* on treatment with methyl alcohol and hydrogen chloride, according to the scheme



These *cycloacetals* polymerise easily, being bimolecular in solution and in the vapour phases at low pressures and temperatures; when strongly heated, they dissociate, but on cooling the bimolecular form is again obtained as crystals. This phenomenon is a property of an  $\alpha\beta$ -oxygen bridge in glucosides, but the three cases mentioned are peculiar, as in the gaseous state they are easily dissociated. The acetals of acetoin and glycollaldehyde are bimolecular over a comparatively wide range of temperature, whereas acetol*cycloacetal* is dissociated at  $100^\circ$  under a pressure of a few millimetres. The derivatives of benzoylcarbinol cannot be examined owing to their high melting points. The following formulæ are suggested for dimeric acetoin*cycloacetal*.



It is known that  $\alpha$ -hydroxy-aldehydes and -ketones themselves polymerise to bimolecular forms, acetoin being an example. Refractometric measurements indicate that the unimolecular liquid form of acetoin possesses an alicyclic hydroxy-carbonyl structure. The change to the bimolecular crystalline form and the slow reverse change (at the ordinary temperature) indicate some structural alteration for which the following scheme is suggested :



Acetoin, b. p.  $140\text{--}144^\circ$ ,  $d_4^{17}$  0.9972,  $n_D^{17.3}$  1.4190, is best prepared from  $\gamma$ -bromobutan- $\beta$ -one by warming with an excess of potassium formate in dry methyl alcohol or with water and freshly precipitated calcium carbonate or potassium hydrogen carbonate. It is converted by acetic anhydride and pyridine into the acetate, b. p.  $169\text{--}173^\circ$ ,  $d_4^{16.5}$  1.038,  $n_D^{16.5}$  1.4157.

Acetoin may be polymerised by the action of granulated zinc at  $-15^\circ$  (cf. Diels and Stephan, A., 1907, i, 1000), when colourless crystals slowly separate, m. p.  $83^\circ$  (cf. von Pechmann and Dahl, A., 1890, 1234). Vapour density determinations in all cases were made by the method of Bleyer and Kohn, whence  $M=91$  (req.=88) at  $140^\circ/2$  mm. *Methyleycloacetal* was prepared from acetoin by the action of 1% methyl-alcoholic hydrogen chloride at  $0^\circ$ ; bis-acetoin may be employed (m. p.  $73\text{--}73.5^\circ$ , b. p.  $196\text{--}198^\circ/745$  mm.). In phenol solution, it is bimolecular and also at  $80^\circ/0.8$  mm., but



at higher temperatures the vapour dissociates and is unimolecular at  $140^{\circ}/2$  mm.

Acetol methylcycloacetal (m. p.  $127^{\circ}$ ), prepared from acetol by means of methyl-alcoholic hydrogen chloride, at  $100^{\circ}/10$  mm. is partly bimolecular, but at  $140^{\circ}/1.5$  mm. it is unimolecular.

Ethylglycoside (cf. Bergmann and Miekeley, *loc. cit.*) is bimolecular at  $140^{\circ}/8$  mm., and unimolecular at  $180^{\circ}/10$  mm.

The methylcycloacetal of benzoylcarbinol, m. p.  $192^{\circ}$ , was unimolecular at  $200^{\circ}$ , but at higher temperatures some secondary changes took place which interfered with the accuracy of the measurements.

A. E. C.

**Isomerism of Thioaldehydes.** E. FROMM and M. SOFFNER (*Ber.*, 1924, **57**, [B], 371—373).—A reply to Hinsberg (*A.*, 1923, i, 1056; cf. Fromm and Schultis, *A.*, 1923, i, 580).—The crude product (m. p.  $216^{\circ}$ ) of the action of hydrogen sulphide on formaldehyde, whether freshly prepared or preserved during several months, loses hydrogen sulphide when treated with lead oxide and sodium hydroxide. It is converted into the substance, m. p.  $247^{\circ}$  (Hinsberg's  $\beta$ -trithioformaldehyde), not only by hydriodic acid, but also by concentrated hydrochloric acid; the change is therefore due to transformation and not to reduction. The sulphoxides derived from trithioformaldehyde, m. p.  $216^{\circ}$ , and from the substance, m. p.  $247^{\circ}$ , are probably identical; their solubilities are the same, and they yield the same product when treated with concentrated hydriodic acid.

The properties of the compound formed from hydrogen sulphide and formaldehyde appear to be in harmony with the formula  $\text{SH}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{SH}$ ; the length of the chain cannot be determined, since there is no available method for the examination of the molecular weight of the compound. Oxidation of trithioformaldehyde or of the polymeric thioaldehyde, m. p.  $247^{\circ}$ , by hydrogen peroxide in acetic acid solution does not afford much insight into their constitution, since it is very probable that either compound is resolved into monomeric thioformaldehyde in the initial stages of the change.

$\alpha$ -Trithioformaldehyde, m. p.  $216^{\circ}$ , is the only compound of the group to which a definite molecular weight can be assigned. The degree of polymerisation of the product, m. p.  $247^{\circ}$ , cannot be ascertained, and it is purely arbitrary to regard it as a trimeride.

H. W.

**Formation of Acetone from Acetates.** E. HÄGGLUND and E. O. HEDMAN (*J. pr. Chem.*, 1924, [ii], **107**, 50—64).—Dry distillation of sodium acetate at  $400^{\circ}$  in a current of steam gives nearly as high a yield of acetone as the distillation of calcium acetate; when inert gases such as nitrogen are used in place of steam, the yield of acetone is not raised in this way. Mixing the sodium acetate with calcium oxide or carbonate or sodium carbonate raises the yield of acetone considerably, and also accelerates the reaction, acetone formation being practically complete in the first hour instead of in 3—4 hours. This accelerating action was also observed

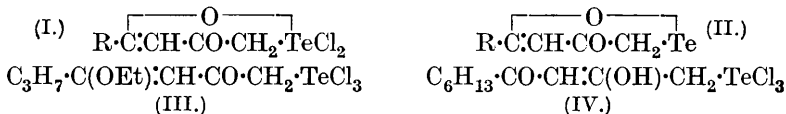
in an atmosphere of nitrogen. Rather more carbon monoxide and less carbon dioxide were produced than in the distillation of calcium acetate. Methane was only produced in quantity when sodium hydroxide was added to the sodium acetate; in this case very little acetone was produced. R. B.

### Density and Viscosity of Acetone at Low Temperatures.

E. H. ARCHIBALD and W. URE (*J. Chem. Soc.*, 1924, **125**, 726—731).—The following values were obtained for the density of acetone at the temperatures given: 0.0°, 0.8140; —10.0°, 0.8251; —20.0°, 0.8370; —30.0°, 0.8473; —40.0°, 0.8575; —50.0°, 0.8777; —70.0°, 0.8884; —80.0°, 0.9002; and —90.0°, 0.9117. Corresponding viscosities (absolute units) are: 0°, 0.00389; —10.6°, 0.00451; —20.4°, 0.00517; —30.3°, 0.00613; —40.0°, 0.00713; —49.9°, 0.00818; —59.7°, 0.00981; —69.7°, 0.01200; —79.7°, 0.01505; and —89.7°, 0.02051. The large increase in viscosity-temperature coefficient may account for the large conductivity-temperature coefficients found for solutions of organic substances in the liquid halogen hydrides. F. G. W.

**Interaction of Tellurium Tetrachloride and the Higher  $\beta$ -Diketones.** I. G. T. MORGAN and H. D. K. DREW (*J. Chem. Soc.*, 1924, **125**, 731—754).—The course of the reaction between tellurium tetrachloride and  $\beta$ -diketones, in chloroform or benzene, is determined by the complexity of the carbon chain of the diketone. If the solvent contains alcohol, the latter may enter into the reaction. The tellurium  $\beta$ -diketones, obtained by reducing the tellurium  $\beta$ -diketone dichlorides with potassium metabisulphite, are powerful bactericides (*Biochem. J.*, 1924, **18**, 190).

[With C. R. PORTER.]—*n*-Butyrylacetone yields, in pure chloroform, tellurium *n*-butyrylacetone dichloride (I), transparent, colourless prisms, m. p. 153—154° after darkening at 144°; in presence of alcohol, tellurium *O*-ethyl-*n*-butyrylacetone trichloride (III), golden-yellow needles, m. p. 105.5—106.5° (decomp.), is also formed.

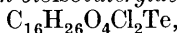


Tellurium *n*-butyrylacetone,  $\text{C}_7\text{H}_{10}\text{O}_2\text{Te}$  (II), forms yellow needles, m. p. 110—112°. *n*-Heptoylacetone yields tellurium *n*-heptoylacetone dichloride (see I), nacreous, compact, or acicular prisms, m. p. 87°, and tellurium *n*-heptoylacetone trichloride (IV), colourless, nacreous, six-sided plates, m. p. 117° (decomp.). Tellurium *n*-heptoylacetone,  $\text{C}_{10}\text{H}_{16}\text{O}_2\text{Te}$  (see II), forms yellow needles or golden-yellow scales, m. p. 86°, and shows residual acidity. The trichloride is not converted into the cyclic dichloride on boiling with pure chloroform, and addition of anhydrous aluminium chloride led to the formation of a crystalline aluminium derivative.

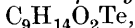
[With I. ACKERMAN.]—Dipropionylmethane yields tellurium dipropionylmethane dichloride,  $\text{C}_7\text{H}_{10}\text{O}_2\text{Cl}_2\text{Te}$ , thin, colourless, six-

sided plates (from acetone or benzene) darkening at  $157^{\circ}$ , and intumescing at  $162^{\circ}$ , or glistening prisms (from methyl alcohol), darkening at  $150^{\circ}$  and intumescing at  $170^{\circ}$  (cf. T., 1921, **119**, 616), and tellurium *O*-ethylpropionylmethane trichloride,  $C_9H_{15}O_2Cl_3Te$ , transparent, lemon-yellow prisms, m. p.  $110$ — $111^{\circ}$  (decomp.). Tellurium dipropionylmethane,  $C_7H_{10}O_2Te$ , forms very tough, golden-yellow needles, m. p.  $151^{\circ}$  (decomp.), sublimes at  $110^{\circ}$  under reduced pressure, and shows no enolic reactions.

Tellurium propionyl-*n*-butyrylmethane dichloride,  $C_8H_{12}O_2Cl_2Te$ , forms silvery flakes, darkening at  $150^{\circ}$ , m. p.  $156^{\circ}$  (decomp.). Tellurium propionyl-*n*-butyrylmethane,  $C_8H_{12}O_2Te$ , forms yellow needles, m. p.  $101$ — $102^{\circ}$  (decomp.). *iso*Butyrylacetone (b. p.  $163^{\circ}/752.5$  mm.; copper salt, light blue, voluminous, crystalline powder, m. p.  $167$ — $168^{\circ}$ ) yields tellurium *O*-ethylisobutyrylacetone trichloride,  $C_9H_{15}O_2Cl_3Te$ , pale yellow flakes or needles, m. p.  $103^{\circ}$  (decomp.). *iso*Valerylacetone (b. p.  $183^{\circ}/741$  mm.; copper salt, m. p.  $154^{\circ}$ ) yields tellurium bisisovalerylacetone dichloride,



transparent, colourless, acicular prisms, or nacreous leaflets, m. p.  $97$ — $98^{\circ}$  (decomp.), and tellurium *O*-ethylisovalerylacetone trichloride, small, compact, lemon-yellow, gem-like crystals, changing at  $88^{\circ}$  to a yellow glass having m. p.  $101$ — $102^{\circ}$  (decomp.).  $\gamma$ -Methylpropionylacetone [copper salt, dark olive-green crystals, m. p.  $174$ — $176^{\circ}$  (decomp.), or greenish-grey needles, m. p.  $175$ — $177^{\circ}$  (decomp.)], yields tellurium  $\gamma$ -methylpropionylacetone dichloride, colourless, glistening prisms, m. p.  $166$ — $167^{\circ}$  (decomp.) after sintering at  $164^{\circ}$ , which is reduced to the neutral tellurium  $\gamma$ -methylpropionylacetone, long, soft, pale golden needles, or elongated prisms, m. p.  $125$ — $126^{\circ}$  (decomp.), subliming at  $100^{\circ}$  in a vacuum.  $\gamma$ -Ethyl-*n*-butyrylacetone, colourless, fragrant oil, b. p.  $101$ — $102^{\circ}/9$  mm. [copper salt, m. p.  $166^{\circ}$  (decomp.)], yields tellurium  $\gamma$ -ethyl-*n*-butyrylacetone dichloride, nacreous rosettes of colourless, prismatic needles, m. p.  $140^{\circ}$  (decomp.). Tellurium  $\gamma$ -ethyl-*n*-butyrylacetone,

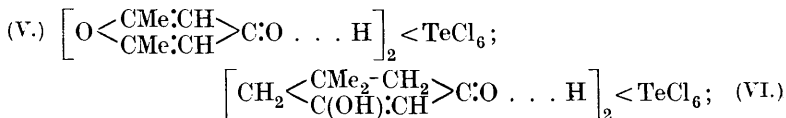


forms yellow needles, sintering at  $110^{\circ}$ , m. p.  $113^{\circ}$ , and is non-enolic.

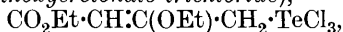
Dipropionylethylmethane,  $Et \cdot CH(CO \cdot Et)_2$ , forms a colourless oil with a pleasant, slightly peppery odour, b. p.  $105$ — $106^{\circ}/13$  mm.,  $202$ — $203^{\circ}/744$  mm. [copper salt, grey, microcrystals (from alcohol), m. p.  $178$ — $180^{\circ}$ , or silver-grey needles (from benzene), m. p.  $174$ — $176^{\circ}$ ]. Tellurium dipropionylethylmethane dichloride forms colourless, transparent, six-sided prisms, darkening from  $172^{\circ}$ , m. p.  $182^{\circ}$  (decomp.), and is reduced to tellurium dipropionylethylmethane, tough, golden needles, m. p.  $137$ — $138^{\circ}$  (decomp.), subliming at  $110^{\circ}$  in a vacuum. Tellurium  $\gamma\gamma$ -diethylacetylacetone dichloride forms colourless, nacreous flakes or prisms, softening at  $177^{\circ}$ , m. p.  $178$ — $180^{\circ}$ . Tellurium  $\gamma\gamma$ -diethylacetylacetone forms brittle, yellow, acicular needles, or needles with characteristically serrated edges, m. p.  $85$ — $86^{\circ}$ , and has no residual acidity.

Diacetylacetone yields a mixture of dimethylpyrone tellurichloride (V), spear-like aggregates of golden-yellow needles, and the oxy-

chloride  $[(C_7H_8O_2)H]_2TeOCl_4$ , colourless crystals, m. p.  $115^\circ$ . Tetraacetylene yields a substance crystallising in pale golden, six-sided plates or needles, blackening at  $135^\circ$ , which is hydrolysed

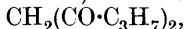


with formation of 3:4-diacetyl-2:5-dimethylfuran, of which it is probably the tellurichloride. Dimethyldihydroresorcinol affords *dimethyldihydroresorcinol tellurichloride* (VI), large, transparent, pale yellow prisms, resinifying at  $130^\circ$ , m. p.  $160-165^\circ$  (decomp.). Ethyl acetoacetate yields *tellurium ethyl O-ethylacetoacetate trichloride* (*tellurium ethyl  $\beta$ -ethoxycrotonate trichloride*),

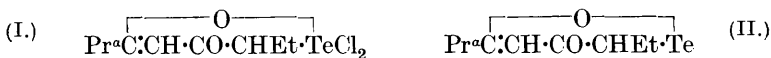


colourless plates, softening at  $88^\circ$ , m. p.  $90-92^\circ$  (decomp.  $140^\circ$ ). Definite products were not obtained by condensing tellurium tetrachloride with ethyl malonate, 3-allylacetylacetone, acetylmesityl oxide, acetylcamphor,  $\omega$ -phenylacetylacetone, benzylidenedisacetylacetone (non-enolic and dienolic forms) and 2-acetylcyclohexanone. The benzeneazo- $\beta$ -diketones yield bright yellow, stable compounds containing tellurium and halogen. F. G. W.

**Interaction of Tellurium Tetrachloride and the Higher  $\beta$ -Diketones.** II. G. T. MORGAN and R. W. THOMASON (J. Chem. Soc., 1924, 125, 754-759).—*Dibutyrylmethane*,



is obtained as a fragrant, colourless liquid, b. p.  $204-205^\circ$ , by the condensation of methyl propyl ketone with *n*-butyl *n*-butyrate or (in better yield) with ethyl *n*-butyrate. It forms a blue copper salt, m. p.  $156^\circ$ , and condenses with *p*-nitrophenylhydrazine to form 1-*p*-nitrophenyl-3:5-di-*n*-propylpyrazole,  $C_{15}H_{19}O_2N_3$ , yellowish-brown needles, m. p.  $53^\circ$ . It condenses with tellurium tetrachloride in chloroform with formation of *tellurium dibutyrylmethane dichloride* (I), vitreous needles (from methyl alcohol), m. p.  $148^\circ$ , or colourless needles (from alcohol or chloroform-petroleum), m. p.  $120-139^\circ$  or  $138-139^\circ$ , and *tellurium dibutyrylmethane trichloride*,  $Pr^aCO \cdot CH:C(OH) \cdot CHEt \cdot TeCl_3$  or  $Pr^aC(OH):CH \cdot CO \cdot CHEt \cdot TeCl_3$ , large, tabular crystals, m. p.  $87-88^\circ$ , with blackening. Both forms of the dichloride are reduced, with alkali hydrogen sulphite, to *tellurium dibutyrylmethane* (II), golden-yellow needles, m. p.  $97^\circ$ .

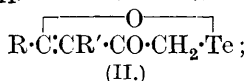
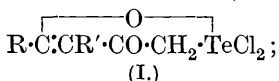


$\gamma$ -Ethylpropionylacetone,  $C_2H_5 \cdot CO \cdot CHEt \cdot CO \cdot CH_3$ , obtained by the action of ethyl iodide on sodium propionylacetone, forms a fragrant oil, b. p.  $192-193/755$  mm. (copper salt, m. p.  $176^\circ$ ). Tellurium  $\gamma$ -ethylpropionylacetone dichloride,  $C_8H_{12}O_2Cl_2Te$ , acicular prisms, m. p.  $167^\circ$  (decomp.), and tellurium  $\gamma$ -ethylpropionylacetone,  $C_8H_{12}O_2Te$ , pale yellow needles, m. p.  $109^\circ$ , are described.

$\gamma$ -*n*-Propylacetylacetone was obtained as a fragrant oil, b. p.

191—192°/745 mm. (*copper salt*, m. p. 215°), by the action of *n*-propyl iodide on sodium acetylacetone at 180° under pressure (cf. T., 1920, 117, 780). *Tellurium γ-n-propylacetylacetone dichloride*,  $C_8H_{12}O_2Cl_2Te$ , forms colourless, acicular prisms, m. p. (indefinite) 180°. *Tellurium γ-n-propylacetylacetone*,  $C_8H_{12}O_2Te$ , forms pale yellow needles, m. p. 106—107°. *γ-isoPropylacetylacetone*, prepared similarly to the *n*-propyl derivative, b. p. 182—183°/745 mm., has an odour of dry hay. It does not form a copper salt, and gives no coloration with ferric chloride. *Tellurium γ-iso-propylacetylacetone dichloride* forms lustrous, colourless, acicular prisms, blackening indefinitely at about 150°. *Tellurium γ-iso-propylacetylacetone* forms yellow needles, m. p. 152—153°. F. G. W.

**Interaction of Tellurium Tetrachloride and the Higher β-Diketones.** III. G. T. MORGAN and E. HOLMES (*J. Chem. Soc.*, 1924, 125, 760—765).—The isolation of the condensation products of tellurium tetrachloride and the β-diketones is rendered more difficult, as the series is ascended, by their increasing fusibility and solubility in organic media. *n*-Valerylacetone, a pungent oil, b. p. 194° (blue *copper salt*, m. p. 143°), is converted by tellurium tetrachloride into *tellurium n-valerylacetone dichloride*,  $C_8H_{12}O_2Cl_2Te$  ( $R=n-C_4H_9$ ,  $R'=H$ , in formula I), colourless needles, m. p. 125°; this is reduced by potassium metabisulphite to *tellurium n-valerylacetone*,  $C_8H_{12}O_2Te$  (see II), yellow needles, m. p. 80°. *n*-Hexoylacetone (blue *copper salt*, m. p. 138°) gives *tellurium n-hexoylacetone dichloride* ( $R=n-C_5H_{11}$ ,  $R'=H$ , in I), colourless



needles, m. p. 102°. *Tellurium n-hexoylacetone* (see II) forms brilliant yellow needles, m. p. 86°.

*γ-n-Butylacetylacetone*, b. p. 210—212°/750 mm. (grey *copper salt*, m. p. 186°) was prepared by the action of *n*-butyl iodide on sodium acetylacetone. *Tellurium γ-n-butylacetylacetone dichloride* ( $R=CH_3$ ,  $R'=n-C_4H_9$ , in I), lustrous, colourless crystals, m. p. 155°, is reduced to *tellurium γ-n-butylacetylacetone* (see II), primrose-yellow needles, m. p. 129°. *γ-n-Butylpropionylacetylacetone*, similarly obtained from propionylacetone, has b. p. 223—224°/745 mm. (*copper salt*, grey needles, m. p. 156°). *Tellurium γ-n-butylpropionylacetone dichloride* ( $R=C_2H_5$ ,  $R'=n-C_4H_9$ , in I), forms colourless leaflets, m. p. 103°. *Tellurium γ-n-butylpropionylacetone* (see II) forms golden-yellow needles, m. p. 93°. Methyl *n*-nonyl ketone was condensed with ethyl acetate and sodium to form *n-decoylacetone*, an oil with a sweet, penetrating odour, b. p. 276°/760 mm. (*copper salt*, pale blue needles, m. p. 114°). *Tellurium n-decoylacetone dichloride* ( $R=n-C_9H_{19}$ ,  $R'=H$ , in I), forms grey crystals, m. p. 49°, and *tellurium n-decoylacetone* (see II), yellow needles, m. p. 64°. F. G. W.

**Bactericidal Action of the Tellurium Derivatives of Aliphatic β-Diketones.** II. G. T. MORGAN, E. A. COOPER, and A. W. BURTT.—(See i, 591.)

**Pentosans. VII. Fusion of Xylan with Potassium Hydroxide.** E. HEUSER and J. ROTH (*J. pr. Chem.*, 1924, [ii], 107, 1—6; cf. A., 1923, i, 1061, 1181).—Fusion of xylan with 10 parts of potassium hydroxide and an equal weight of water for  $\frac{1}{2}$  hour to 2 hours gives oxalic, acetic, and formic acids in amounts depending on the temperature. Oxalic acid is formed most readily at 220—250° (yield 53%), with some evolution of hydrogen. Below 200° much xylan remains unchanged. The yields of acetic acid and formic acid at 230—280° vary from 13—15% and 9—12%, respectively. The presence of succinic acid has been proved, but its amount could not be determined. Succinic acid is not formed in the fusion and subsequently decomposed, for this acid was recovered practically unchanged after fusion with potassium hydroxide. Traces of pyrocatechol and protocatechuic acid have been detected, but the presence of these and other aromatic substances is attributed to the presence of impurities in the xylan. The amount of formic acid produced leads to the conclusion that the oxalic acid results from decomposition of the formate, as in the fusion of cellulose, a conclusion which was confirmed by measuring the hydrogen evolved when the fusion was conducted in a stream of nitrogen.

R. B.

**Mutarotation of the Sugars.** R. GILMOUR (*J. Chem. Soc.*, 1924, 125, 705—706).—A question of priority (cf. Gilmour, P., 1909, 25, 225; Baker, Ingold, and Thorpe, this vol., i, 262).

F. G. W.

**Chemical Effects of  $\gamma$ -Rays of Radium.** A. SLOSSE (*Compt. rend. Soc. Biol.*, 1923, 89, 96—98; from *Chem. Zentr.*, 1924, i, 33—34).—The effect of the radiations from radium bromide enclosed in a sealed tube and immersed in a solution of pure dextrose was to produce a small decrease in optical activity, attributed to a partial transformation of  $\beta$ - into  $\gamma$ -dextrose. The presence of formaldehyde was established; no other degradation products of dextrose were found. After subjection to radiation, the dextrose solution became much more readily oxidisable by potassium permanganate and sulphuric acid.

G. W. R.

**Glucose [Dextrose] from  $\alpha$ - and  $\beta$ -Glucosides.** H. COLIN and [MLLE.] A. CHAUDUN (*Compt. rend.*, 1924, 178, 779—782).—The hydrolysis of  $\alpha$ - and  $\beta$ -methyl-, of  $\alpha$ - and  $\beta$ -ethyl-glucosides, and of salicin, has been followed polarimetrically and by copper titration. Salicin hydrolyses initially to give a glucose of low rotatory power (increasing with time) and is therefore a  $\beta$ -glucoside.

E. E. T.

**Acetone-sugars and their Derivatives. I. The Constitution of Glucosediacetone [Diisopropylidene-glucose] and a new Benzoylglucosemonoacetone.** H. OHLE (*Ber.*, 1924, 57, [B], 403—409).—The action of aniline hydrochloride on benzoylglucosediacetone (Fischer and Noth, A., 1918, i, 226) in boiling, absolute alcoholic solution leads to the formation of a second

*benzoylglucosemonoacetone*,  $\text{CMe}_2\cdot\text{C}_6\text{H}_5\text{O}_5\cdot\text{OBz}$ ,  $[\alpha]_D^{20} -26^\circ$  in alcoholic solution, which could not be caused to crystallise. In so far as hydrolysis does not occur, it is stable towards dilute acids, but is rapidly converted by traces of alkali into the crystalline benzoylglucosemonoacetone of Fischer and Noth (*loc. cit.*). The constitution of the new derivative has not been established completely, but it is considered to be the primary product of the action from which Fischer's compound is obtained by isomerisation. Since Fischer, Pfähler, and Brauns (A., 1920, i, 840) have shown that the wandering of acyl groups occurs from the secondary to the primary alcoholic hydroxy group, it is assumed that the crystalline product is  $\zeta$ -benzoylglucosemonoacetone. This hypothesis is supported by the observations that it is the sole isolable product of the action of benzoyl chloride on glucosemonoacetone in the presence of pyridine, and that both benzoylglucosemonoacetones are convertible into the same tribenzoylglucosemonoacetone, the experimental conditions being such that isomerisation is excluded.

Glucosemonoacetone reacts with acetone to form glucosediacetone as readily in the presence of anhydrous copper sulphate as in that of hydrogen chloride. A similarly ready reaction is observed in the cases of glycerol and of glyceryl  $\alpha$ -benzoate.

It is suggested that the wandering of acyl and alkyl groups is more frequent than has been assumed previously in the chemistry of the sugars. The discordant results obtained by Irvine and Patterson (T., 1922, 121, 2146) and by Levene and Meyer (A., 1923, i, 92) by the oxidation of methylglucosediacetone are probably attributable to this cause.

H. W.

**Crystallisation of Sucrose.** J. A. KUCHARENKO (*Louisiana Planter*, 1923, 71, 211—213, 231—232).—The concentration of supersaturated solutions of sucrose at the instant of crystallisation was determined at various temperatures; by the correlation of surface,  $S$ , and weight,  $P$ , in the equation  $S^3=kP^2$ , the rate of crystallisation of solutions of various degrees of supersaturation could be accurately measured. The speed of crystallisation was found to vary directly with the degree of supersaturation and with the temperature employed.

CHEMICAL ABSTRACTS.

**The System Maltose-Water.** J. GILLIS (*Rec. trav. chim.*, 1924, 43, 135—143).—The author has studied the lowering of the melting point of ice for high concentrations of maltose both in pure water and in the presence of ammonia. The resulting curve is shown together with the solubility curve of maltose between  $0^\circ$  and  $96.5^\circ$ . From the latter, the inference is drawn that the monohydrate of  $\beta$ -maltose exists as the solid phase in equilibrium with the solution up to the neighbourhood of  $100^\circ$ . The solubility curve is compared with the curves of lactose (Gillis, A., 1921, i, 11) and of dextrose (Jackson and Silsbee, A., 1922, i, 986).

H. J. E.

**Acetobromomaltose.** H. FISCHER and F. KÖGL (*Annalen*, 1924, 436, 219—228; cf. E. and H. Fischer, A., 1910, i, 716; Karrer, A., 1921, i, 310, 313, 768).—The authors question the

purity of the acetobromomaltose obtained by Karrer's method, as from this specimen a yield of only 30% of hepta-acetylmaltose is obtainable, whereas from their specimen a 70% yield is produced. Further, the acetobromomaltose obtained by Karrer's method has a very high bromine content, which indicates that some secondary reaction has taken place. Pure acetobromomaltose is prepared by allowing maltose to stand with acetyl bromide for 20–40 minutes at 0°; it is an amorphous solid which after 7 months' drying gave  $[\alpha]_D^{15.5} +171.5^\circ$  in chloroform. Hepta-acetylmaltose, microscopic needles, m. p. 174–175°, was obtained by the action of sodium acetate and acetic acid on the bromo compound, the total yield being 70%. The specific rotation increased to a constant value on preservation, and, after 48 hours, is  $[\alpha]_D^{10} +103.01^\circ$  in *s*-tetrachloroethane.

*Hepta-acetylbenzylmaltoside*, colourless prisms, m. p. 125°,  $[\alpha]_D^{16.5} +27.76^\circ$  in *s*-tetrachloroethane, was prepared from an absolute ethereal solution of the bromo compound by shaking with silver carbonate and benzyl alcohol. It is hydrolysed by methyl-alcoholic ammonia at 0° to *benzylmaltoside*, m. p. 147–148°,  $[\alpha]_D^{17} +47.64^\circ$  in aqueous solution.

*Hepta-acetylethylmaltoside*, prepared in the same way as the benzyl derivative, crystallises in prisms, m. p. 132°,  $[\alpha]_D^{14} +48.93^\circ$  in *s*-tetrachloroethane. It is hydrolysed to *ethylmaltoside*, m. p. 168–169°.

*Hepta-acetylmethylmaltoside*, m. p. 130–131°, is prepared in the same manner as the ethyl homologue. *Hexa-acetylmaltal* is obtained by the reduction of a solution of the acetobromomaltose in 50% acetic acid by zinc dust at 10°; it crystallises in colourless prisms, m. p. 134°,  $[\alpha]_D^{16.5} +64.15^\circ$ . It adds on one atomic proportion of bromine in chloroform solution and on warming with water loses one acetyl group, leaving the penta-acetyl derivative as fine needles, m. p. 123°. This on acetylation with acetic anhydride and pyridine gives a substance, m. p. 113–114°, which has not been further examined.

A. E. C.

**Lactosan.** A. PICTET and M. M. EGAN (*Helv. Chim. Acta*, 1924, 7, 295–297).—When lactose is carefully heated at 120–130° at 4–6 mm., it loses its water of crystallisation, and at 185° in 10 to 12 hours it is converted into the anhydride, *lactosan*,  $C_{12}H_{20}O_{10}$ , a white, amorphous powder, m. p. 200–202° (decomp.),  $[\alpha]_D^{16} +65.5-66.0^\circ$ , without mutarotation. It is readily soluble in water, and its reducing power in terms of Fehling's solution is 61% of that of dextrose. Brewer's yeast does not ferment it. With phenylhydrazine, it gives the osazone of lactose, and when acetylated it gives octa-acetyl-lactose. Lactosan is polymerised by heating at 105°/15 mm. for  $\frac{1}{4}$  hour with a trace of zinc chloride, forming a *tetralactosan*,  $(C_{12}H_{20}O_{10})_4$ , m. p. 245–246° (decomp.), which does not reduce Fehling's solution. By fuming hydrochloric acid, lactosan is partly converted into lactosyl chloride. The properties of lactosan indicate that it is  $\epsilon$ -galactosylglucosan.

E. H. R.



**Degradation of Starch by Salts.** W. S. ILJIN (*Biochem. Z.*, 1924, **145**, 14—17; cf. also Iljin, A., 1923, i, 172; Haehn, A., 1923, i, 443; Biedermann, A., 1923, i, 665).—Further experiments are described in which starch in dilute solution is hydrolysed by various concentrations of sodium, lithium, and calcium chlorides without the intervention of an enzyme. Potassium, magnesium, and barium chlorides are said to give similar results. J. P.

**Action of Weak Bases on Cellulose Nitrate.** G. G. GIANNINI (*Gazzetta*, 1924, **54**, 79—85).—Determinations of the compositions and of the molecular weights in freezing acetic acid exhibited by two preparations of the product obtained by Angeli by the action of pyridine on cellulose nitrate (A., 1919, i, 196; 1922, i, 922) containing, respectively, 8.98% and 10.08% N, as well as analyses of the gaseous mixtures emitted during their preparation, suggest that pyridine produces in cellulose nitrate a gradual denitration varying in velocity with the temperature. T. H. P.

**Triphenylmethyl Ethers of Cellulose and Starch.** B. HELFERICH and H. KOESTER (*Ber.*, 1924, **57**, [B], 587—591; cf. A., 1923, i, 331).—Cellulose, preferably in the form of material which has been regenerated from the xanthate (1 part), is converted by triphenylmethyl chloride (6 parts) and pyridine (14 parts) at 100° during 14—32 hours into *cellulose triphenylmethyl ether*,  $C_{25}H_{24}O_5$ , a pale pink, voluminous powder, m. p. about 260° (decomp.), which swells in contact with many organic media and gives colloidal solutions in pyridine, chloroform, and bromoform. Further prolongation of the reaction or use of a larger excess of triphenylmethyl chloride does not lead to the etherification of more hydroxyl groups. The ether is readily hydrolysed by hydrogen chloride in chloroform solution, yielding triphenylmethyl chloride (or the carbinol if water is present) and a carbohydrate which is identical analytically with the original material. If triphenylmethylcellulose is heated with acetic anhydride and pyridine on the water-bath, approximately one acetyl group is introduced into each dextrose component; with chloroacetyl chloride and pyridine, esterification takes place to a greater extent. Rice starch yields *starch triphenylmethyl ether*,  $C_{25}H_{24}O_5$ , which closely resembles the corresponding cellulose ether. H. W.

**Adsorption of Aluminium Hydroxide from Aluminium Sulphate Solutions by Cotton and Wood Cellulose.** C. G. SCHWALBE (*Z. angew. Chem.*, 1924, **37**, 125—128).—The contradictions which occur in the literature as to whether aluminium hydroxide is adsorbed from aluminium sulphate solutions by cotton and wood cellulose are ascribed to the fact that the adsorptive power of fibres is conditioned by a large number of variable factors such as the period and temperature of steeping, the concentration of the solution in which the fibre is steeped, and especially the previous history of the fibre, circumstances which have an important effect on the nature of its surface. Cotton cellulose which had been stored for 7 years in a dry place failed to adsorb aluminium

from solutions of the sulphate or acetate or from sodium aluminate even after milling for 7 hours in a ball mill. In order to study the effects of the presence of hydrocellulose and oxycellulose, strips of cotton fabric were treated with 3% sulphuric acid and heated for 4 hours at 70°, and others were over-bleached before being used in adsorption experiments. The ash content of the samples so treated was found to increase very appreciably after steeping in an aluminium sulphate solution and subsequent washing. It is uncertain whether this increase in the adsorptive power of the fabric is due to the presence of hydrocellulose and oxycellulose or to a change in the nature and extent of the surface. Sized wood cellulose pulp is capable of adsorbing much greater quantities of aluminium hydroxide than the undamaged fibres, and the adsorptive power increases with the fineness of comminution up to a certain point, and thereafter remains approximately constant. The swelling of wood cellulose fibres exerts a great influence on their power of adsorbing aluminium hydroxide. The number of factors which affect the adsorptive power of wood cellulose is even greater than in the case of cotton cellulose, owing to the varying quantities of pentosans and hexosans which may be present. H. C. R.

**Quantitative Determination of the Fluorescent Powers (the Spectro-fluorescometry) of Cellulose and its Derivatives. IV.**

S. J. LEWIS (*J. Soc. Dyers and Col.*, 1924, **40**, 111—114).—A continuation of work previously described (this vol., i, 374). No essential differences were found in the fluorescent properties of yarn and ribbon prepared from the same solution of viscose, of hydrocellulose prepared by the action of sulphuric or hydrochloric acid on cotton linters, or of oxycellulose prepared by means of a hypochlorite or potassium permanganate. Experiments with cellulose tendered, by means of acids and exposure to daylight, indicate that changes in fluorescent power appear to be more noticeable in the region of  $\lambda$  2900. Paper, after exposure for 3 weeks to radium, showed no fluorescence. It is again concluded that the physical condition of the material has but little effect on its fluorescent properties. A. J. H.

**Polysaccharides. XXV. Methylation Products of Reserve Cellulose (Lichenin).**

P. KARRER and K. NISHIDA (*Helv. Chim. Acta*, 1924, **7**, 363—370).—Continuing previous work (this vol., i, 373), fresh evidence is put forward confirming the chemical similarity between lichenin or reserve cellulose and structural cellulose. Exhaustive methylation of lichenin gives a product containing 41.9% of methoxyl, compared with a maximum of 42—43% in the case of cotton. Methylated lichenin dissolves in cold water to a colloidal solution which coagulates on warming. In some respects, it resembles methylated hydrocellulose more than methylated cellulose, but, unlike the former, it does not depress the freezing point of water. The methylated lichenin, when heated with 1% methyl-alcoholic hydrogen chloride, gives trimethyl- and dimethyl-methylglucosides in similar proportions to those obtained from fully methylated cellulose by Irvine and Hirst (*T.*, 1923, **123**,

529). The yield of trimethylglucose obtained by hydrolysis of the glucoside is smaller, however, than the 85% obtained by Irvine and Hirst. E. H. R.

**Galegine.** E. SPÄTH and S. PROKOPP (*Ber.*, 1924, **57**, [B], 474—480; cf. Tanret, A., 1914, i, 859).—Galegine is converted by hydrogen in the presence of palladised charcoal to *dihydrogalegine*,  $\text{CHMe}_2 \cdot [\text{CH}_2]_2 \cdot \text{N} \cdot \text{C}(\text{NH}_2)_2$ , the constitution of which is deduced from its conversion by barium hydroxide into carbamide and *isoamylamine* and its synthesis from *isoamylamine* and cyanamide. Since galegine on oxidation with permanganate yielded acetone but no trace either of formaldehyde or *isobutaldehyde*, it must have the composition  $\text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{N} \cdot \text{C}(\text{NH}_2)_2$  (cf. Barger and White, this vol., i, 272). An improved method for the isolation of galegine is described, consisting essentially in extracting the free base from its aqueous solution by means of amyl alcohol. Dihydrogalegine sulphate, white crystals, the *picrate*, yellow crystals, m. p. 173—174°, and *m-nitrobenzoyl* derivative of *isoamylamine*, m. p. 81—82°, are described. F. A. M.

**Composition of Japanese Petroleum.** I. S. KOMATSU and S. KUSUMOTO (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 77—84).—The fraction of petroleum from Nishiyama, Echigo, distilling below 90°, is shown to consist mainly of methylcyclopentane, b. p. 71—72°,  $d_4^{25}$  0.7295,  $n_D^{25}$  1.3965, and cyclohexane, b. p. 80—81°,  $d_4^{25}$  0.765,  $n_D^{25}$  1.414. [Cf. *B.*, 1924, 408.] W. A. S.

**The Hydrogenating, Reducing, and Oxidising Action of Hydrazine on Organic Compounds.** E. MÜLLER and H. KRAEMER-WILLENBERG (*Ber.*, 1924, **57**, [B], 575—583).—Benzyl alcohol reacts with 2 mols. of nearly anhydrous hydrazine at 180° to give nitrogen and toluene; if 4 mols. of hydrazine are used, hexahydrotoluene is obtained. At 280° benzene gives cyclohexane, together with a small proportion of adipic acid (the requisite oxygen is derived from the trace of water present in the hydrazine). Toluene, *o*-, *m*-, and *p*-xylenes, mesitylene, and cymene are similarly transformed into their hexahydro-derivatives, hydrogenation occurring under milder experimental conditions with respect to temperature and duration as the number of carbon atoms in the hydrocarbon molecule increases. Pyridine and quinoline are not affected by hydrazine at any temperature up to 330°. Hydrobenzoin yields diphenylethylene oxide, m. p. 56°.

Monohydric phenols are not hydrogenated by hydrazine. At 100°, phenol gives the compound  $(\text{Ph} \cdot \text{OH})_2 \cdot \text{N}_2\text{H}_4$ , m. p. 63°, which is unchanged by hydrazine at 200°. *p*-Cresol and *s*-xylenol yield similar salts, the *p*-cresol compound forming colourless needles, m. p. 61—62°. Polyhydric phenols are oxidised by hydrazine, as is evidenced by the copious formation of ammonia. *Quinol hydrazine*,  $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2$ , long, colourless needles, m. p. 154°, and resorcinol yield solid, nitrogenous products the constitution of which could not be elucidated.

Ethylene glycol is reduced by hydrazine at 200° to ethyl alcohol.

Glycerol is transformed into methyl alcohol, formic, acetic, and racemic acids. Erythritol yields oxalic acid, whereas dulcitol gives a hexose which is converted by phenylhydrazine into an osazone,  $C_{18}H_{22}O_4N_4$ , pale yellow needles, m. p.  $205^\circ$ . *d*-Mannitol yields dextrose. Cellulose is oxidised by hydrazine. H. W.

**The System *cyclo*Hexane-Aniline.** E. H. BUCHNER and D. KLEYN (*Rec. trav. chim.*, 1924, **43**, 153—157).—The critical temperatures of mixtures of *cyclo*hexane and aniline containing up to 40.1% of the latter were determined. The curve is regular and on extrapolation gives  $427^\circ$  as the critical temperature of aniline (cf. Guye and Malet, A., 1902, ii, 302). As no maximum was observed, the system is regarded as an exception to the general rule, and doubt is cast on the conclusions drawn by Buchner (A., 1918, ii, 9) in another case. The mutual solubilities of the two substances were also investigated; above  $31.3^\circ$ , there is complete miscibility in all proportions. H. J. E.

**Catalytic Preparation of Amines.** E. BRINER, P. FERRERO, and E. DE LUSERNA (*Helv. Chim. Acta*, 1924, **7**, 282—294).—Attempts were made to obtain aniline (i) by passing a mixture of benzene and ammonia vapours over a heated catalyst, (ii) from phenol and ammonia in a similar manner. From benzene and ammonia only traces of aniline could be obtained under any conditions; the observations of Wibaut are therefore confirmed (A., 1917, i, 386). The result is only to be expected, as the reaction is endothermic,  $C_6H_6 + NH_3 = NH_2Ph + H_2 - 23.6$  Cal. The second reaction gives appreciable yields of aniline, up to 12% of the theoretical, the best results being obtained using alumina as catalyst at  $420^\circ$ , with excess of ammonia and prolonged contact. The reaction in this case is exothermic,  $PhOH + NH_3 = NH_2Ph + H_2O + 0.4$  cal. With thoria as the catalyst, only traces of aniline are obtained, but appreciable quantities of diphenyl ether and phenylene oxide; these products are obtained also in absence of ammonia. When methyl alcohol mixed with phenol and ammonia vapours is passed over heated alumina, a mixture of methyl- and dimethylanilines is obtained, the former predominating, but the yields are smaller than those from phenol and ammonia alone. In presence of thoria some anisole is formed. E. H. R.

**Freezing-point Curves for the System 2-Chloroacetanilide-4-Chloroacetanilide.** K. J. P. ORTON and G. OWEN (*J. Chem. Soc.*, 1924, **125**, 766—767).—Owen's method (*J. Chem. Soc.*, 1923, **123**, 3393) has been applied to an examination of the freezing-point curves for the system 2-chloroacetanilide-4-chloroacetanilide. The results were in harmony with the behaviour of the system 2 : 4-dichloroacetanilide-4-chloroacetanilide, the lower-melting polymorph of 4-chloroacetanilide previously observed (*J. Chem. Soc.*, 1909, **95**, 1059) never separating from the liquid mixture in bulk but only when small quantities were cooled very slowly in capillary tubes. R. B.

**Action of Hydrogen Chloride on a Dry Solution of a Chloroamine.** F. G. SOPER (*J. Chem. Soc.*, 1924, **125**, 768—769).—The action of dry hydrogen chloride on a solution of 2:4-dichloro-*N*-chloroacetanilide in glacial acetic acid gives no trace of chlorine except in presence of moisture. This result suggests that hydrolysis,  $\text{:NCl} + \text{H}_2\text{O} \rightleftharpoons \text{:NH} + \text{HOCl}$ , is the first step in the production of chlorine and that the appearance of this gas is due to a subsequent interaction,  $\text{HCl} + \text{HOCl} \rightleftharpoons \text{Cl}_2 + \text{H}_2\text{O}$ . R. B.

**Solubility of Anilinesulphonic Acids.** J. C. PHILIP and R. S. COLBORNE (*J. Chem. Soc.*, 1924, **125**, 492—500).—The solubility relations previously found to obtain between sulphanilic acid and water (*J. Chem. Soc.*, 1913, **103**, 284) have now been found to be characteristic of the anilinesulphonic acids generally. A notable feature of these acids is the readiness with which they form supersaturated solutions, from which under suitable conditions unstable hydrates may readily be produced. Solubility determinations show that these hydrates are not stable at any temperature on the solubility curve, but are either completely labile or are metastable over a small temperature range in the neighbourhood of 0°. Aniline-*o*-sulphonic acid forms a *monohydrate*, stable below 13.5°; above this temperature, the anhydrous acid is the stable solid phase. Aniline-*m*-sulphonic acid forms a sesquihydrate which separates below 20° as a metastable phase, with a greater solubility than that of the anhydrous acid. *p*-Bromoaniline-*o*-sulphonic acid gives, below 30°, a monohydrate which is metastable with respect to the anhydrous acid even at 0°, although its solubility can be readily measured up to 25°. *p*-Bromoaniline-*m*-sulphonic acid exists in two enantiotropic forms, the rhombic, stable above 100°, the monoclinic, stable at the ordinary temperature, and separation of the metastable monohydrate furnishes the most striking example of the class. This hydrate separates as a felted mass of crystals, which only slowly changes to the less soluble anhydrous acid. *p*-Chloroaniline-*o*-sulphonic acid with water at 0° slowly changes to a stable monohydrate, but no unstable hydrate was observed. *p*-Chloroaniline-*m*-sulphonic acid at 0° forms small tablets of a metastable monohydrate. R. B.

**Chemotherapeutical Researches in the Series 205 Baeyer. Carbamates of the Aminobenzoylaminonaphthalenesulphonic Acids.** E. FOURNEAU, J. TRÉFOUËL, (MME.) J. TRÉFOUËL, and J. VALLÉE (*Ann. Inst. Pasteur*, 1924, **38**, 81—114).—A more detailed account of work already noted (this vol., i, 382).

**Absorption Spectra of some Derivatives of Phenol and other Substances.** J. E. PURVIS.—(See this vol., ii, 219.)

**Fluorescence Spectra. II. Phenol and Phenolic Ether Vapours.** J. K. MARSH.—(See this vol., ii, 219.)

**Action of the Oxides and the Oxy-acids of Nitrogen on Diphenyl Ether.** H. RYAN and P. T. DRUMM (*Sci. Proc. Roy. Dubl. Soc.*, 1924, **17**, 313—320).—Diphenyl ether treated with

nitrogen peroxide alone or in carbon tetrachloride solution, or with nitrous fumes in the same solvent, gave a mixture of *op'*- and *pp'*-dinitrodiphenyl ethers (cf. Mailhe and Murat, A., 1912, i, 346; 1913, i, 44), with some 2:4-dinitrophenol; with nitrous fumes in acetic acid solution, the main product was the *p*-mono-nitro derivative. The latter was also formed when the ether was treated with nitric acid (*d* 1.4) either alone or in carbon tetrachloride or acetic acid. With fuming nitric acid (*d* 1.5) a mixture of the *pp'*-dinitro- and 2:2':4:4'-tetranitro-diphenyl ether, m. p. 195°, was formed. This derivative was also obtained from 2:4-dinitrochlorobenzene and 2:4-dinitrophenol and by further nitration of 2:4-dinitrodiphenyl ether and of 2:4:4'-trinitrodiphenyl ether (cf. Cook, A., 1910, i, 731). 2:4:6-Trinitrodiphenyl ether (from picryl chloride and potassium phenoxide) and the 2:4:6:2'-tetranitro compound (prepared in a similar way) both gave on further nitration 2:4:6:2':4'-pentanitrodiphenyl ether, colourless needles, m. p. 210°. W. A. S.

**Action of the Oxides and the Oxy-acids of Nitrogen on Phenyl Benzyl Ether.** H. RYAN and J. KEANE (*Sci. Proc. Roy. Dublin Soc.*, 1924, 17, 287—295).—Treatment of phenyl benzyl ether in the cold, and for a long time if necessary, with nitrogen peroxide, gaseous or in carbon tetrachloride solution, with nitrous fumes or with nitric acid, alone or in carbon tetrachloride solution (cf. A., 1919, i, 13; 1923, i, 323), gave mostly *p*-nitrophenyl benzyl ether, a little *p*-nitrophenyl *p*-nitrobenzyl ether (cf. Kumpf, A., 1884, 1005), and varying amounts of decomposition products. Nitration seemed not to proceed with nitric acid in acetic acid or ether solution. Further nitration of *p*-nitrophenyl benzyl ether was brought about by treatment with nitric acid in carbon tetrachloride solution, but again not in acetic acid or alcohol. The product was the above dinitro derivative. With nitric acid alone, a mixture of *o*-*p*-dinitrophenyl *p*-nitrobenzyl ether, colourless prisms, m. p. 207—208°, and *o*-*p*-dinitrophenyl *o*-nitrobenzyl ether, needles, m. p. 188°, was formed. These compounds were also obtained by treating *o*-nitrophenyl benzyl ether in a similar way. Both trinitro derivatives were converted by the action of a mixture of fuming sulphuric and nitric acids into the same product, viz. *o*-*o*-*p*-trinitrophenyl *o*-*p*-dinitrobenzyl ether, scales, m. p. 146°. An attempt to prepare a hexanitro derivative of the ether resulted only in the isolation of a decomposition product, m. p. 139—140°. W. A. S.

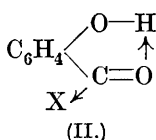
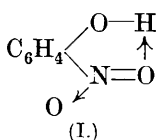
**Action of the Oxides and the Oxy-acids of Nitrogen on Diphenyl Ethylene Ether.** H. RYAN and T. KENNY (*Sci. Proc. Roy. Dublin Soc.*, 1924, 17, 305—311).—Diphenyl ethylene ether,  $\text{Ph}\cdot\text{O}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{Ph}$ , treated with gaseous nitrogen peroxide, or nitrogen peroxide in carbon tetrachloride solution, or with nitric acid (*d* 1.5), alone or in carbon tetrachloride solution, gave mostly the *pp'*-dinitro derivative, m. p. 143° (cf. Weddige, A., 1881, 1136), accompanied by 2:4-dinitrophenol and decomposition products. Nitration did not take place with nitric acid dissolved in acetic acid. Phenyl *o*-nitrophenyl ethylene ether, rectangular plates, m. p.

97°, and the corresponding *p*-nitro derivative, prisms, m. p. 86°, were prepared by interaction of the corresponding potassium nitrophenoxide and  $\omega$ -bromophenetole. Di-*o*-nitrophenyl ethylene ether was prepared similarly (Weddige, *loc. cit.*). From the *o*-nitro and this di-*o*-nitro derivative, by further nitration, *o*-nitrophenyl *o*-*p*-dinitrophenyl ethylene ether, m. p. 172°, was obtained. All these lower nitrated derivatives gave ultimately *di*-2:4-dinitrophenyl ethylene ether, pale yellow, flat prisms, m. p. 214°, and continued action of nitric acid destroyed the molecule. *o*-Nitrophenyl *p*-nitrophenyl ethylene ether, rectangular prisms, m. p. 117·5°, was also prepared synthetically. W. A. S.

**Solubility of the Aminophenols.** N. V. SIDGWICK and R. K. CALLOW (*J. Chem. Soc.*, 1924, **125**, 522—527).—As regards solubility in water and benzene, the aminophenols are an abnormal group, their abnormality resembling that of the phenylenediamines (*Chem. Soc. Trans.*, 1923, **123**, 2817) rather than the usual type. The *o*-compound is less soluble in water than the *p*-isomeride; in benzene, the solubilities are about the same. The *m*-compound is more soluble in water and less soluble in benzene than either of its isomerides. *m*-Aminophenol very readily forms supersaturated solutions in water, consequently it was possible to follow the two-liquid curve up to 60—70° below the saturation point, and even to measure the metastable ice curve in dilute solutions. This appears to be a general property of *m*-derivatives (cf. *Chem. Soc. Trans.*, 1922, **121**, 2256). The following boiling points were determined at 11 mm. pressure: *m*-aminophenol, 164° (with very slight decomp.); *p*-aminophenol, 174° (after melting with decomp.). *o*-Aminophenol sublimes rapidly at 153°. (Cf. following abstract.) R. B.

**Abnormal Benzene Derivatives.** N. V. SIDGWICK and R. K. CALLOW (*J. Chem. Soc.*, 1924, **125**, 527—538).—The results of a series of investigations (*Chem. Soc. Trans.*, 1915, **107**, 1202; 1920, **117**, 389, 396; 1921, **119**, 979, 1001, 1013; 1922, **121**, 1844, 1853, 2256, 2263, 2586; 1923, **123**, 2813, 2819, and preceding abstract) on the volatility and solubility in the liquid state of certain classes of benzene derivatives are summarised and a possible explanation of the phenomena is discussed. The benzene derivatives in question are described as abnormal because the isomerides differ widely in their vapour pressures and solubility relations. Such abnormality depends on the presence in the molecule of two active or alterable substituents (OH, CO<sub>2</sub>H, NH<sub>2</sub>, CHO, NO<sub>2</sub>, Cl, etc., as opposed to unalterable such as the alkyls) and of these two, one must be OH, NH<sub>2</sub> (or substituted NH<sub>2</sub>), or CO<sub>2</sub>H. Apparently one group makes the compound sensitive and the other augments this sensitiveness. The relations holding among the substituted phenols differ in many respects from those observed with the amines and acids, which again differ from one another. Among the phenols, abnormality was found in all cases examined where the second substituent was other than alkyl. The meta- and para-compounds resemble one another closely as normal isomerides, but differ markedly from the ortho-compounds in being (*a*) less volatile,

(b) more miscible with water, and (c) less miscible with benzene, properties characteristic of polar as opposed to non-polar substances. Consideration of other properties confirms the view that the ortho-series is abnormal and from the fact that in these compounds the polar character due to the hydroxylic hydrogen is suppressed in much the same way as if this hydrogen were replaced by methyl, the suggestion is put forward of a co-ordinate linking of the phenolic



hydrogen with some atom of the second group. This is expressed in the annexed formulæ, in which the arrow ( $\rightarrow$ ) points to the atom receiving the two unshared electrons. These formulæ represent

the most stable type of chelate ring known, and formula (II) explains the abnormality of the hydroxybenzoic acids, their esters and aldehydes ( $\text{X}=\text{OH}$ ,  $\text{OAlk}$ , or  $\text{H}$ ). With other active groups (halogens,  $\text{OH}$ ,  $\text{OAlk}$ , and perhaps  $\text{NH}_2$ ), a five-atom ring must be

assumed,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{Cl} \diagdown \\ \text{O} \end{array} \text{H}$  or  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \diagdown \\ \text{O} \end{array} \text{H}$ , which is less common,

but occurs in the cupferron compounds and is possible in a large class of mordant dyes. Such chelate compounds always tend to be non-polar (cf. acetylacetones) and this ring structure explains why *o*-nitrophenol cannot form compounds with aniline, *p*-toluidine, benzamide, and acetamide, whereas the *m*- and *p*-nitrophenols can; and why if the phenol has an active substituent both in the ortho- and in the para-positions, the influence of the ortho-group predominates and the compound is non-polar. An explanation is also afforded of Auwers' conclusion (A., 1903, ii, 268) that a substituent group which when occupying the ortho-position in a solute gives abnormality, for example, in benzene solution, when introduced into the solvent tends to reduce the abnormality. The behaviour of abnormal derivatives other than phenol is much less easy to explain, and co-ordination through the hydrogen atom is only one of several possibilities. With the chloro- and nitro-acids, the difference between meta- and para-compounds is as great as that between the meta- and ortho-, whilst solubilities both in water and in benzene are in the order  $o > m > p$ . The amino-compounds are somewhat less abnormal, and this is probably connected with their basicity. The introduction of an acetyl group into the chloro- and nitro-anilines tends to increase the abnormality. Among the amino-compounds the meta-derivative occupies an exceptional position, being less volatile than the para-derivative, and its solubility both in benzene and in water is much nearer to (and sometimes less than) the ortho- than is the case with the other classes of abnormal benzene derivatives, a distinction which points to direct chemical influence rather than to either ring-formation or steric effect. R. B.

**Action of the Oxides and Oxy-acids of Nitrogen on  $\beta$ -Naphthyl Ethyl Ether.** H. RYAN and J. KEANE (*Sci. Proc. Roy. Dubl. Soc.*, 1924, 17, 297—303).— $\beta$ -Naphthyl ethyl ether on



treatment with nitrogen peroxide, nitrous fumes, or nitric acid in glacial acetic acid or carbon tetrachloride solution, gave mainly 1-nitro-2-naphthyl ethyl ether, and with gaseous nitrogen peroxide or nitric acid (more than before) in carbon tetrachloride solution or alone, a mixture of 1:6- and 1:8-dinitro-2-naphthyl ethyl ether. The ether itself, its 1-nitro-, 1:6-dinitro-, and 1:8-dinitro-derivatives were all converted by the further action of nitric acid into 1:6:8-trinitro-2-naphthyl ethyl ether, colourless prisms or scales, m. p. 189—190° (cf. Staedel, A., 1883, 863), the constitution of which was thus proved. Heated with alcoholic ammonia, it gave 1:6:8-trinitro- $\beta$ -naphthylamine, m. p. 300—301°. W. A. S.

**Conversion of Eugenol into isoEugenol.** S. K. GOKHALE, J. J. SUDBOROUGH, and H. E. WATSON (*J. Indian Inst. Sci.*, 1923, **6**, 241—255).—The composition of mixtures of eugenol and iso-eugenol is best estimated from the refractive index. The earlier method (McKie, *Chem. Soc. Trans.*, 1921, **119**, 777) is troublesome and untrustworthy. Eugenol has  $n_D^{30}$  1.53664 and isoeugenol  $n_D^{30}$  1.57237. The curve showing the relationship between composition and refractive index for mixtures is a straight line. The temperature coefficient of the refractive index is about 0.0004 per degree for both substances.

When eugenol is fused with sodium hydroxide at 200—210°, little if any conversion and much decomposition takes place; with potassium hydroxide (4 parts), 85% of the theoretical yield of isoeugenol is obtained (cf. Einhorn and Frey, A., 1894, i, 578). A mixture of 2 parts of sodium hydroxide and 1 part of potassium hydroxide also gives a good yield. When eugenol is heated with 6 to 8 parts of 50% potassium hydroxide solution in an autoclave at 170—180°, almost complete conversion takes place. W. A. S.

**Adrenaline Compounds.** C. FUNK and L. FREEDMAN (U. S. Pat. 1472298).— $\beta$ -Methylamino-4- $\alpha$ -ethoxyethylpyrocatechol hydrochloride, thin, rectangular prisms, m. p. 169°, is prepared by heating *r*-adrenaline (or its hydrochloride) for several hours in a reflux apparatus with absolute ethyl alcohol containing dry hydrogen chloride equivalent to 1—4 mols. of adrenaline, and cooling. A substance (hydrochloride, rectangular prisms, m. p. 180—183°), possibly a lactonic compound of 2 mols. of adrenaline, is also formed.

CHEMICAL ABSTRACTS.

**Properties of Neighbouring Hydroxy Groups Attached to a Benzene Nucleus.** R. L. ALIMCHANDANI (*J. Chem. Soc.*, 1924, **125**, 539—543).—The hypothesis that the carbon atoms of the benzene nucleus are charged alternately positively and negatively finds support in the properties of the three vicinal methoxy groups of 3:4:5-trimethoxy-2-trichloromethylphthalide and 3:4:5-trimethoxybenzenesulphonic acid. When chloral hydrate is condensed with 3:4:5-trimethoxybenzoic acid by means of 90% sulphuric acid, the product consists mainly of 3:4:5-trimethoxy-2-trichloromethylphthalide, rectangular plates, m. p. 76—77°.

from which the simultaneously formed 4-hydroxy-3 : 5-dimethoxy-2-trichloromethylphthalide is separated by means of dilute sodium hydroxide. The trimethoxyphthalide by treatment with 98% sulphuric acid is converted into 4-hydroxy-3 : 5-dimethoxy-2-trichloromethylphthalide, m. p. 172—173°, and with sodium hydroxide into 3 : 4 : 5-trimethoxyphthalide-2-carboxylic acid, m. p. 147—149°. Hydrolysis of this acid with 96—98% sulphuric acid gives 4-hydroxy-3 : 5-dimethoxyphthalide-2-carboxylic acid. 3 : 4 : 5-Trimethoxyphthalide similarly yields 4-hydroxy-3 : 5-dimethoxyphthalide, m. p. 144°. The action of 96—98% sulphuric acid on pyrogallyl trimethyl ether gives in varying proportions 3 : 4 : 5-trimethoxybenzenesulphonic acid, leaflets, containing 1.5H<sub>2</sub>O, m. p. 95—97° (the *barium*, *sodium*, and potassium salts are described), and 4-hydroxy-3 : 5-dimethoxybenzenesulphonic acid, leaflets, 1.5H<sub>2</sub>O, m. p. 128—129° (the *barium* and sodium salts are described), which is not hydrolysed by sulphuric acid even in hot solution and on oxidation yields 2 : 6-dimethoxy-*p*-benzoquinone. Treatment with bromine gives 1 : 2 : 3-tribromo-5-hydroxy-4 : 6-dimethoxybenzene, slender prisms, m. p. 134—135°, which by methylation with methyl sulphate gives 1 : 2 : 3-tribromo-4 : 5 : 6-trimethoxybenzene, prisms, m. p. 75—76°. This compound was also obtained by the action of bromine on 3 : 4 : 5-trimethoxybenzenesulphonic acid, the sulphonic group being displaced. Hydrolysis of the trimethoxybenzenesulphonic acid to pyrogallyl trimethyl ether readily takes place in hot sulphuric acid. R. B.

**Methyl Ether of Diphenylphenylacetylenylcarbinol.** K. ZIEGLER and K. TRIPP (*Ber.*, 1924, 57, [B], 420; cf. A., 1923, i, 921).—The carbinol is readily methylated by dissolving it in hot methyl alcohol and adding 1 to 2% of sulphuric acid, previously diluted with methyl alcohol. On cooling, the methyl ether crystallises out almost quantitatively, and after recrystallisation forms leaflets, m. p. 123—124°. It is decomposed by acids to give phenyl β-phenylstyryl ketone, m. p. 86—87° (cf. A., 1922, i, 556). F. A. M.

**Benzeins.** R. MEYER and W. GERLOFF (*Ber.*, 1924, 57, [B], 591—599; cf. A., 1923, i, 230).—Benzaurin dissolves in aqueous alkali to an intense carmine solution which gradually fades; the fading is not due to atmospheric action as suggested by Doebner (*Ber.*, 1879, 12, 1464), but probably to the transformation of coloured *p*-hydroxyfuchson into colourless dihydroxytriphenylcarbinol. On passing carbon dioxide into the colourless solution, the original benzaurin is reprecipitated. It is considered to be *p*-hydroxyfuchson hydrate, OH·C<sub>6</sub>H<sub>4</sub>·CPh·C<sub>6</sub>H<sub>4</sub>·O, H<sub>2</sub>O. Benzaurin forms a crystalline *bisulphite* compound, (OH·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C(Ph)SO<sub>3</sub>Na, which decomposes on keeping. It was not found possible to prepare an oxime, phenylhydrazone, or semicarbazone. Treatment of an alkaline solution of benzaurin with potassium cyanide gave the *nitrile*, (OH·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C(Ph)CN, an oil which slowly solidified to crystals, m. p. 203—204°; attempts to hydrolyse the nitrile to the corresponding dihydroxytriphenylmethanecarboxylic acid were unsuccessful. On treatment with acetic anhydride, the nitrile

yielded a *diacetyl* derivative, colourless crystals, m. p. 140—141°, and on benzylation gave *dihydroxytriphenylmethanecarboxylamide dibenzoate*,  $(\text{OBz}\cdot\text{C}_6\text{H}_4)_2\text{C}(\text{Ph})\text{CONH}_2$ ; on hydrolysing this with alcoholic potassium hydroxide and acidifying the resultant solution, the original nitrile was recovered. *Benzaurin diethyl ether* and *dibenzyl ether* are colourless, crystalline substances melting at 75—76° and 110°, respectively. Bromination of benzaurin in acetic acid in presence of iron gives *tetrabromobenzaurin*, dark red crystals which lose no water on moderate heating (*sodium salt*, brown needles with green iridescence). Benzaurin is reduced by alcoholic ammonia to *pp'*-diaminotriphenylmethane; using strong aqueous ammonia, *p*-aminofuchsonimine is formed.

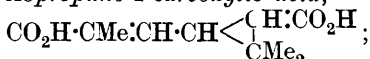
Resorcinolbenzein dried in a vacuum has the formula  $\text{C}_{19}\text{H}_{14}\text{O}_4$ . At 140°, it loses 1 mol. of water, leaving a product,  $\text{C}_{19}\text{H}_{12}\text{O}_3$ , as found by Kehrmann; the authors therefore give the hydrated substance the formula  $\text{OH}\cdot\text{C}_6\text{H}_3\cdot\text{C}_6\text{H}_3\cdot\text{O} \cdot \cdot \cdot \text{H}_2\text{O}$ . The following derivatives of resorcinolbenzein were prepared: *diacetate*, yellow needles, m. p. 145°; *dibenzoate*, colourless needles, m. p. 152°; dibromo derivative, reddish-yellow powder which loses  $\text{H}_2\text{O}$  at 140°; tetrabromo derivative, crystals which lose 1 mol. of  $\text{HBr}$  at 140—150°; *pentabromo* derivative, brown needles, which sublime with decomposition at 140—150° (*sodium salt*, brownish-red needles with green iridescence). *Dinitroresorcinolbenzein nitrate*, obtained by warming the benzein with strong nitric acid, forms a brilliant red, crystalline powder which decomposes with a slight explosion on heating.

F. A. M.

**Insecticides. II. Constitution of Chrysanthemum-mono- and -di-carboxylic Acids.** H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 201—211).—Three acids were obtained by hydrolysis of the semicarbazones of the active constituents of insect powder (cf. p. 523). The first, chrysanthemumcarboxylic acid,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ , is readily separated from the others on account of its volatility in steam, and is shown to be 2:2-dimethyl-3-isobutenylcyclopropane-1-carboxylic acid,

$\text{CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CMe}_2$   
 $[\alpha]_{\text{D}}^{20} + 20.1^\circ$ . Its *methyl ester* is a colourless liquid, b. p. 99°/14 mm., 86—87°/10 mm.,  $[\alpha]_{\text{D}}^{20} + 20.74^\circ$ , having a faint odour of insect powder; *chloride*,  $\text{C}_{10}\text{H}_{15}\text{OCl}$ , colourless oil, b. p. 85°/12 mm., 58°/0.03 mm.; *anilide*, white needles, m. p. 101°; *amide*, white needles, m. p. 131°; *anhydride*, viscous oil, b. p. 125°/15 mm. When reduced by the Paal-Skita method, the acid takes up two atoms of hydrogen, giving 2:2-dimethyl-3-isobutenylcyclopropane-1-carboxylic acid, a colourless, mobile oil, b. p. 124—126°/10 mm. Its *chloride* has b. p. 89—90°/12 mm.; *amide*, white crystals, m. p. 132—132.5°; and *anilide*, large, colourless crystals, m. p. 82—83°. *Methyl l-trans-caronate*,  $\text{C}_7\text{H}_{14}\text{O}_4$ , obtained by decomposing chrysanthemumcarboxylic acid ozonide, forms a mass of white crystals, m. p. 37—38°, b. p. 93°/25 mm.,  $[\alpha]_{\text{D}} - 8.26^\circ$  in benzene. The second acid obtained from insect powder, chrys-

anthemumdicarboxylic acid, has the composition  $C_{10}H_{14}O_4$ , and the third,  $C_{11}H_{16}O_4$ , is its monomethyl ester. It is the latter which is present in the active constituent of the insect powder, the former being formed from it by hydrolysis. By the action of ozone, the second acid gives *l-trans*-caronic acid and pyruvic acid, whilst the third gives *l-trans*-caronic acid and methyl pyruvate. Chrysanthemumdicarboxylic acid is therefore 2:2-dimethyl-3- $\beta$ -carboxypropenylcyclopropane-1-carboxylic acid,



it has  $[\alpha]_D^{17} +72.8^\circ$ . The *chloride*,  $C_{10}H_{12}O_2Cl_2$ , forms white crystals, m. p. 48—50°, b. p. 151°/12 mm.; *anilide*, m. p. 204—205°. The

monomethyl ester,  $CO_2H \cdot \begin{array}{c} \text{CMe}_2 \\ \text{C} \end{array} \cdot CH \rightarrow CH \cdot CH \cdot CMe \cdot CO_2Me$ , is a viscous oil,

b. p. 129—130°/0.03 mm.,  $[\alpha]_D^{18} +103.9^\circ$ ; the *chloride* is a colour-oil, b. p. 114°/0.5 mm. The *dimethyl* ester is a colourless oil, b. p. 149°/16 mm., 87—88°/0.25 mm. When chrysanthemumdicarboxylic acid is distilled at atmospheric pressure, it partly decomposes into carbon dioxide and 2:2-dimethyl-3-propenylcyclopropane-1-carboxylic acid, a mobile oil, b. p. 133°/12 mm.; *chloride*, b. p. 95°/12 mm. With pyrethrolone, this acid forms an ester having weak insecticidal properties. The ester obtained from reduced chrysanthemumcarboxylic acid and pyrethrolone is inactive.

E. H. R.

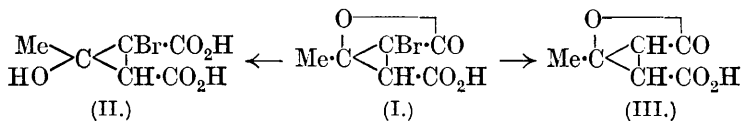
**3-Methylcyclopropene-1:2-dicarboxylic Acid.** F. FEIST (*Annalen*, 1924, **436**, 125—153; cf. Feist, A., 1893, i, 404; Goss, Ingold, and Thorpe, *J. Chem. Soc.*, 1923, **123**, 327).—When bromoisodehydracetic acid is treated with alkali, an acid (A) is produced, m. p. 200°, which on dibromination and reduction with sodium amalgam yields an isomeride (B), m. p. 189°. Only one formula is possible for both these isomeric methylcyclopropenedicarboxylic acids, namely,  $CMe \begin{array}{c} \text{CH} \cdot CO_2H \\ \text{C} \cdot CO_2H \end{array}$ , since both are racemic acids

which can be resolved into their optically active components. The acid A (*silver* salt, and *phenylhydrazine* salt, white needles, m. p. 138°) was resolved by means of its quinine salt into *d*- and *l*-acids having the rotations  $[\alpha]_D +215^\circ$  and  $-156^\circ$ . They both melt at 200°. The methyl ester, needles, m. p. 32°, has b. p. 122°/20 mm.,  $d_4^{20}$  1.142,  $n_D^{20}$  1.4672. The ethyl ester, m. p. 38°, b. p. 135°/15 mm., the *anilide*, white powder, m. p. 246°, and *carbamide* salt, m. p. 215°, are described.

The acid B was resolved by means of its brucine and quinine salts; the extreme values obtained for the *d*- and *l*-acids were  $[\alpha]_D +179.8^\circ$  and  $-118^\circ$ . The methyl ester of B has m. p. 30.5° and b. p. 116°/20 mm.;  $d_4^{20}$  1.140,  $n_D^{20}$  1.4669. It is not identical with the methyl ester of A and on hydrolysis regenerates B. The latter is converted into A by concentrated sulphuric acid or by heating with concentrated alkali.

By dibromination of the acids or their esters and subsequent reduction with sodium amalgam, B is produced. The dibromo-

acid derived from A melts at  $244^{\circ}$  and gives an *ethyl* ester, b. p.  $183\text{--}184^{\circ}/13$  mm.,  $d_4^{20}$  1.590,  $n_D^{20}$  1.5026. The *methyl* ester forms white needles, m. p.  $77^{\circ}$ . The dibromo-acid derived from B melts at  $232^{\circ}$  and yields an *ethyl* ester, b. p.  $177^{\circ}/13$  mm.,  $d_4^{20}$  1.566,  $n_D^{20}$  1.500. This dibromo-acid on warming with water or concentrated alkali yields a monobasic lactonic acid,  $C_6H_5O_3Br$ , m. p.  $171^{\circ}$ , 2-bromo-3-hydroxy-3-methylcyclopropane-1:3-dicarboxylolactonic acid (I), which is readily transformed by alkali into the corresponding hydroxy-acid,  $C_6H_7O_3Br$  (II). The *methyl* ester of the lactonic acid has m. p.  $98^{\circ}$ , b. p.  $166^{\circ}/15$  mm. By reduction of the lactonic acid with sodium amalgam, bromine is removed and the lactone of so-called oxalbutyric acid, m. p.  $140\text{--}141^{\circ}$ , is left (III).



The lactonic acid (m. p.  $171^{\circ}$ ) is identical with the lactone of so-called oxalbromobutyric acid. On oxidation with alkaline permanganate, it yields a tribasic acid,  $C_6H_5O_6Br$  (m. p.  $225^{\circ}$ ), which gives a *dimethyl* ester, m. p.  $76^{\circ}$ .

Reduction of 3-methylcyclopropane-1:2-dicarboxylic acids (A or B) by means of colloidal palladium and hydrogen yields two isomeric 3-methylcyclopropane-1:2-dicarboxylic acids (m. p.  $147^{\circ}$  and  $108^{\circ}$ ). A third isomeride, m. p.  $138\text{--}140^{\circ}$ , has also been obtained as a by-product in the reduction of the dibromomethylcyclopropane-dicarboxylic acid by means of sodium amalgam. Of the three possible isomerides, two have been already described, one, m. p.  $108^{\circ}$ , by Preiswerk (A., 1903, i, 459), and the other by Kötze and Stalman (A., 1903, i, 741), who isolated a syrup. The acid, m. p.  $147^{\circ}$ , is thought to be the *trans* acid, as it gives no anhydride. The methyl ester has b. p.  $208.5\text{--}209^{\circ}/760$  mm.,  $100^{\circ}/14$  mm., and on hydrolysis yields an acid, m. p.  $138^{\circ}$ . The acid, m. p.  $147^{\circ}$ , after exposure to moisture melts at  $138^{\circ}$ , but after drying its melting point rises to  $147^{\circ}$ . Acid A gives an *ozonide*,  $C_6H_6O_7$  (horny solid), which on hydrolysis yields oxalic and acetic acids, through acetyl-oxalacetic acid. The methyl ester gives an *ozonide* (colourless oil) which on hydrolysis yields methyl acetoacetate and methyl oxalacetate.

A. E. C.

**Anhydrides.** W. AUTENRIETH and G. THOMAE. (See i, 485).

**Constitution of Sparassol.** A. ST. PFAU (*Ber.*, 1924, 57, [B], 468—470).—The product, m. p.  $67\text{--}68^{\circ}$  (sparassol), obtained by Wedekind and Fleischer (this vol., i, 174) from the fungus *Sparassia ramosa*, is proved to be identical with a product obtained by Pfau from a fungus, *Evernia prunastri*. It is identical with the methyl ester of everninic acid, 6-hydroxy-4-methoxy-*o*-toluic acid, and is not methyl 4-hydroxy-6-methoxy-*o*-toluate as suggested by Wede-

kind and Fleischer. Sparassol does not exist as such in the fungus, but is formed by the alcoholysis of the evernic acid present. On hydrolysis with 10% aqueous sodium hydroxide, sparassol yields evernic acid. F. A. M.

**Sparassol.** E. SPÄTH and K. JESCHKI (*Ber.*, 1924, **57**, [B], 471–474; cf. preceding abstract).—The constitution of sparassol was proved in the following manner. Orcinol was converted into orcyraldehyde by the method of Gattermann and Köbner (A., 1899, i, 363) and this into orsellinic acid (4:6-dihydroxy-*o*-toluic acid). The last was methylated by means of diazomethane to the 4-methyl ether of methyl orsellinate (methyl everninate), which melted at 67–68° and was identical with Wedekind and Fleischer's sparassol. The *acetyl* derivative (*acetylsparassol*) has m. p. 63–64°. The *dimethyl* ether of methyl orsellinate has m. p. 41–42°, and the *nitro* derivative of methyl everninate, m. p. 168–169°. F. A. M.

**Physical Constants of Stereoisomeric Compounds.** K. VON AUWERS and B. OTTENS (*Ber.*, 1924, **57**, [B], 437–446).—Systematic investigation of the benzenoid hydrocarbons (cf. A., 1916, i, 130; 1919, i, 578) and of derivatives of *cyclohexane* (A., 1920, i, 721) has shown that the propinquity of side chains or other substituents to one another causes an increase in density and index of refraction and a decrease in molecular refractivity. It is to be expected, therefore, that the *cis*-forms of stereoisomeric compounds as a consequence of the closer juxtaposition of their substituents would resemble the *ortho*- or 1:2-derivatives and have a higher density and refractive index but a lower molecular refraction than their *trans*-isomerides. This hypothesis has already been utilised to some extent in the elucidation of the configuration of compounds (cf. Skita, A., 1920, i, 27; 1923, i, 671; Hückel, this vol., i, 31); its general validity is now tested by an examination of several well-defined pairs of isomerides.

Ethyl hexahydrophthalate and ethyl 4-amino-2:6:6-trimethylhexahydrobenzoate exhibit well-marked differences which are in harmony with the rule mentioned above; with the ethyl esters of hexahydroterephthalic and hexahydrohomophthalic acids, the differences are so slight as to be inconclusive, whilst with the ethyl hexahydroisophthalates the slight differences are contrary to the rule. The latter observation, combined with the experience of Skita (A., 1923, i, 671), indicates that for the present physical data cannot be regarded as trustworthy aids in elucidating the configuration of *meta*- or 1:3-derivatives. The values observed with trithioaldehyde and trithioacetone are in harmony with those which are anticipated; this is also the case with the isomeric  $\beta\epsilon$ -dihydroxy- $\beta\epsilon$ -dimethyl- $\Delta\gamma$ -hexenes,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}_2\cdot\text{OH}$  (cf. Zalkind, A., 1923, i, 176). The stereoisomeric dimethylsuccinic and dimethylglutaric esters show similar small, scarcely utilisable differences in their constants such as are observed with the hydrogenated *tere*- and *homo-phthalic* esters. The further accumulation of methyl groups in the succinic molecule produces the expected effects. The physical constants of pairs of stereoisomeric alkyl-

glutaconic esters are very similar. This is to be expected if Feist's view that these substances are geometrical isomerides is accepted, since marked differences in the spectroscopic constants are only observed with simple, stereoisomeric acids and esters of the acrylic series, and these tend to disappear as the molecule becomes more complicated, even to only a limited extent. On the other hand, exaltations such as would be expected if Thorpe's formulation is adopted are not observed.

Physical constants are recorded for the following compounds. *Ethyl cis-hexahydrophthalate*, b. p.  $133^{\circ}/10$  mm.,  $d_4^{20}$  1.054,  $n_{\text{He}}^{13.9}$  1.45296,  $n_{\text{He}}^{20}$  1.453. *Ethyl trans-hexahydrophthalate*, b. p.  $135^{\circ}/11$  mm.,  $d_4^{20}$  1.040,  $n_{\text{He}}^{20}$  1.450. *Ethyl cis-hexahydroisophthalate*, b. p.  $142^{\circ}/11$  mm.,  $d_4^{20}$  1.045,  $n_{\text{He}}^{20}$  1.452. *Ethyl trans-hexahydroisophthalate*, b. p.  $142^{\circ}/12$  mm.,  $d_4^{20}$  1.047,  $n_{\text{He}}^{20}$  1.453. *Ethyl cis-hexahydrotetraphthalate*, b. p.  $151^{\circ}/13$  mm.,  $d_4^{20.6}$  1.0516,  $n_{\text{He}}^{20.6}$  1.45222. *Ethyl trans-hexahydrotetraphthalate*, lustrous, flattened needles, m. p.  $43-44^{\circ}$ ,  $d_4^{64.4}$  1.0105,  $n_{\text{He}}^{64.4}$  1.43367. *Ethyl cis-hexahydrohomophthalate*, b. p.  $273^{\circ}$ ,  $d_4^{20}$  1.040,  $n_{\text{He}}^{20}$  1.454. *Ethyl trans-hexahydrohomophthalate*, b. p.  $275^{\circ}$ ,  $d_4^{20}$  1.038,  $n_{\text{He}}^{20}$  1.453. *Ethyl cis-4-amino-2:6:6-trimethylhexahydrobenzoate*, b. p.  $127^{\circ}/11$  mm.,  $d_4^{20}$  0.990,  $n_{\text{He}}^{20}$  1.475. *Ethyl trans-4-amino-2:6:6-trimethylhexahydrobenzoate*, b. p.  $127^{\circ}/11$  mm.,  $d_4^{20}$  0.980,  $n_{\text{He}}^{20}$  1.473.

*Ethyl succinate*, b. p.  $217^{\circ}$ ,  $d_4^{20}$  1.041,  $n_{\text{He}}^{20}$  1.420. *Ethyl methylsuccinate*, b. p.  $218^{\circ}$ ,  $d_4^{20}$  1.011,  $n_{\text{He}}^{20}$  1.419. *Ethyl cis- $\alpha\beta$ -dimethylsuccinate*, b. p.  $221^{\circ}$ ,  $d_4^{20}$  0.996,  $n_{\text{He}}^{20}$  1.423. *Ethyl trans- $\alpha\beta$ -dimethylsuccinate*, b. p.  $220^{\circ}$ ,  $d_4^{20}$  0.995,  $n_{\text{He}}^{20}$  1.421. *Ethyl  $\alpha\alpha$ -dimethylsuccinate*, b. p.  $218^{\circ}$ ,  $d_4^{20}$  0.993,  $n_{\text{He}}^{20}$  1.421. *Ethyl trimethylsuccinate*, b. p.  $226^{\circ}$ ,  $d_4^{20}$  0.993,  $n_{\text{He}}^{20}$  1.436. *Ethyl tetramethylsuccinate*, b. p.  $219^{\circ}$ ,  $d_4^{20}$  0.995,  $n_{\text{He}}^{20}$  1.436. *Ethyl cis- $\alpha\gamma$ -dimethylglutarate*, b. p.  $231^{\circ}$ ,  $d_4^{20}$  0.980,  $n_{\text{He}}^{20}$  1.423. *Ethyl trans- $\alpha\gamma$ -dimethylglutarate*, b. p.  $231^{\circ}$ ,  $d_4^{20}$  0.977,  $n_{\text{He}}^{20}$  1.422.

*Ethyl cis- $\beta$ -methylglutaconate*, b. p.  $131^{\circ}/19$  mm.,  $d_4^{20}$  1.034,  $n_{\text{He}}^{20}$  1.452. *Ethyl trans- $\beta$ -methylglutaconate*, b. p.  $127^{\circ}/12$  mm.,  $d_4^{20}$  1.034,  $n_{\text{He}}^{20}$  1.452. *Ethyl cis- $\alpha\beta$ -dimethylglutaconate*, b. p.  $128^{\circ}/13$  mm.,  $d_4^{20}$  1.024,  $n_{\text{He}}^{20}$  1.454. *Ethyl trans- $\alpha\beta$ -dimethylglutaconate*, b. p.  $125^{\circ}/12$  mm.,  $d_4^{20}$  1.031,  $n_{\text{He}}^{20}$  1.454. *Ethyl cis- $\alpha$ -ethyl- $\beta$ -methylglutaconate*, b. p.  $127^{\circ}/12$  mm.,  $d_4^{20}$  1.019,  $n_{\text{He}}^{20}$  1.455. *Ethyl trans- $\alpha$ -ethyl- $\beta$ -methylglutaconate*, b. p.  $139^{\circ}/18$  mm.,  $d_4^{20}$  1.014,  $n_{\text{He}}^{20}$  1.453.

Trithioacetone,  $\text{C}_9\text{H}_{18}\text{S}_3$ , has m. p.  $22^{\circ}$ ,  $d_4^{20}$  1.068,  $n_{\text{He}}^{20}$  1.542. *cis*-Trithioacetaldehyde, m. p.  $101^{\circ}$ , and *trans*-trithioacetaldehyde, m. p.  $126^{\circ}$ , in addition to trithioacetone have been examined in quinoline solution; the solvent is shown to be suitable for this purpose.

*cis*- $\beta\epsilon$ -Dihydroxy- $\beta\epsilon$ -dimethylhexene, m. p.  $76^{\circ}$ ,  $d_4^{20}$  0.869,  $n_{\text{He}}^{20}$  1.423. *trans*- $\beta\epsilon$ -Dihydroxy- $\beta\epsilon$ -dimethylhexene, m. p.  $69^{\circ}$ ,  $d_4^{20}$  0.864,  $n_{\text{He}}^{20}$  1.422. H. W.

**Synthesis of Polyhydroxyphenylalanines.** F. SCHAAF and A. LABOUCHÈRE (*Helv. Chim. Acta*, 1924, 7, 357—363).—For the synthesis of 2:5-dihydroxyphenylalanine, gentisaldehyde dimethyl

ether (2 : 5-dimethoxybenzaldehyde) was condensed with hippuric acid, and the resulting  $\alpha$ -benzoylamino-2 : 5-dimethoxycinnamic acid reduced to  $\alpha$ -benzoylamino-2 : 5-dimethoxy- $\beta$ -phenylpropionic acid, from which the 2 : 5-dihydroxyphenylalanine was obtained. This method was inapplicable for the synthesis of trihydroxyphenylalanine as the cinnamic acid derivative could not be reduced. The following method was, however, successful. 2 : 3 : 4-*Trimethoxybenzaldehyde* was obtained by Gattermann's synthesis from pyrogallol and hydrocyanic acid; it forms glistening prisms, m. p. 37°. It condenses with hydantoin to give 2 : 3 : 4-*trimethoxybenzylidenehydantoin*,  $\text{C}_6\text{H}_2(\text{OMe})_3\text{CH}:\text{C} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$ , pale yellow

needles, m. p. 197°, which is reduced by sodium amalgam in water to 2 : 3 : 4-*trimethoxybenzylhydantoin*, thin, white needles, m. p. 154°. This is hydrolysed by boiling barium hydroxide to 2 : 3 : 4-*trimethoxyphenylalanine*, forming star-shaped aggregates of needles, m. p. 216°. If the hydrolysis is not carried to completion,  $\alpha$ -*carbamido*- $\beta$ -2 : 3 : 4-*trimethoxyphenylpropionic acid* is obtained, m. p. 189°. The trimethoxyphenylalanine is demethylated by boiling with hydriodic acid (*d* 1.70), giving 2 : 3 : 4-*trihydroxyphenylalanine*, crystallising in short, stout needles, m. p. 225° (decomp.). Its neutral solution reduces silver nitrate in the cold and gives a permanent blue colour with ferric chloride.

3 : 4 : 5-*Trihydroxyphenylalanine* was synthesised in a similar manner. It forms stout prisms, m. p. 290° (decomp.). In its low solubility it resembles 3 : 4-dihydroxyphenylalanine, but both the trihydroxyphenylalanines differ from this in not giving the characteristic reaction with the pigment-forming ferment, dopa-oxydase. 3 : 4 : 5-*Trimethoxybenzylidenehydantoin* forms yellow needles, decomp. 250—260°; 3 : 4 : 5-*trimethoxybenzylhydantoin*, long, white prisms, m. p. 172°; 3 : 4 : 5-*trimethoxyphenylalanine*, white needles, decomp. 220°.

E. H. R.

**Constitution of Phthalonic Acid.** CORNILLON (*Compt. rend.*, 1924, 178, 713—715; cf. this vol., i, 294).—Phthalonic anhydride (1 mol.) is converted by phosphorus pentachloride (1 mol.), in presence of toluene, into  $\alpha$ -*chlorophthalide*- $\alpha$ -*carboxylic chloride*,  $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \end{smallmatrix} \text{CCl}\cdot\text{COCl}$ , prisms, m. p. 70°, b. p. 120°/2 mm. The latter in moist air passes into the corresponding *acid*, white needles, m. p. 133°. The acid is stable in air; cold alkali slowly, and warm alkali very rapidly, affords phthalonic acid. The chloro-acid, or its chloride, is at once converted by alcohols into the corresponding esters. The *methyl* ester, stable, has m. p. 92°; the *ethyl* ester, m. p. 48°, b. p. 164°/5 mm., is gradually affected by moist air. The chloride, with aniline, affords the corresponding *anilide* (m. p. 137.5°), this being converted by concentrated alkali into phthalonanilic acid.

Phthalonic anhydride and methyl alcohol afford *methyl hydrogen phthalonate*,  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{CO}_2\text{Me}$ , m. p. 94°; this ester separates from alcoholic solutions with 1 mol. of solvent of crystallisation



(removable in a vacuum), and is converted by phosphorus pentachloride into methyl  $\alpha$ -chlorophthalide- $\alpha$ -carboxylate. E. E. T.

**Isomerism of the Oximes. XVI. Action of Ultra-violet Light on Aldoximes and their Derivatives.** O. L. BRADY and G. P. MCHUGH (*J. Chem. Soc.*, 1924, 125, 547—554).—The action of ultra-violet light on nineteen aromatic aldoximes has been investigated. In nine cases, viz., *p*-methoxy- and 3 : 4-methylenedioxybenzantialdoximes, benzantialdoxime, *o*-, *m*-, and *p*-nitro-, and *o*-, *m*-, and *p*-chloro-benzantialdoximes, conversion from the *anti*- to the *syn*-isomeride was accomplished, but in all these cases the *syn*-isomeride has been prepared by other means. It is evident, however, that the conversion is not dependent, as Ciusa supposed (A., 1907, i, 137), on the presence of a negative substituent in the benzene ring. Eight cases were examined in which the *syn*-isomeride had not been prepared by other means: *o*-methoxy-, 5-bromo-*o*-methoxy-, 2 : 4-dinitro-, 3-nitro-*p*-dimethylamino-, 6-nitro-3 : 4-methylenedioxy-, 5-nitro-3 : 4-dimethoxy-, 6-nitro-3 : 4-dimethoxy-, and 5-bromo-4-hydroxy-3-methoxy-benzantialdoximes, and in no case did conversion take place under the influence of ultra-violet light. With 3 : 4-dimethoxybenzantialdoxime no isomeric change occurred, although the *syn*-compound has been obtained by special means. 5-Bromo-3 : 4-dimethoxybenzantialdoxime suffered demethylation when exposed to ultra-violet light, giving 5-bromo-4-hydroxy-3-methoxybenzantialdoxime.

A number of derivatives of the *anti*-oximes have been examined, and of these the three *O*-ethers, viz., the methyl ethers of *m*- and *p*-nitrobenzantialdoximes and the benzyl ether of *p*-nitrobenzantialdoxime, were converted into the *syn*-isomeride, although not so completely as the oximes. Of the two nitrogen ethers investigated, the *N*-methyl ether of benzaldoxime is decomposed, yielding benzonitrile, whilst the *N*-methyl ether of *m*-nitrobenzaldoxime undergoes no change. R. B.

**Configuration of Stereoisomeric Oximes and the Structure of Oxime-*N*-ethers and *aci*-Nitro Derivatives.** K. VON AUWERS and B. OTTENS (*Ber.*, 1924, 57, [B], 446—461).—The spectrochemical behaviour of a series of oximes is found to be closely similar to that of their *O*-alkyl and acyl derivatives. Since the latter substances necessarily contain the group :C:N·OR, it follows that the oximes themselves must have the constitution :C:N·OH. Confirmation of this view is found in the observation that the benzylideneamines, which undoubtedly contain the similar, conjugated group, :C:C·CH:N<sup>-</sup>, have molecular exaltations which are of the same order of magnitude as those of the oximes. A consideration of the magnitudes of the physical constants of the oximes renders it very improbable that a three-membered ring,  $\text{>C} \begin{smallmatrix} \text{N}^- \\ \diagup \text{O} \end{smallmatrix}$ , is present,

although a direct estimation of the influence of the ring is impossible, since there is no known compound in which its presence has been established definitely. It is, however, scarcely conceivable that

such a ring, even when conjugated with a double linking, could produce the observed remarkable increase in index of refraction and dispersive power, particularly since heterocyclic rings containing nitrogen, such as  $\begin{smallmatrix} \cdot\text{C} \\ \cdot\text{C} \end{smallmatrix} > \text{N}\cdot$  and  $\begin{smallmatrix} \cdot\text{N} \\ \cdot\text{N} \end{smallmatrix} > \text{C}$ , are optically indifferent. The "nitron" formula,  $\text{:C:NH:O}$ , for the oximes is excluded, since their *N*-ethers are characterised by unusually high dispersive power, which could scarcely fall to a small fraction in the oximes themselves if the latter substances yielded the *N*-ethers simply by the replacement of hydrogen by alkyl without any structural change.

Attempts to discriminate between the *cis*- and *trans*-forms of stereoisomeric oximes, on the hypothesis that the former varieties exhibit higher densities and refractive indices but smaller molecular refractions and dispersions than the *trans*-compounds, are described. In the cases of the benzaldoximes and their ethers, it is found that the  $\alpha$ -oxime has the *syn*-configuration; this is opposed to the customary view, but is in harmony with the recent observations of Meisenheimer (A., 1922, i, 152) and Beckmann (A., 1923, i, 228). In a number of other instances, the interpretation of the observed results is much more difficult; at present, it is not possible to form a definite opinion as to the value of spectrochemical evidence in this field.

The optical behaviour of the *N*-ethers of oximes is strongly against the existence of a three-membered ring,  $\text{:C} < \begin{smallmatrix} \text{N}\cdot\text{R} \\ \text{O} \end{smallmatrix}$ , the presence of

which could not explain the observed powerful exaltations; it is consonant with the structure  $\text{:C:NR:O}$ , experimental evidence for which has been adduced by Semper and Lichtenstadt (A., 1918, i, 437) and by Staudinger (A., 1919, i, 584).

The optical properties of the carbamidoximes (cf. Conduché, A., 1908, i, 12, 154), of the *aci*-forms of the nitroparaffins and of tetranitromethane are in agreement with the constitutions,  $\text{RR'C:N(O)CO}\cdot\text{NH}_2$ ,  $\text{RR'C:N(O)OH}$ , and  $(\text{NO}_2)_2\text{C:N(O)O}\cdot\text{NO}_2$ , respectively.

The physical constants have been observed partly with homogeneous material, partly with substances dissolved in quinoline which is found to be a very suitable solvent for this purpose. The following data, amongst others, are recorded. Heptaldoxime,  $d_4^{99.3}$  0.8219,  $n_{\text{He}}^{99.8}$  1.41514.  $\alpha$ -Mesityl oxideoxime, b. p.  $84^\circ/11$  mm.,  $d_4^{100}$  0.876,  $n_{\text{He}}^{100}$  1.450.  $\beta$ -Mesityl oxideoxime, b. p.  $95^\circ/11$  mm.,  $d_4^{100}$  0.881,  $n_{\text{He}}^{100}$  1.462.  $\alpha$ -Mesityl oxideoxime acetate, b. p.  $101^\circ/11$  mm.,  $d_4^{20}$  0.986,  $n_{\text{He}}^{20}$  1.474.  $\beta$ -Mesityl oxideoxime acetate, b. p.  $107^\circ/14$  mm.,  $d_4^{20}$  0.990,  $n_{\text{He}}^{20}$  1.478.  $\alpha$ -Mesityl oxideoxime benzyl ether, b. p.  $131^\circ/11$  mm.,  $d_4^{20}$  0.987,  $n_{\text{He}}^{20}$  1.533.  $\alpha$ -Benzaldoxime, m. p.  $35^\circ$ ,  $d_4^{20}$  1.110,  $n_{\text{He}}^{20}$  1.593.  $\alpha$ -Benzaldoxime *O*-methyl ether, b. p.  $79^\circ/11$  mm.,  $d_4^{20}$  1.020,  $n_{\text{He}}^{20}$  1.548.  $\beta$ -Benzaldoxime *O*-methyl ether, b. p.  $79^\circ/11$  mm.,  $d_4^{20}$  1.028,  $n_{\text{He}}^{20}$  1.550.  $\alpha$ -Benzaldoxime acetate,  $d_4^{20}$  1.107,  $n_{\text{He}}^{20}$  1.544.

Heptaldoxime *N*-benzyl ether,  $d_4^{99.6}$  0.9293,  $n_{\text{He}}^{99.6}$  1.49714. Furfur-

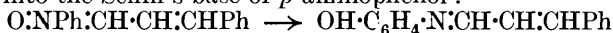
aldoxime *N*-methyl ether,  $d_4^{99.8}$  1.1185,  $n_{He}^{99.8}$  1.56351. Furfuraldoxime *N*-benzyl ether,  $d_4^{99.7}$  1.1270,  $n_{He}^{99.7}$  1.59871.  $\beta$ -Benzaldoxime *N*-methyl ether,  $d_4^{99.9}$  1.0528,  $n_{He}^{99.9}$  1.59189. *o*-Chlorobenzaldoxime *N*-phenyl ether, coarse, pale yellow crystals, m. p. 81.5–82.5° (from *o*-chlorobenzaldehyde and phenylhydroxylamine),  $d_4^{100.3}$  1.2008,  $n_{He}^{100.3}$  1.64853. Phenylnitromethane,  $d_4^{24.7}$  1.1540,  $n_{He}^{24.7}$  1.52850. *aci*-Phenylnitromethane methyl ether, from nitromethane, methyl sulphate, and sodium hydroxide, a pale yellow liquid with an odour of bitter almonds, b. p. 117°/15 mm., ca. 83°/1.5 mm.,  $d_4^{15.0}$  1.1241,  $n_{He}^{15.0}$  1.58708. Tetranitromethane,  $d_4^{16.9}$  1.6425,  $n_{He}^{16.9}$  1.43976.

Benzylidenemethylamine, CHPh:NMe, b. p. 185°,  $d_4^{20}$  0.962,  $n_{He}^{20}$  1.553. Benzylidene-ethylamine, b. p. 195°,  $d_4^{20}$  0.937,  $n_{He}^{20}$  1.541. Benzylideneisopropylamine, b. p. 245°,  $d_4^{20}$  0.906,  $n_{He}^{20}$  1.519. Benzylideneaniline, b. p. 300°,  $d_4^{30.3}$  1.0041,  $n_{He}^{30.3}$  1.61041. Benzylidene-*o*-toluidine, b. p. 314°,  $d_4^{20}$  1.041,  $n_{He}^{20}$  1.635. H. W.

**Reactions of Cinnamalphenylnitrone.** D. BIGIARI and M. MARRI (*Gazzetta*, 1924, **54**, 99–113).—Among the products obtained by Weitnauer (Dissertation, Basle, 1904) on reducing phenylisocinnamaloxime by means of sodium or sodium amalgam and absolute alcohol were two compounds described by this author as (1) liquid secondary base, b. p. 190–190.5°/8 mm., and (2) solid secondary base, m. p. 90–90.5°, and regarded as having the structures,  $\text{NHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ , and  $\text{NHPh}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ , respectively. The authors show that the solid base, m. p. 90°, is actually hydrocinnamanilide, its formation being the result of migration of the oxygen atom of the phenylisocinnamaloxime from the nitrogen to the adjacent carbon atom, followed by hydrogenation of the cinnamanilide thus formed:  $\text{O:NPh:CH}\cdot\text{CH:CHPh} \rightarrow \text{NHPh}\cdot\text{CO}\cdot\text{CH:CHPh} \rightarrow \text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ . Similar transpositions are exhibited by a large number of compounds, including nitrones (cf. Miescher, "Nitronen und Nitrene," Zurich, 1918, 20). By acetic anhydride, cinnamalphenylnitrone is converted quantitatively into the acetyl derivative of cinnamanilide as the result of an intensely exothermic reaction, hydrolysis then yielding the anilide:  $\text{O:NPh:CH}\cdot\text{CH:CHPh} \rightarrow \text{NHPh}\cdot\text{CO}\cdot\text{CH:CHPh}$ ; catalytic reduction of cinnamanilide by means of hydrogen and platinum black yields hydrocinnamanilide, identical with the product obtained by heating aniline with hydrocinnamic acid.

By catalytic reduction, Cusmano (A., 1922, i, 143) has converted nitrones into hydroxylamines. From cinnamalphenylnitrone this author has obtained, by reduction with hydrogen and platinum black, a compound which is apparently a hydroxylamine. This marked divergence in behaviour must be due to the presence of conjugated double bonds in the molecule of cinnamalphenylnitrone.

By dilute sulphuric acid, cinnamalphenylnitrone is readily converted into the Schiff's base of *p*-aminophenol:



(cf. Angeli, Alessandri, and Pegna, A., 1910, i, 552). Analogous reactions produced by dilute sulphuric acid are:  $\text{O:NH}_2\text{Ph} \rightarrow \text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ ;  $\text{O:NPh:NPh} \rightarrow \text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N:NPh}$ ;  $\text{O:NPhMe}_2$

→  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ . On other nitrones, the acid exerts a hydrolysing action, the original aldehyde or ketone and arylhydroxylamine being regenerated.

The *acetyl* derivative of cinnamanilide,  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}$ , forms acicular crystals, m. p. 138–139°.

*Hydrocinnamanilide*,  $\text{C}_{15}\text{H}_{15}\text{ON}$ , crystallises in lustrous, white needles, m. p. 98°, and exhibits the normal molecular weight in acetic acid. It is stable towards alcoholic potassium hydroxide, but is rapidly hydrolysed when heated with dilute sulphuric acid. Sodium and alcohol reduce it to aniline and another base, which is probably Weitnauer's liquid secondary base. With nitrous acid, it appears to yield a nitrosoamine. Its *acetyl* derivative,  $\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}$ , forms minute, refractive crystals, m. p. 45°. T. H. P.

**Oxides of the Stereoisomeric Trithiobenzaldehydes.** O. HINSBERG (*Ber.*, 1924, **57**, [B], 417–419).—A detailed reply to the criticisms of Fromm and Schultis (*A.*, 1923, i, 580) on the author's work (*A.*, 1914, i, 185). Contrary to the views of Fromm and Schultis,  $\alpha$ -trithiobenzaldehyde pentoxide (disulphone-sulphoxide) must be regarded as a homogeneous substance. The individuality of  $\delta$ -trithiobenzaldehyde tetroxide is not, however, established with equal certainty, and it is possible that the product is a difficultly separable mixture of the tri-, tetra-, and pent-oxides, but this is not conclusively proved by the experiments of Fromm and Schultis. Valid evidence against the existence of  $\delta$ -trithiobenzaldehyde has not been adduced. H. W.

**Pinacolin Transformation in the Dehydration of 1 : 2-Dimethylcyclohexane-1 : 2-diol.** S. NAMETKIN and N. DELEKTORSKY (*Ber.*, 1924, **57**, [B], 583–587).—1 : 2-Dimethylcyclohexane-1 : 2-diol, m. p. 92–93°, prepared by hydrating the corresponding oxide at the ordinary temperature with very dilute sulphuric acid, was heated at 150–160° for 3 hours with acidulated water. On cooling, the pinacolin separated as an oil possessing a peppermint-like odour and distilling, after purification by means of its semicarbazone, at 60.5°/20 mm. It was found to be identical with 1-methyl-1-cyclopentyl methyl ketone (Meerwein, *A.*, 1919, i, 162). The pinacolin transformation is therefore accompanied by the change from a six-ring to a five-ring. The reverse change occurs on dehydrating 1-methyl-1- $\alpha$ -hydroxyethylcyclopentane, the product being 1 : 2-dimethyl- $\Delta^1$ -cyclohexene (Meerwein, *loc. cit.*). F. A. M.

**Oxidation of Sabinene with Chromyl Chloride. A Correction.** G. G. HENDERSON and J. M. ROBERTSON (*J. Chem. Soc.*, 1924, **125**, 765–766).—The supposed 4-isopropylidene-cyclohexanone obtained by the oxidation of sabinene with chromyl chloride (*Chem. Soc. Trans.*, 1922, **121**, 2717) has now been found to be *p*-tolyl methyl ketone. The alcohol obtained by its reduction is therefore *p*-tolylmethylcarbinol. The formation of this ketone from sabinene is attributed to oxidation of part of the sabinene to cymene, which with chromyl chloride forms the compound  $\text{C}_{10}\text{H}_{14}\cdot 2\text{CrO}_2\text{Cl}_2$ , from which *p*-tolyl methyl ketone is formed on decomposition with water. R. B.

**Change of State of Aggregation and Polymorphism. III. Polymorphism of Benzophenone.** K. SCHAUUM and K. UNGER (*Z. anorg. Chem.*, 1924, **132**, 90—98; cf. A., 1916, i, 405).—The instability of the metastable form of benzophenone makes the investigation of its pseudo-binary character difficult. On this account, the *p*-halogen and *p*-hydroxy derivatives were examined. These were found to be monotropic trimorphic, but the m. p. of the three forms lie very close together, not more than 0·5° apart. The effect of previous history on the m. p. of benzophenone was examined. No difference could be detected after heating for different periods of time at different temperatures. H. T.

**Preparation of 3 : 3'-Dinitrobenzophenone.** E. DE B. BARNETT and M. A. MATTHEWS (*J. Chem. Soc.*, 1924, **125**, 767).—By nitration of benzophenone in sulphuric acid solution with nitric acid (*d* 1·50) at 25—30°, a yield of 50% of theory of crude 3 : 3'-dinitrobenzophenone was obtained, which after one crystallisation from methyl ethyl ketone melted at 155°. R. B.

**Valency. I. Estimation of the Strength of the Bond between a Radical and Carbon.** A. SCHONBERG, R. ABELSDORFF, H. KIRCHRATH, W. MALCHOW, and A. ROSENBAACH (*Annalen*, 1924, **436**, 205—218).—The reaction between benzophenone and sodamide, first studied by Haller (A., 1908, i, 987), has been applied to substituted aromatic ketones. Benzophenone, in toluene solution, gives as a final product benzamide:  $\text{Ph}_2\text{CO} + \text{NaNH}_2 \rightarrow \text{Ph}_2\text{C}(\text{NH}_2)\text{ONa} \rightarrow \text{C}_6\text{H}_6 + \text{Ph}\cdot\text{CO}\cdot\text{NHNa} \rightarrow \text{Ph}\cdot\text{CO}\cdot\text{NH}_2$ . With an unsymmetrical substituted benzophenone, the reaction may proceed in two ways, giving benzene and a substituted benzamide, or a substituted benzene and benzamide. It is shown that Haller's explanation (*loc. cit.*) of the reaction is incorrect; for instance, diphenyl phenyl ketone with sodamide in toluene solution gives diphenyl, which agrees with the above scheme. The yields in this reaction are practically quantitative, so that by determining the proportions of the free acids (obtained by hydrolysis of the amides) formed, it is possible to determine the relative affinity of the various radicals for carbonyl carbon, and comparative numerical values can be assigned to each radical. Taking the affinity of the phenyl radical as the unit, the following values are assigned to substituted phenyl radicals containing the substituent groups indicated:—*m*-chloro-, 0·05—0·32; *m*-bromo-, 0·08—0·38; *p*-chloro-, 0·18—0·51; *p*-bromo-, 0·18—0·65; *p*-methoxy-, 1·12—2·16; and *p*-dimethyl-amino-, about 1·23. The value for the radicals  $\text{CPh}_3\cdot$  and  $\text{CPh}_2(\text{ONa})\cdot$  is less than 0·14. If the ketone is not decomposed by sodamide, for example, phenyl triphenylmethyl ketone, hydrolysis with alkali is resorted to, the final products being triphenylacetic acid and benzoic acid, in proportions depending on the relative affinities of the triphenylmethyl and phenyl radicals. The method fails with aliphatic ketones, a sodium compound of the ketone being formed.

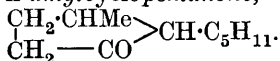
*p*-Methylmercaptobenzophenone, colourless prisms, m. p. 79°, was synthesised from benzoyl chloride, methyl phenyl sulphide, and

aluminium chloride in carbon disulphide solution; (*phenylhydrazone*, colourless crystals, m. p. 90°). *p*-Methylmercaptobenzoic acid, by the action of sodamide on the ketone in toluene solution, forms prisms, m. p. 192°. 4:4'-Dimethylmercaptobenzophenone, from thioanisole and oxalyl chloride in presence of aluminium chloride in ice-cold carbon disulphide solution, forms colourless scales, m. p. 125.5° (anil, yellow prisms, m. p. 135°). A. E. C.

**Isomeric *p*'-Methylchalkones [*p*-Tolyl Styryl Ketones].** C. WEYGAND (*Ber.*, 1924, **57**, [B], 413—417).—*p*-Tolyl methyl ketone, condensed with benzaldehyde and sodium ethoxide, yields *p*-methylchalkone (*p*-tolyl styryl ketone), m. p. 590 (cf. Sorge, A., 1902, i, 379); on recrystallising several months later, it was suddenly converted into the isomeric form, m. p. 77°, described by Kostanecki (A., 1896, i, 688), and during the night all the other uncovered preparations were converted into the same modification. All subsequent preparations gave only the 77° form, which on heating to 135° and cooling deposits the form, m. p. 59°; this is at once changed into the 77° modification when touched with a crystal of the latter. Both forms could be crystallised from suitable solvents at first, but once the 77° form had appeared it became nearly impossible to recover the 59° form from solution except by working at low temperatures or in air-tight vessels. Both forms give orange-yellow solutions in concentrated sulphuric acid, the 77° form being deposited on dilution; both yield the same  *dibromide*  as a white, crystalline powder, m. p. 175—176°, the same  *compound*  with stannic chloride, m. p. 85° (not sharp), and the same aniline additive  *compound* , m. p. 141°. At 21°, 100 g. of benzene dissolve about 55.8 g. of the 77° form, and 166.8 g. of the 59° form. Both forms have normal molecular weights in benzene. F. A. M.

#### Insecticides. IV. Constitution of Tetrahydropyrethron.

H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, **7**, 236—244).—It was shown in a previous paper (p. 523) that reduction of pyrethrolone by the Paal-Skita method gives tetrahydropyrethrolone. When the reduction is pushed to the limit, the hydroxyl group is also reduced, tetrahydropyrethron being formed. Complete reduction is effected more readily with the acetate or the methyl ether than with pyrethrolone itself. *Tetrahydropyrethron* is a colourless, mobile liquid with a faint, ethereal odour, b. p. 100—101°/12 mm. Its constitution, determined from its oxidation products, is 3-methyl-2-n-amylocyclopentanone,



The *semicarbazone* varies in melting point from 160° to 194°, according to the manner in which the ketone is prepared. That of m. p. 194°, from the ketone obtained by reduction of pyrethrolone acetate, is the *lævo* form; that having m. p. 160° is the *racemic* form. The *p*-nitrophenylhydrazone (*r*-form) forms yellow needles, m. p. 87°. By oxidation of tetrahydropyrethron with potassium permanganate, hexoic and lævulic acids were obtained. Their

formation is compatible with two possible formulæ, a *cyclopentane* derivative with the keto group in the ring or a *cyclobutane* derivative with the keto group in the side chain. The oxime of the former should give a lactam by the Beckmann change, whilst the oxime of the latter should give an acid amide. The oxime of tetrahydropyrethrone is a colourless oil, b. p. 84–85°/0.1 mm., which, by treatment with concentrated sulphuric acid, is converted into the iso-oxime, a viscous oil, b. p. 120°/0.1 mm. The latter is converted by boiling hydrochloric acid into  $\delta$ -amino- $\gamma$ -methyldecoic acid, which by treatment with nitrous acid is converted into the lactone of  $\delta$ -hydroxy- $\gamma$ -methyldecoic acid. The constitution of tetrahydropyrethrone as 3-methyl-2-*n*-amylcyclopentanone is therefore established.

E. H. R.

**Insecticides. V. Synthesis of Tetrahydropyrethrone, the Reduction Product of Pyrethrolone.** H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 245–259).—The constitution of tetrahydropyrethrone, which was concluded to be 3-methyl-2-*n*-amylcyclopentanone (preceding abstract), has been confirmed by synthesis as follows: Ethyl  $\alpha$ -bromoheptoate (colourless oil, b. p. 106–107°/12 mm.) was condensed with ethyl lævulate, forming the  $\gamma$ -lactone of ethyl hydrogen  $\gamma$ -hydroxy- $\gamma$ -methylnonane- $\alpha\delta$ -dicarboxylate,  $\text{C}_5\text{H}_{11}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CMe}\cdot\text{[CH}_2\text{]}_2\cdot\text{CO}$ , a colourless,

viscous oil, b. p. 130°/0.1 mm. When hydrolysed with 25% potassium hydroxide, the lactone ester is decomposed to a great extent into heptoic and lævulic acids, and only a small yield of  $\gamma$ -hydroxy- $\beta$ -methylnonane- $\alpha\delta$ -dicarboxylic acid lactone is obtained, white crystals, m. p. 86–87°. When the disodium salt of the free adipic acid is heated, it loses water and carbon dioxide, forming  $\gamma$ -methyl- $\Delta^7$ -decenoic acid,  $\text{C}_5\text{H}_{11}\cdot\text{CH}\cdot\text{CMe}\cdot\text{[CH}_2\text{]}_2\cdot\text{CO}_2\text{H}$ , a viscous oil of peculiar odour, b. p. 160–163°/15 mm. (*p*-toluidide, m. p. 44–45°;  $\alpha$ -naphthylamide, m. p. 63–64°), which is reduced by the Paal-Skita method to  $\gamma$ -methyldecoic acid, a colourless oil, b. p. 150–152°/12 mm. (*p*-toluidide, m. p. 34–36°;  $\alpha$ -naphthylamide, m. p. 61–62°).

When the condensation of ethyl  $\alpha$ -bromoheptoate and ethyl lævulate with zinc was continued for a prolonged period at 150°, one of the reaction products was a butylene derivative, ethyl hydrogen  $\gamma$ -methyl- $\Delta^7$ -nonylene- $\alpha\delta$ -dicarboxylate ( $\delta$ -carbethoxy- $\gamma$ -methyl- $\Delta^7$ -decenoic acid),  $\text{C}_5\text{H}_{11}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CMe}\cdot\text{[CH}_2\text{]}_2\cdot\text{CO}_2\text{H}$ , a colourless oil, b. p. 150°/0.4 mm., which could not be reduced with hydrogen (Paal-Skita) or sodium amalgam; the ethyl ester has b. p. 170–180°/15 mm. When the ester was boiled with sodium and xylene, and the sodium compound of the resulting methylamylcyclopentanonecarboxylate boiled with 20% sulphuric acid, 3-methyl-2-amyl- $\Delta^2$ -cyclopentenone was obtained, a colourless oil, b. p. 115–117°/12 mm. (*semicarbazone*, m. p. 175–176°; *p*-nitrophenylhydrazone, m. p. 118–119°). The unsaturated ketone could only be reduced by passing its vapour with hydrogen over nickel at 240–250°. The resulting 3-methyl-2-amylcyclopentanone was identical with tetrahydropyrethrone.

The following compounds were obtained in unsuccessful attempts to effect the synthesis : 3-*Methyl-5-n-amylocyclopentanone*, colourless liquid, b. p. 107—109°/14 mm. (*semicarbazone*, m. p. 147—148°; *p-nitrophenylhydrazone*, m. p. 134—135°), by condensing ethyl  $\beta$ -methyladipate to a *cyclopentanonecarboxylic acid* by Dieckmann's method (A., 1900, i, 297) and heating the sodium salt of this acid with amyl bromide. *Ethyl  $\beta$ -methylbutane- $\alpha\alpha$ -tricarboxylate*, colourless oil, b. p. 135°/0.4 mm. (from ethyl malonate and ethyl  $\gamma$ -bromovalerate, in presence of sodium), reacted slowly with *n*-amyl bromide in presence of alcoholic sodium ethoxide, giving the same methylamylcyclopentanone as above and by-products.

E. H. R.

### Insecticides. III. Constitution of Pyrethrolone. H.

STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 212—235).—The alcoholic constituent of the active substances in insect powder, pyrethrolone,  $C_{11}H_{16}O_2$ , is obtained from the semicarbazone already described by careful cold hydrolysis with potassium hydrogen sulphate in presence of benzene and water. It forms a viscous oil, b. p. 111—112°/0.05 mm.,  $[\alpha]_D^{20} -6.2^\circ$  (approx.). Pyrethrolone probably has the constitution 1-*methyl-2-pentadienyl-cyclopentane-4-ol-3-one*,

$$\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ | \\ \text{OH} \cdot \text{CH} - \text{CO} \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{CH} : \text{C} : \text{CHMe};$$

it forms a *p-nitrophenylosazone*, a brown, microcrystalline powder, decomposing above 350°; and an *acetate*,  $C_{13}H_{18}O_3$ , a colourless, mobile oil, b. p. 104—105°/0.5 mm.,  $[\alpha]_D^{15} -23.79^\circ$ , which forms a crystalline *semicarbazone*, m. p. 143—145°. When treated with alkali it undergoes autoxidation, forming *dehydropyrethrolone*, a mobile oil, b. p. 82°/0.05 mm., which gives a *semicarbazone*, m. p. 251°, and a second oxidation product, a viscous oil, probably a polymerised form of the first; both are weakly acidic. By methylation with methyl alcohol and concentrated sulphuric acid, pyrethrolone semicarbazone forms a *methyl ether*, m. p. 183°, which, by removal of the semicarbazone group gives the *methyl ether* of pyrethrolone, a mobile oil, b. p. 82—83°/0.25 mm. Pyrethrolone itself can be methylated with methyl sulphate to give the same product, but with methyl alcohol and sulphuric acid it gives a different product forming a *semicarbazone*, m. p. 207°. The *ethyl ether* of pyrethrolone is a colourless liquid, b. p. 102—103° in the highest vacuum; *semicarbazone*, m. p. 179—180°.

When pyrethrolone is reduced by the Paal-Skita method, it takes up 2 mols. of hydrogen, forming *tetrahydropyrethrolone*, which is shown (p. 521) to be 1-*methyl-2-n-amylocyclopentane-4-ol-3-one*; it is a viscous oil, b. p. 160—162°/10 mm., 108—110°/0.1 mm.;  $[\alpha]_D^{20} -11.32^\circ$ , with strong reducing properties. When esterified with chrysanthemumyl chloride, it gives a product having no insecticidal properties. Tetrahydropyrethrolone forms a *p-nitrophenylosazone*, decomposing above 350°; a *semicarbazone*, m. p. 189—190° (decomp.); an *acetate*, a mobile oil, b. p. 110°/0.16 mm., and a *methyl ether*, a colourless, mobile oil, b. p. 128°/12 mm., obtained by reduction of pyrethrolone methyl ether. By oxid-



ation with potassium permanganate, tetrahydropyretrolone gives hexoic acid. Decomposition of the mono-ozonide of pyretrolone gives acetaldehyde and acetic acid, showing the presence of an ethylidene group. Malonic acid was also obtained by further oxidising the products obtained from the ozonide with hydrogen peroxide. By ozonisation of pyretrolone acetate, an acid was obtained which appeared to be an *acetoxymethylcyclopentenone-homocarboxylic acid*,  $\begin{array}{c} \text{CH}-\text{CHMe} \\ | \\ \text{C(OAc)}-\text{CO} \end{array} > \text{CH}-\text{CH}_2 \cdot \text{CO}_2\text{H}$ ; m. p. 136—138°.

The above observations, together with the fact that pyretrolone only absorbs 1 mol. of bromine with ease, support the view that the side chain contains the allene grouping, although this grouping has not previously been found in a natural product. E. H. R.

**Hydroxyhydrindone and Chromanone.** F. MAYER and L. VAN ZÜTPHEN (*Ber.*, 1924, **57**, [B], 618).—A correction. In a previous paper (this vol., i, 410) the authors claimed to have synthesised chromanone by the action of aluminium chloride on *o*-hydroxyphenyl  $\beta$ -chloroethyl ketone. The product is now admitted to be 7-hydroxyhydrindone, b. p. 128°/13 mm. The benzylidene compound is coloured yellow by sodium hydroxide solution, but is not dissolved even on boiling. (Cf. Krollpfeiffer and Schultze, following abstract.) F. A. M.

**Formation of Hydroxyhydrindones from Phenyl Esters of  $\beta$ -Halogenpropionic Acids by Heating with Aluminium Chloride.** F. KROLLPFEIFFER and H. SCHULTZE (*Ber.*, 1924, **57**, [B], 600—601; cf. this vol., i, 411).—*p*-Tolyl  $\beta$ -bromopropionate is obtained in quantitative yield by heating *p*-cresol with  $\beta$ -propionyl chloride and is a colourless oil, b. p. 162°/14 mm. When it is heated with twice its weight of aluminium chloride at 100—120°, and the product decomposed with iced hydrochloric acid, 80% of the theoretical yield of 1-hydroxy-4-tolyl  $\beta$ -bromoethyl ketone is obtained, forming small, colourless plates, m. p. 72—73°. At 160—170° the product is 4-methyl-7-hydroxyhydrindone, m. p. 110—111°, the yield being 60% of theory. This provides strong evidence that the “ $\gamma$ -chromanone” obtained by Mayer and van Zütphen (this vol., i, 410) is really 7-hydroxyhydrindone. (Cf. Mayer and Zütphen, preceding abstract.) F. A. M.

**Synthesis of *m*-Dimethoxyphenyl Ethyl and Methyl Ketones.** F. MAUTHNER (*J. pr. Chem.*, 1924, [ii], **107**, 103—108).—To obtain better yields of 3:5-dimethoxyphenyl ethyl ketone than were obtained from 3:5-dimethoxybenzoyl chloride and zinc ethyl iodide (A., 1922, i, 457), methyl 3:5-dimethoxybenzoate was condensed with ethyl acetate by the Claisen method and the ethyl 3:5-dimethoxybenzoate, a pale yellow oil (pyrazolone derivative with phenylhydrazine, m. p. 153—154°), was converted by treatment with methyl iodide and sodium ethoxide, followed by hydrolysis with 25% sulphuric acid, into 3:5-dimethoxyphenyl ethyl ketone, colourless needles, m. p. 34—35° (semicarbazone, colourless needles, m. p. 130—131°). Hydrolysis of ethyl 3:5-di-

methoxybenzoylacetate with 25% sulphuric acid yields 3:5-dimethoxyphenyl methyl ketone, colourless needles, m. p. 42—43°, b. p. 151—152°/10 mm. (p-nitrophenylhydrazone, reddish-yellow needles, m. p. 157—158°; semicarbazone, colourless needles, m. p. 186—187°). Condensation of 3:5-dimethoxybenzaldehyde and sodium propionate by the Perkin reaction gives 3:5-dimethoxy- $\alpha$ -methylcinnamic acid, colourless needles, m. p. 153—154°, but attempts to convert this into 3:5-dimethoxypropenylbenzene through loss of carbon dioxide failed. 3:5-Dimethoxyphenylethylcarbinol, b. p. 170—171°/12 mm. (phenylurethane, colourless plates, m. p. 86—87°), was obtained by the Grignard reaction from 3:5-dimethoxybenzaldehyde and ethyl iodide; with excess of Grignard reagent 3:5-dimethoxypropenylbenzene was formed but rapidly polymerised.

R. B.

### Quinones of Linear Ring Systems with Reactive Halogen in the Non-quinonoid Nucleus. K. FRIES and E. KÖHLER

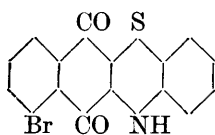
(Ber., 1924, 57, [B], 496—510).—A continuation of previous work (Fries and Kerkow, A., 1922, i, 577). 5-Bromoacetnaphthalide can be prepared by the reduction of 5-bromo-1-nitronaphthalene with iron filings and acetic acid or with zinc dust and ammonium chloride and subsequent acetylation of the product or, more economically, by means of iron powder and glacial acetic acid and subsequent treatment of the solution with acetic anhydride. It is converted by a mixture of glacial acetic acid and nitric acid ( $d$  1.48) at  $-2^\circ$  into a mixture of 5-bromo-2-nitroacetnaphthalide and 5-bromo-4-nitroacetnaphthalide (m. p. 225°), which can be only incompletely separated by fractional crystallisation. Treatment of the mixture with aqueous-alcoholic sodium hydroxide solution leads to the ready isolation of 5-bromo-4-nitro- $\alpha$ -naphthylamine, reddish-brown needles or prismatic crystals, m. p. 192° (monoacetate, pale yellow, lustrous needles, m. p. 225°; diacetate, pale brown leaflets, m. p. 170°), and 5-bromo-2-nitroacetnaphthalide, m. p. 240°. 5-Bromo-4-nitro- $\alpha$ -naphthylamine is reduced by stannous chloride and hydrochloric acid in glacial acetic acid solution to 5-bromo-1:4-naphthylenediamine, slender, pale green needles, m. p. 132° (dihydrochloride, slender, colourless needles; diacetyl compound, colourless needles, m. p. 257°). 5-Bromo-1:4-naphthaquinone, golden-yellow prisms, m. p. 160°, and 5-bromo-2-anilino-1:4-naphthaquinone, red, prismatic leaflets, m. p. 219°, are described. The diamine hydrochloride (or the stannic double salt) is transformed by exhaustive chlorination in the presence of glacial acetic and concentrated hydrochloric acids into 2:2:3:3-tetrachloro-5-bromo-1:4-diketo-1:2:3:4-tetrahydronaphthalene,  $C_6H_3Br \begin{smallmatrix} \text{CO} \cdot \text{CCl}_2 \\ | \\ \text{CO} \cdot \text{CCl}_2 \end{smallmatrix}$ , needles or monoclinic crystals, m. p. 120°, which is reduced by stannous chloride to 2:3-dichloro-5-bromo-1:4-dihydroxynaphthalene, colourless needles, m. p. 196° (acetate, needles, m. p. 154°). The latter substance is oxidised by ferric chloride to 2:3-dichloro-5-bromo-1:4-naphthaquinone, pale yellow, prismatic crystals, m. p. 180°, which, with aniline, gives 3-chloro-5-bromo-2-anilino-1:4-naphtha-

quinone, dark red needles, m. p. 239° (the assumption that the chlorine atom in position 2 suffers replacement is arbitrary).

[With G. SCHÜRMANN.]—A similar sequence of changes starting from 8-chloro-4-nitro- $\alpha$ -acetylnaphthalide (which is the main product of the nitration of 8-chloro- $\alpha$ -acetylnaphthalide) leads to the production of 5-chloro-1:4-naphthaquinone and its derivatives. The following compounds are described: 8-Chloro-4-nitro- $\alpha$ -naphthylamine, brownish-red, lustrous plates, m. p. 203° (acetyl derivative, needles, m. p. 167°); 5-chloro-1:4-naphthylenediamine, slender, pale yellow needles, m. p. about 116° (decomp.) (diacetyl derivative, slender, colourless needles, m. p. 269°); 5-chloro-1:4-naphthaquinone, yellow needles, m. p. 163°; 5-chloro-2-anilino-1:4-naphthaquinone, red needles with a bronzy lustre, m. p. 219°; 2:2:3:3:5-pentachloro-1:4-dihydroxy-1:2:3:4-tetrahydronaphthalene, colourless leaflets, m. p. (indefinite) 82°; 2:3:5-trichloro-1:4-dihydroxynaphthalene, colourless needles, m. p. 204° (acetate, needles, m. p. 162°); 2:3:5-trichloro-1:4-naphthaquinone, coarse yellow needles, m. p. 156°; 3:5-dichloro-2-anilino-1:4-naphthaquinone, dark red needles, m. p. 225°; 3-chloro-2:5-dianilino-1:4-naphthaquinone, needles, m. p. 221°.

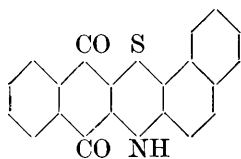
5-Bromo-2-nitro- $\alpha$ -naphthylamine, orange-red needles, m. p. 223°, is obtained by hydrolysing the corresponding monoacetyl derivative (see above) with sulphuric acid (diacetyl derivative, m. p. 133°). The acetyl compound is converted by boiling, 2N-sodium hydroxide solution into 5-bromo-2-nitro- $\alpha$ -naphthol, golden-yellow leaflets, m. p. 142°. 5-Bromo-1:2-naphthylenediamine, colourless plates or slender needles, m. p. 122°, is obtained by reduction of the nitro-amine with tin and hydrochloric acid; the corresponding diacetyl derivative, prismatic crystals, m. p. 287°, is transformed by boiling alcoholic sodium hydroxide solution into 6-bromo-2-methyl- $\alpha\beta$ -naphthiminazole, colourless, slender needles, m. p. 242°, which is also obtained by the reduction of 5-bromo-2-nitro- $\alpha$ -naphthylamine with stannous chloride in glacial acetic acid solution. The diamine condenses with benzil in alcoholic solution to form the quinoxaline derivative,  $C_{24}H_{15}N_2Br$ , pale yellow needles, m. p. 214°. 3:5-Dichloro-5-bromo-1:2-diketo-1:2:3:4-tetrahydronaphthalene (obtained by chlorination of the diamine), apparently monoclinic crystals, m. p. 93°, 3-chloro-5-bromo-1:2-dihydroxynaphthalene, colourless needles, m. p. 176° (diacetyl derivative, coarse crystals, m. p. 147°), and 3-chloro-5-bromo-1:2-naphthaquinone, small, red plates, m. p. 177°, are described.

3-Chloro-5-bromo-2-anilino-1:4-naphthaquinone, dark red needles, m. p. 239°, is converted by treatment with sodium sulphide and oxidation of the product by air into 7-bromo- $\beta\beta$ -naphthaphenthiazine-6:11-quinone (annexed formula), bluish-green, prismatic crystals, m. p. 325°; the corresponding sulfoxide, brownish-red, coarse crystals, m. p. 270°, and the sulphone, orange-red, lustrous leaflets, m. p. above 360°, are described. Boiling acetic anhydride and zinc dust convert the quinone into the triacetyl derivative of 7-bromo-6:11-dihydroxy-



$\beta\beta$ -*naphthaphenthiazine*, lustrous leaflets, m. p.  $299^{\circ}$ . 7-*Anilino*- $\beta\beta$ -*naphthaphenthiazine-6:11-quinone* crystallises in slender, dark violet needles, m. p.  $265^{\circ}$ ; it gives a yellow vat with hyposulphite. 7-*p-Anisidino*- $\beta\beta$ -*naphthaphenthiazine-6:11-quinone* forms dark violet crystals, m. p.  $230^{\circ}$ .

3-*Chloro-2- $\beta$ -naphthylamino-1:4-naphthaquinone*, m. p.  $194^{\circ}$ , prepared from 2:3-dichloro-1:4-naphthaquinone and  $\beta$ -naphthyl-



amine, is transformed in the usual manner into 1:2-*benzo*- $\beta\beta$ -*naphthaphenthiazine-6:11-quinone* (annexed formula), dark, greenish-blue, prismatic crystals, m. p.  $300^{\circ}$ ; the corresponding sulphone crystallises in orange-red leaflets, m. p. above  $400^{\circ}$ . Zinc dust and boiling acetic anhydride transform the quinone derivative of 6:11-*dihydroxy-1:2-benzo*- $\beta\beta$ -*naphthaphenthiazine*, colourless crystals, m. p.  $217^{\circ}$ . H. W.

### Reduction Products of the Hydroxyanthraquinones. V.

F. L. GOODALL and A. G. PERKIN (*J. Chem. Soc.*, 1924, 125, 470—476).—Hydroxyanthranols can be readily prepared in excellent yield by digesting hydroxyanthraquinones with a boiling 20% solution of stannous chloride in 33% hydrochloric acid. The method is serviceable only in those cases in which anthranol formation has been effected by other methods. With purpurin and purpuroxanthin, reduction is incomplete, whilst quinizarin yields quantitatively deep orange-red crystals of 1:4:9-trihydroxyanthrone, m. p.  $152\text{--}154^{\circ}$  (A., 1920, i, 745).

The following anthranols have been obtained by this method: 1- and 3-hydroxy-, 3:6-, 3:7-, and 4:8-dihydroxy-anthranols, anthrapurpurin anthranol, and anthragallol anthranol. Deoxyalizarin (3:4-dihydroxyanthranol), when acetylated and oxidised with ferric chloride, yields 3:4:5':6'-*tetrahydroxydianthrone*, small, yellow needles, m. p.  $268\text{--}270^{\circ}$  (decomp.); *hexa-acetyl* derivative,  $C_{40}H_{30}O_{12}$ , colourless needles, m. p.  $236\text{--}238^{\circ}$ . With alcoholic sulphuric acid, it gives *dihydroxy-3:6'-diethoxydianthrone*,  $C_{32}H_{22}O_6$ , small plates, m. p.  $271\text{--}274^{\circ}$ , which on careful oxidation with chromic acid yields alizarin  $\beta$ -ethyl ether, orange needles, m. p.  $188\text{--}189^{\circ}$ . *Tetra-acetyldiethoxydianthranol* has m. p.  $248\text{--}250^{\circ}$ . By treatment with methyl sulphate and alkali the dihydroxydiethoxydianthrone is converted into 3:4:5':6'-*tetramethoxydianthrone*, colourless needles, m. p.  $255\text{--}256^{\circ}$ . Attempts to convert the tetrahydroxydianthrone into the corresponding helianthrone were unsuccessful. Both deoxyalizarin and tetrahydroxydianthrone are mordant dyes. With bromine in carbon disulphide solution, deoxyalizarin dimethyl ether is converted into 10-bromo-3:4-dimethoxyanthranol, from which by the action of dimethylamine or of alcoholic potassium hydroxide only alizarin dimethyl ether is obtained. Acetyldeoxyalizarin, on treatment with nitric acid in alcohol or acetic acid, yields 10-nitro-3:4-*dihydroxyanthranol diacetate*,  $C_{18}H_{13}O_7N$ , colourless needles, m. p.  $156^{\circ}$  (decomp.). The violet colour observed when nitric acid is added to a solution

of deoxyalizarin in sulphuric acid is due to the production of nitro-dihydroxyanthrone. R. B.

**Derivatives of  $\beta$ -Methylantraquinone. IV. Nitro Derivatives of  $\beta$ -Methylantraquinone and some of their Transformation Products.** R. EDER, C. WIDMER, and R. BÜTLER (*Helv. Chim. Acta*, 1924, 7, 341—357).—The nitro- $\beta$ -methylantraquinone prepared by Römer and Link by nitration of  $\beta$ -methylantraquinone (A., 1883, 1138) has been supposed to be 1-nitro-3-methylantraquinone, on the ground that the hydroxymethylantraquinone prepared from it, m. p. 177—178°, is identical with the 1-hydroxy-3-methylantraquinone prepared synthetically by Bentley, Gardner, and Weizmann (T., 1907, 91, 1626). Repetition of this work shows that the hydroxy compound from nitro- $\beta$ -methylantraquinone really has m. p. 181—182° and is identical with synthetic 1-hydroxy-2-methylantraquinone. The nitro compound is therefore 1-nitro-2-methylantraquinone. It is converted into  $\alpha$ -aminoanthraquinone through the 1-aminoanthraquinone-2-carboxylic acid by boiling the latter with potassium stannite solution. The nitro compound is best prepared by Römer and Link's method; at higher temperatures, red by-products are formed.

Dinitration of  $\beta$ -methylantraquinone or nitration of 1-nitro-2-methylantraquinone gives a mixture of two isomerides, the 1:5- and 1:8-dinitro compounds. 1:5-Dinitro-2-methylantraquinone forms yellow needles, m. p. 329—331°, subliming with partial decomposition in white needles; it is soluble in 50 parts of boiling pyridine, 450 of boiling acetic acid, very sparingly soluble in other solvents. By oxidation with chromic acid in boiling nitric acid solution it gives 1:5-dinitroanthraquinone-2-carboxylic acid, needles, m. p. 337—339°. By distillation of the silver salt (a red powder), 1:5-dinitroanthraquinone is obtained, m. p. above 350°, giving by reduction 1:5-diaminoanthraquinone, m. p. 309—310°, not 319° as given by Noelling and Wortmann (A., 1906, i, 291). Conversion of this into anthrarufin proved its constitution. In a similar manner, the constitution of 1:8-dinitro-2-methylantraquinone, m. p. 293—295°, was established. It forms white to pale yellow needles, sparingly soluble in organic solvents, but more soluble than the 1:5-isomeride. Attempts to obtain higher nitrated derivatives of  $\beta$ -methylantraquinone were unsuccessful. (Cf. Schaarschmidt and Stahlschmidt, A., 1913, i, 95.) E. H. R.

**Neorobin.** P. MASUCCI and G. A. SLOTHOWER (*J. Amer. Pharm. Assoc.*, 1923, 12, 335—338).—"Neorobin," which is prepared by reduction of chrysarobin with tin and acetic acid, is neither a compound of tin nor an acetate. It is at least 50% more active as a reducing agent than chrysarobin, and can be determined by addition of ammoniacal silver nitrate to its solution in acetone, followed by determination of the reduced silver in the usual way.

CHEMICAL ABSTRACTS.

**1:2:8-Trimethoxy-6-methylantraquinone and 1:2:8-Trimethoxy-7-methylantraquinone.** J. L. SIMONSEN (*J. Chem. Soc.*, 1924, 125, 721—726; cf. *ibid.*, 1921, 119, 1339).—The

condensation of hemipinic anhydride with *m*-cresol using aluminium chloride and boric acid as condensing agents yields mainly 2'-hydroxy-3:4-dimethoxy-4'-methyl-2-benzoylbenzoic acid, glistening needles, m. p. 229—230°, which on methylation with methyl sulphate gives 2':3:4-trimethoxy-4'-methyl-2-benzoylbenzoic acid, glistening prisms, m. p. 198—199°, a small quantity of a *phthalein*,  $C_{24}H_{22}O_6$ , m. p. 285—287°, being obtained as a by-product in the condensation. Concentrated sulphuric acid at 150° converts the 2'-hydroxy-3:4-dimethoxy-4'-methyl-2-benzoylbenzoic acid into the corresponding anthraquinone, but in poor yield, and from the crude hydroxyanthraquinone 1:2:8-trimethoxy-6-methylanthraquinone, fine yellow needles, m. p. 164—165°, was obtained by methylation. With *o*-cresol the condensation gave mainly 2'-hydroxy-3:4-dimethoxy-3'-methyl-2-benzoylbenzoic acid, bevelled prisms, m. p. 250—251°, accompanied by considerable quantities of a *phthalein*,  $C_{24}H_{22}O_6$ , m. p. 237—238°, when a large excess of *o*-cresol was used. Methylation converted the benzoylbenzoic acid derivative into 2':3:4-trimethoxy-3'-methyl-2-benzoylbenzoic acid, hexagonal prisms, m. p. 199° (methyl ester, prisms, m. p. 153—155°), whilst heating with sulphuric acid gave an almost quantitative yield of the crude hydroxyanthraquinone, which was methylated with difficulty to 1:2:8-trimethoxy-7-methylanthraquinone, yellow needles, m. p. 209—210°. R. B.

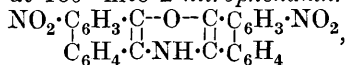
**Phenanthrene Series. XXXV. Transformations of Chlorophenanthrenes.** J. SCHMIDT and E. ÄCKERLE (*Ber.*, 1924, 57, [B], 363—369).—An extension of the work of Schmidt and Spoun (*A.*, 1922, i, 665). The preparation of 9:9- and 10:10-dichloro-2-nitrophenanthrones from 2-nitrophenanthraquinone and phosphorus pentachloride in the presence of benzene is described in detail (the position of the chlorine atoms in these compounds is assigned arbitrarily). 9:9-Dichloro-2-nitrophenanthrone is reduced by hydroxylamine hydrochloride or phenylhydrazine to 9-chloro-2-nitro-10-hydroxyphenanthrene, yellow needles, m. p. 223° (acetate, m. p. 228°; benzoate, m. p. 220°). 10:10-Dichloro-2-nitrophenanthrone is converted similarly by hydroxylamine hydrochloride into 10-chloro-2-nitro-9-hydroxyphenanthrene, small, yellow crystals, m. p. 193°. It appears therefore that the halogen atoms of the chloro-2-nitrophenanthrones are retained with unexpected firmness; this view is confirmed by the observation that the  $\alpha$ -compound is stable towards molecular silver in the presence of boiling benzene.

4-Nitrophenanthraquinone is converted by phosphorus pentachloride in the presence of benzene into a mixture of 9:9-dichloro-4-nitrophenanthrone ( $\alpha$ -compound), pale yellow crystals, m. p. 203°, and 10:10-dichloro-4-nitrophenanthrone ( $\beta$ -compound), m. p. 137°. The former substance is transformed by hydroxylamine hydrochloride or phenylhydrazine into 9-chloro-4-nitro-10-hydroxyphenanthrene, m. p. 203° (acetate, pale yellow powder, m. p. 223°; benzoate, small, colourless crystals, m. p. 196°). 10-Chloro-4-nitro-9-hydroxyphenanthrene has m. p. 153—154° (benzoate, m. p. 188—189°).

4-Nitrophenanthraquinone is converted by phosphorus pentachloride under pressure at 120° into 9 : 9 : 10 : 10-tetrachloro-4-nitro-dihydrophenanthrene, slender, brownish-yellow needles, m. p. 164—165°, which is transformed by phenylhydrazine or molecular silver into 9 : 10-dichloro-4-nitrophenanthrene, m. p. 136—137°; the chlorine atoms are retained with extraordinary firmness in these compounds, particularly in the latter.

*Di-9-chloro-2-nitro-10-phenanthryl ether*,  $(\text{C}_6\text{H}_4 \leftarrow \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CCl} \rightarrow \text{C})_2\text{O}$ ,

a brown substance which does not melt below 370°, is obtained as a by-product of the action of acetic anhydride on 9-chloro-2-nitro-10-hydroxyphenanthrene. The latter substance is converted by alcoholic ammonia at 160° into 2-nitrophenanthroxazine,



which does not melt below 370°.

H. W.

**Enolisation of Camphor.** M. BREDT-SAVELSBERG, C. A. HEINEMANN, P. CATHARINUS, and H. EIBEL (*J. pr. Chem.*, 1924, [ii], **107**, 65—86).—The method of Tschugaev and Zerevitinov (A., 1907, ii, 509) for the determination of hydroxyl groups has been applied to a study of the enolisation of camphor. When camphor, which in ether, benzene, or alcohol solution is known to possess the ketonic structure, is brought into contact with a Grignard reagent, enolisation takes place and its extent is determined from the hydrocarbon produced corresponding with the alkyl or aryl group in the Grignard reagent used. Thus magnesium methyl halides give methane, magnesium phenyl bromide gives benzene. The extent of the enolisation depends on a number of factors. (1) The alkyl or aryl group in the Grignard reagent. Equimolecular quantities of camphor and Grignard reagent in ether solution show 29% enolisation with magnesium methyl iodide, 14% with magnesium ethyl iodide, and 25% with magnesium  $\alpha$ -naphthyl bromide. In the second case, ethylene is produced as well as ethane, in the ratio of about 3 : 10 at 30°. In amyl ether solution, magnesium phenyl bromide shows 21% enolisation (in ethyl ether solution it was very difficult to determine the benzene formed). (2) The halogen present in the Grignard reagent. With the magnesium methyl halides the enolisation of the camphor increases with the electronegative character of the halogen, from about 14·8% in the case of the iodide to 28·2% with the chloride. (3) The proportions of Grignard reagent and camphor. Excess of Grignard reagent favours enolisation of the camphor. With the proportions  $\frac{1}{2}$ , 1, 2, and 3 mols. of camphor to 1 mol. of Grignard reagent the enolisation figures were 32·6, 14·9, 16·3, and 16·9%, respectively. (4) The time of reaction. Equilibrium is only reached after a prolonged period. With magnesium methyl iodide, periods of  $\frac{1}{2}$ , 5, 10, 25, and 40 hours showed enolisation of 13·0, 14·1, 14·9, 30·4, and 44·7%, respectively. (5) The character of the solvent. In amyl ether solution, magnesium methyl iodide enolises camphor to the extent of about 3·6%, against 44·7% in ethyl ether. In a

solvent free from oxygen (benzene) the enolisation is 32.5%. (6) The temperature of reaction. With magnesium methyl iodide the enolisation figures in 10 hours were found to be 6.85% at 0° and 14.9% at 20°. The enolisation of camphor by Grignard reagents explains the low yields of tertiary borneols which have been obtained by the Grignard method, as only the keto-form yields a complex from which tertiary borneols are formed. R. B.

**Pyroelectricity of Two Derivatives of Camphor.** M. R. LUCAS.—(See ii, 224.)

**Oxidation of *allo*-Ocimene, Ocimene, and Myrcene.** C. J. ENKLAAR (*Chem. Weekblad*, 1924, **21**, 101—102; cf. A., 1906, i, 377).—A sample of *allo*-ocimene (b. p. 98—102°/32 mm.) on treatment with permanganate in dry acetone at 0° was only partly oxidised. The only oxidation product obtained was a neutral substance, *allo-ocimene* oxide, probably  $C_{10}H_{16}O$ , b. p. 105°/13 mm.,  $d^{20}_D$  0.909, which is neither aldehyde, ketone, nor glycol. By the action of permanganate on ocimene in acetone solution at 56°, an acid (lead salt, crystallising in rhombs) was obtained; this lead salt is suitable for the identification of the terpene. Myrcene under these conditions yields an acid of which the lead salt crystallises in fine needles, readily distinguishable from the ocimene lead salt. By exhaustive treatment of ocimene with permanganate, a mixture was obtained in which only oxalic acid could be identified. S. I. L.

**Catalytic Action. IV. A Function of Reduced Copper.** S. KOMATSU (*Mem. Coll. Sci. Kyōto*, 1924, **7**, 85—91).—When menthol is passed over reduced copper at 320°, besides the expected menthone, some menthene is formed. The copper therefore acts, like thoria, as a dehydrating agent. In the same way, ethyl alcohol yields acetaldehyde and ethylene, and *isopropyl* alcohol (at 300°) gives acetone and propylene. *cyclo*Hexanol is likewise dehydrogenated and dehydrated; *cyclo*hexene, *cyclo*hexanone, *dicyclo*hexyl ether, and water are produced in quantities agreeing with the author's explanation of the reaction, based on the supposition that dehydration takes place in three directions simultaneously.

W. A. S.

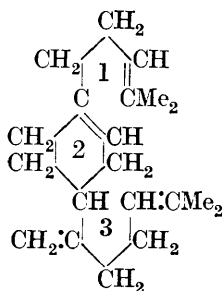
**Higher Terpene Compounds. XX. Sesquiterpenes and Sesquiterpene Alcohols of Camphor Oil.** L. RUZICKA and M. STOLL (*Helv. Chim. Acta*, 1924, **7**, 260—270).—So-called heavy camphor oil, b. p. 110—140°/12 mm., contains, besides cadinene and bisabolene, a monocyclic *hydrocarbon*,  $C_{15}H_{24}$ , which was not more exactly characterised, but forms a very stable *dihydrochloride*, an oil, b. p. 125°/0.3 mm., and a bicyclic *hydrocarbon*,  $C_{15}H_{24}$ , a colourless oil, b. p. 128—135°/12 mm., which must be of the cadinene type since, when dehydrogenated by boiling with sulphur, it gives cadaline. The sesquiterpene alcohol fraction of camphor oil, b. p. 150—160°/12 mm., gives cadaline when dehydrogenated with sulphur. Purification of this alcohol fraction through the benzoate gives 15% of an alcohol, b. p. 155—160°/12 mm., which agrees in properties with Semmler and Rosenberg's sesquicamphenol (A., 1913,



i, 378). When this purified alcohol was dehydrogenated with sulphur and the product fractionated, the fraction of b. p. 140—145°/12 mm. contained eudaline whilst that of b. p. 150—165°/12 mm. contained cadaline. Camphor oil therefore contains compounds of both cadinene and eudesmol types, and is unique in this respect. The alcohol fraction was separated by means of phthalic anhydride into primary, secondary, and tertiary constituents. The *primary* sesquicamphenol has b. p. 156—158°/12 mm.,  $[\alpha]_D +2.2^\circ$ ,  $d_4^{18}$  0.9568,  $n_D^{18}$  1.5045. It is reduced by hydrogen in presence of platinum black to a *dihydrosesquicamphenol*,  $C_{15}H_{28}O$ , a colourless, viscous oil, b. p. 152—153°/12 mm.,  $d_4^{22}$  0.9150,  $n_D^{22}$  1.4755. From the purified sesquiterpene alcohols a *secondary* sesquicamphenol, b. p. 160—162°/12 mm.,  $[\alpha]_D -5.2^\circ$ ,  $d_4^{20}$  0.9720,  $n_D^{20}$  1.5066, was obtained, which by catalytic reduction gave a dihydrosesquicamphenol, b. p. 150—152°/12 mm.,  $d_4^{15}$  0.9510,  $n_D^{15}$  1.4892; whilst from a crude fraction of alcohols, b. p. 140—170°/12 mm., the secondary alcohol appeared to be a mixture of  $C_{15}H_{26}O$  and  $C_{15}H_{24}O$ . One of these alcohols is of the cadinene type. The tertiary alcohol fraction, obtained from the sesquiterpene alcohols purified through the benzoate, had b. p. 156°/12 mm.,  $d_4^{30}$  0.9665,  $n_D^{20}$  1.5050, and by dehydrogenation gave both eudaline and cadaline. Two tertiary sesquiterpene alcohols are therefore present in camphor oil.

E. H. R.

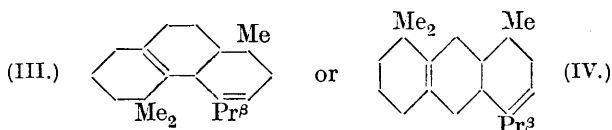
**Higher Terpene Compounds. XXI. Constitution and Isomerisation of  $\alpha$ -Camphorene.** L. RUZICKA and M. STOLL (*Helv. Chim. Acta*, 1924, 7, 271—282).— $\alpha$ -Camphorene, the diterpene found by Semmler and Rosenberg in camphor oil (A., 1913, i, 378), is known to be a monocyclic compound related to myrcene, but its constitution has not been determined. Myrcene is probably a mixture of isomerides,  $CMe_2 \cdot CH \cdot [CH_2]_2 \cdot C \cdot (CH_2) \cdot CH \cdot CH_2$  (I) and  $CH_2 \cdot CMe \cdot [CH_2]_3 \cdot C \cdot (CH_2) \cdot CH \cdot CH_2$  (II), but experiments on its decomposition by ozone indicate that (I) predominates, since only succinic acid was obtained and no trace of glutaric acid. Assuming



that myrcene polymerises to  $\alpha$ -camphorene by a process similar to the polymerisation of isoprene to dipentene, the annexed formula is obtained for  $\alpha$ -camphorene. This formula harmonises with the physical constants of  $\alpha$ -camphorene, and with its isomerisation products. When boiled with 95% formic acid,  $\alpha$ -camphorene is converted into a *bicyclic diterpene*, a viscous oil, b. p. 192—194°/12 mm.,  $d_4^{14}$  0.9086,  $n_D^{14}$  1.5104. The side chain 1 of the above formula has the configuration of a geranyl derivative, and ring closure is to be expected.

More prolonged heating of  $\alpha$ -camphorene or of the bicyclic compound with formic acid results in the formation of a *tricyclic diterpene*, b. p. 180—181°/12 mm.,  $d_4^{14}$  0.9475,  $n_D^{14}$  1.5201. In the above formula, the ring 2 and the first three carbon atoms of side chain 3 have the dipentene structure, and a wandering of the

double bond into the ring may take place, analogous to the isomerisation of dipentene to  $\alpha$ - and  $\gamma$ -terpenes. This would give configurations leading, after ring closure, to the formation of either a phenanthrene or an anthracene derivative,



By oxidation with manganese dioxide and sulphuric acid the tricyclic  $\alpha$ -camphorene gave, besides mellophanic acid, which might result from either formula, pyromellitic acid, which can, as far as is known, only result from the anthracene structure. It is probable, therefore, that the tricyclic compound has structure IV, for which the name *isotricyclocamphorene* is proposed, III being designated *tricyclocamphorene*. By catalytic hydrogenation, only two atoms of hydrogen were taken up, *dihydro*(?iso)*tricyclocamphorene* being formed, a colourless, viscous oil, b. p.  $176^\circ/12$  mm.,  $d_4^{20}$  0.9410,  $n_D^{20}$  1.5118. Oxidation of octahydro- $\alpha$ -camphorene with manganese dioxide and sulphuric acid gave, besides mellophanic acid and pyromellitic acid, terephthalic acid, which is additional evidence in support of the suggested  $\alpha$ -camphorene formula. To the two known types of the diterpene series, the abietic acid and dextropimaric acid types, must now be added the camphorene type; in all of these the carbon skeleton is composed of four associated isoprene residues. (Cf. A., 1923, i, 818—819.) E. H. R.

**Classification of the Resinic Acids from Conifers.** O. ASCHAN (*Chem.-Ztg.*, 1924, 48, 149—150).—The acids occurring in pine resins together with some of their derivatives may be divided into three classes, viz., the natural acids such as pimaric and sapic acids; the colophony acids (*isopimaric* and *abietic* acids) which are formed by heating the natural sapic acids; and the sylvic acids formed by treating other resinic acids with mineral acids. Of the acids of the first group, the pimaric acids are stable in the air and difficultly soluble in organic solvents, have high melting points, and absorb two atoms of hydrogen in the presence of platinum black; the sapic acids, on the other hand, are very unstable, have low melting points, and dissolve readily in organic solvents. The *isopimaric* acids are unstable in air, absorb two or four atoms of hydrogen, are fairly easily soluble in hot organic solvents, and melt between  $150^\circ$  and  $160^\circ$ , whilst the *abietic* acids absorb only two atoms of hydrogen, are difficultly soluble in organic solvents, and melt at about  $200^\circ$ . The true sylvic acids formed by treating the natural acids with hydrochloric or sulphuric acid are stable in the air, absorb four atoms of hydrogen or four hydroxyl groups when treated with permanganate, are difficultly soluble in organic solvents, and have high melting points, whilst the *isosylvic* acids, formed by splitting off water or hydrogen halide from the corresponding additive products of other resinic acids, are relatively easily soluble in organic solvents and have low melting points. A. R. P.

**Synthesis of 7-Ethoxy-4'-dimethylaminoflavone.** H. NÄGELI and J. TAMBOR (*Helv. Chim. Acta*, 1924, 7, 333—336).—Condensation of *p*-dimethylaminobenzaldehyde in alcoholic potassium hydroxide solution with resacetophenone monoethylether (2-hydroxy-4-ethoxyacetophenone) gives 2-hydroxy-4-ethoxy-4'-dimethylaminochalkone (2-hydroxy-4-ethoxyphenyl 4-dimethylaminostyryl ketone), red needles, m. p. 149°, giving an intense green fluorescence in organic solvents. The acetyl derivative forms yellow needles, m. p. 88°. Treatment of the acetyl compound in carbon tetrachloride solution with pyridine dibromide gave a chalkone dibromide which, without further examination, was converted by alcoholic potassium hydroxide into 7-ethoxy-4'-dimethylaminoflavone, orange needles, m. p. 183°. Its solution in concentrated sulphuric acid is yellow with a weak green fluorescence; in organic solvents the fluorescence is intense.

2 : 4-Diethoxyphenyl 4-dimethylaminostyryl ketone, from resacetophenone diethyl ether, as above, forms bright yellow needles, m. p. 128°. *o*-Hydroxyphenyl *p*-dimethylaminostyryl ketone forms red needles, m. p. 176°. The corresponding *p*-hydroxyphenyl *p*-dimethylaminostyryl ketone forms orange leaflets, m. p. 205°; acetyl derivative, brownish-yellow needles, m. p. 136°; methyl ether, yellow leaflets, m. p. 126°; ethyl ether, orange leaflets, m. p. 113°. 2 : 3-Dimethoxyphenyl *p*-dimethylaminostyryl ketone forms brown needles, m. p. 80°, and *o*-anisyl *p*-dimethylaminostyryl ketone, yellow leaflets, m. p. 101°. E. H. R.

**Action of the Oxides and the Oxy-acids of Nitrogen on Diphenylene Oxide.** H. RYAN and N. CULLINANE (*Sci. Proc. Roy. Dubl. Soc.*, 1924, 17, 321—326).—Whilst diphenylene oxide is unaffected by mixtures of cold nitric and glacial acetic acids, nitric acid in carbon tetrachloride solution, fuming nitric acid in warm acetic acid solution, nitrous fumes, or nitrogen peroxide in carbon tetrachloride or acetic acid, converts it mainly into 3-nitrodiphenylene oxide (cf. Borsche and Bothe, A., 1908, i, 528). Gaseous nitrogen peroxide gives the 3 : 6-dinitro derivative (Mailhe, A., 1912, i, 548), which also results when the mononitro derivative is nitrated. By still more vigorous nitration, first 1 : 3 : 6(?)-trinitrodiphenylene oxide (blunt prisms, m. p. 223°), and then 1 : 3 : 6 : 8(?)-tetranitrodiphenylene oxide (colourless plates, m. p. 283°) are produced (cf. Mailhe, *loc. cit.*; Borsche and Scholten, A., 1917, i, 390).

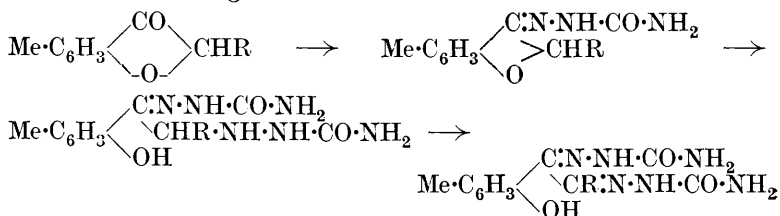
W. A. S.

**Valency Requirements of Alkyl [Radicals].** K. VON AUWERS and G. WEGENER (*J. pr. Chem.*, 1923, [ii], 106, 226—252).—When the silver compound of benzamide is treated with methyl iodide at the ordinary temperature, 52% undergoes change in 11 days, the product affording, with picric acid, ammonium and benzimino methyl ether picrates. When ethyl iodide is used (91% interaction in 5.5 days) the corresponding products are ethyl benzoate, benzonitrile, ammonium picrate, and benzimino ethyl ether dipicrate (?), m. p. 146—147°. When allyl iodide is used, the initial products isolated are benzamide and benzimino *n*-propyl

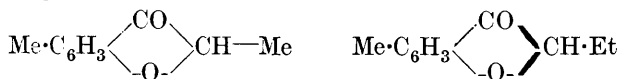
ether (a colourless oil, b. p. 113—116°/12 mm.), the latter with picric acid affording ammonium picrate (cf. Wheeler, A., 1898, i, 185). In none of the above cases were *N*-ethers, described by Wheeler, detected.

*s*-Formylphenylhydrazine, when treated with methyl iodide in presence of sodium ethoxide, gives a mixture of products; with allyl bromide as alkylating agent the hydrazine is rapidly and quantitatively converted into  $\beta$ -formyl- $\alpha$ -allyl- $\alpha$ -phenylhydrazine, white prisms, m. p. 57—58°, b. p. 183°/13 mm. When benzyl chloride is used,  $\beta$ -formyl- $\alpha$ -benzyl- $\alpha$ -phenylhydrazine (white prisms, m. p. 108—109°) is formed.

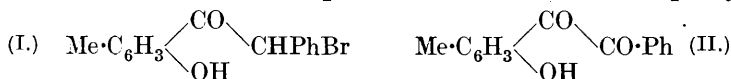
The authors have studied the scission of 4-methyl-1-alkylcoumaranones, using semicarbazide :



The coumaranone (1 mol.) was left in aqueous-alcoholic solution at 45—50° in presence of 2.5 mols. of semicarbazide hydrochloride and sodium acetate and the time required for the initial separation of the disemicarbazone noted. The times (hours) required were as follows : R=Me, 4; R=Et, 14; R=Pr<sup>a</sup>, 4; R=Pr<sup>a</sup>CH<sub>2</sub>, 6.5; R=*n*-pentyl, 7.5; R=Ph·CH<sub>2</sub>, 14.5. These results agree well with those *e.g.* of Meerwein (A., 1920, i, 2), as is evident from the following formulæ :



A phenyl radical (possessing greater valency requirements than an alkyl radical) in position 1 facilitates scission of coumaranones to such an extent that it is impossible to convert (I) into 1-phenyl-



coumaranone satisfactorily, the latter substance being accompanied by (II) and a little *o*-benzoyl-*p*-cresotic acid (produced by the oxidation of 1-phenylcoumaranone). Since coumaranones not alkylated in position 1 cannot be split with semicarbazide, hydrogen must have a lower valency requirement than an alkyl radical. 1 : 1-Dialkylcoumaranones are less readily split by reagents than coumaranone itself, only giving monosemicarbazones with difficulty; this is probably due to steric hindrance. Coumaranones containing the 1-grouping >CR(OR), where R=H or alkyl, are readily split, but this may be attributed to the interaction of the ·OR radical with semicarbazide.

The authors compare and contrast the scission of coumaranones with that of benzoxazoles (Skraup, A., 1919, i, 598) and of phthalides (Teppema, A., 1923, i, 256), from the point of view of valency requirements of the groups present.

A number of new compounds are described:  $\alpha$ -Bromo-n-valeryl bromide is a colourless liquid, b. p.  $190^{\circ}$ ;  $\alpha$ -bromo-n-hexanoyl bromide is a colourless liquid, b. p.  $201\text{--}210^{\circ}$ /ordinary press. (decomp.) or  $85\text{--}90^{\circ}/12\text{--}13$  mm.;  $\alpha$ -bromo-n-heptanoyl bromide, a pale yellow liquid, has b. p.  $101\text{--}102^{\circ}/9$  mm.;  $\alpha$ -bromopalmityl bromide is a white solid, charring when heated. These bromides, condensed with *p*-cresol methyl ether (A., 1918, i, 27), give rise to ketones: 3- $\alpha$ -bromo-n-valeroyl-*p*-cresol forms yellow plates, m. p.  $51\text{--}52^{\circ}$ ; 3- $\alpha$ -bromo-n-hexanoyl-*p*-cresol, yellow needles, has m. p.  $30.5\text{--}31.5^{\circ}$ ; 3- $\alpha$ -bromo-n-heptanoyl-*p*-cresol, yellow needles, has m. p.  $49\text{--}50^{\circ}$ ; 3- $\alpha$ -bromopalmitoyl-*p*-cresol forms yellow crystals, m. p.  $46\text{--}47^{\circ}$ . The ketones, with alcoholic sodium acetate, afford coumaranones: 4-methyl-1-n-propylcoumaranone, a yellow oil, has b. p.  $133\text{--}134^{\circ}/11$  mm.,  $d_4^{20}$  1.064,  $n_D^{20}$  1.5445; 4-methyl-1-n-butylcoumaranone, a yellow oil, has b. p.  $166\text{--}168^{\circ}/17$  mm., and cannot be purified through the semicarbazone, since the disemicarbazone is formed even in the cold; 4-methyl-1-n-pentylcoumaranone, a yellow oil, has b. p.  $175^{\circ}/18$  mm.; 4-methyl-1-n-tetradecylcoumaranone forms waxy white crystals, m. p.  $68\text{--}69^{\circ}$ , and when heated in alcoholic solution with *p*-nitrophenylhydrazine hydrochloride affords the pp-dinitro-osazone of *p*-cresyl tetracaidecyl ketone,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{C}(\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{C}(\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)\cdot\text{C}_{14}\text{H}_{29} + 1$  (or 2)  $\text{H}_2\text{O}$ , red crystals, m. p.  $164\text{--}165^{\circ}$  (with previous softening); 4-methyl-1-benzylcoumaranone, from 2-hydroxy-4-methylcoumarilic ester, sodium ethoxide, and benzyl chloride, forms white prisms or needles, m. p.  $50\text{--}51^{\circ}$ , b. p.  $200\text{--}210^{\circ}/13\text{--}14$  mm. The benzyl compound is accompanied by 2-benzoxyl-4-methylcoumarilic acid, white needles, m. p.  $146\text{--}147^{\circ}$ , and is converted by *p*-nitrophenylhydrazine hydrochloride into the pp-dinitro-osazone of *p*-cresyl benzyl diketone, decomp.  $223^{\circ}$  (if heated rapidly). 4-Methyl-1:1-dibenzylcoumaranone forms colourless needles or rhombohedra, m. p.  $122\text{--}123^{\circ}$ .

The following were obtained by treating coumaranones with semicarbazide: disemicarbazone of *p*-cresyl *n*-propyl diketone, decomp.  $212\text{--}213^{\circ}$  (rapid heating); disemicarbazone of *p*-cresyl *n*-butyl diketone, m. p. or decomp.  $213\text{--}214^{\circ}$  (rapid heating); disemicarbazone of *p*-cresyl *n*-pentyl diketone, m. p.  $208\text{--}216^{\circ}$ ; disemicarbazone of *p*-cresyl benzyl diketone, m. p.  $222^{\circ}$  (rapid heating).

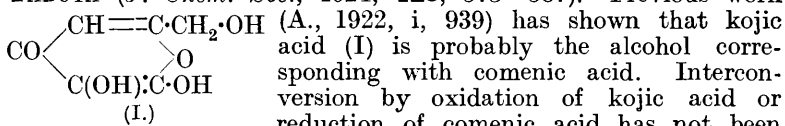
E. E. T.

**Hydroxyhydrindone and Chromanone.** F. MAYER and L. VAN ZÜTPHEN (*Ber.*, 1924, 57, [B], 618).—The product, m. p.  $111^{\circ}$ , obtained by the action of aluminium chloride on  $\alpha$ - $\beta$ -chloropropionylphenol and considered to be 4-ketochroman (Mayer and van Zütphen, this vol., i, 410) is shown to be 7-hydroxy- $\alpha$ -hydrindone (Knahe and Salkowski, A., 1916, i, 820; von Auwers and Hilliger, A., 1917, i, 38).

H. W.

**Synthesis of 7-Methoxychromanone.** A. E. TSCHITSCHIBABIN (*Ber.*, 1924, 57, [B], 617).—The synthesis of 7-methoxychromanone by Pfeiffer and Oberlin (cf. this vol., i, 413) from resorcinol monomethyl ether and iodopropionic acid had already been effected by Tschitschibabin and Nikitin in 1911 (*A.*, 1911, i, 1007). F. A. M.

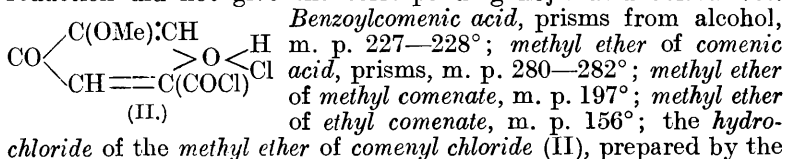
**The Constitution of Kojic Acid, a  $\gamma$ -Pyrone Derivative formed by *Aspergillus oryzae* from Carbohydrates.** T. YABUTA (*J. Chem. Soc.*, 1924, 125, 575—587).—Previous work



accomplished, but both compounds furnish the same 4 : 5-dihydroxy-2-methylpyridine. Kojic acid on treatment with thionyl chloride yields 5-hydroxy-2-chloromethyl- $\gamma$ -pyrone, needles, m. p. 166—167°. The latter gives the corresponding 5-benzoyloxy derivative, prisms, m. p. 117—118°, and the 5-methoxy derivative, needles, m. p. 119—121°, and on reduction with zinc dust and acetic acid gives allomaltol (5-hydroxy-2-methyl- $\gamma$ -pyrone), prisms, m. p. 166°. Allomaltol is distinct from maltol (Brand, *A.*, 1894, i, 270) and from isomaltol (Backe, *A.*, 1910, i, 225, 544), the distinction being confirmed by the preparation of the following derivatives. Allomaltol methyl ether (5-methoxy-2-methyl- $\gamma$ -pyrone), prisms, m. p. 70—71°, b. p. (approx.) 93°/0.1 mm.; benzoylallomaltol (3-benzoyloxy-6-methyl- $\gamma$ -pyrone), prisms, m. p. 128—129°; phenylcarbamate of allomaltol,  $\text{NHPh} \cdot \text{CO} \cdot \text{C}_6\text{H}_5\text{O}_3$ , plates, m. p. 186—188°; bromoallomaltol (6-bromo-5-hydroxy-2-methyl- $\gamma$ -pyrone), crystals, m. p. 171—173°. Benzeneazoallomaltol (6-benzeneazo-5-hydroxy-2-methyl- $\gamma$ -pyrone), by treating allomaltol in solution with diazobenzene acetate, forms reddish-brown needles, no definite m. p.

Oxidation of the following kojic acid derivatives did not give the corresponding comenic acid derivatives: monobenzoyl kojic acid; monoethyl ether of kojic acid (5-ethoxy-2-hydroxymethyl- $\gamma$ -pyrone), prepared by the interaction of kojic acid, ethyl *p*-toluenesulphonate, and sodium ethoxide in alcohol, needles, m. p. 110°; 5-ethoxy-2-hydroxymethyl-4-pyridine, prepared from kojic acid monoethyl ether, and isolated as the picrate, needles, m. p. 184—185°; 5-hydroxy-2-chloromethyl- $\gamma$ -pyrone and its methyl ether; 5-hydroxy-2-iodomethyl- $\gamma$ -pyrone, prepared from the corresponding chloro-compound as crystalline plates; 5-methoxy-2-iodomethyl- $\gamma$ -pyrone, prisms, m. p. 135—137°.

The following derivatives of comenic acid were prepared, but reduction did not give the corresponding kojic acid derivatives.

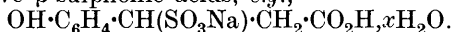


action of thionyl chloride on comenic acid methyl ether, prisms, m. p.  $103^{\circ}$ ; the *methyl ether of comenyl chloride*, prepared from the previous compound by the action of sodium acetate, m. p.  $148^{\circ}$ ; *comenamide methyl ether*, prepared by the action of ammonia on (II), needles, m. p.  $178^{\circ}$ . The catalytic reduction of the methyl ether of comenyl chloride by Rosenmund's method (A., 1918, i, 300; 1921, ii, 320, 392) failed owing to the instability of the pyrone nucleus. *Comenamic acid methyl ether* (5-methoxy-4-pyridone-2-carboxylic acid) was prepared by the action of ammonia on comenic acid methyl ether; *ammonium salt*, needles, m. p.  $269^{\circ}$ ; *hydrochloride*, prisms. Thionyl chloride introduces chlorine into the 4-position of the methyl ether, giving *4-chloro-5-methoxypyridine-2-carboxylic acid chloride*, which Rosenmund's method also failed to reduce. The acid chloride was converted into *4-chloro-5-methoxypyridine-2-carboxylic acid*, prisms, m. p.  $209^{\circ}$ , into the *amide*, needles, m. p.  $207-208^{\circ}$ , into the *methyl ester*, prisms, m. p.  $167^{\circ}$ , and into the *ethyl ester*, prisms, m. p.  $140^{\circ}$ .

*alloMaltol methyl ether*, prepared either by the methylation of *allomaltol* or by the reduction of 5-methoxy-2-chloromethyl-4-pyrone, when heated with ammonia in a closed tube at  $100^{\circ}$  gives *5-methoxy-2-methyl-4-pyridone*, needles, m. p.  $115^{\circ}$ , which gives a *picrate*, needles, m. p.  $205-206^{\circ}$ . The dimethyl ether of kojic acid, when similarly treated, yields the corresponding pyridine derivative, which distils at  $200^{\circ}/1$  mm., and on heating with red phosphorus and hydriodic acid gives *4:5-dihydroxy-2-methyl pyridine*, prisms, decomp.  $280^{\circ}$ , and crystallising  $+1\text{H}_2\text{O}$  at low temperatures.

Comenic acid when heated with ammonia under pressure gives comenamic acid, which when treated with phosphorus pentachloride and then reduced with tin and hydrochloric acid gives the same *4:5-dihydroxy-2-methylpyridine*. The dihydroxypicolines obtained thus from both acids gave on methylation the same *5-methoxy-1:2-dimethyl-4-pyridone* ( $+3\text{H}_2\text{O}$ ), colourless needles, m. p.  $98^{\circ}$ . This compound is also formed by treating *allo-maltol methyl ether* with methylamine, thus confirming the position of the methyl groups. Comenamic acid on methylation gives similarly *5-methoxy-1-methyl-4-pyridone-2-carboxylic acid* ( $+4\text{H}_2\text{O}$ ), needles, m. p.  $208^{\circ}$ .  
F. G. M.

**Action of Sodium Sulphite on Coumarins.** B. B. DEY and K. K. ROW (*J. Chem. Soc.*, 1923, 125, 554-564).—Coumarins and many substituted coumarins react readily with sodium hydrogen sulphite to give  $\beta$ -sulphonic acids, *e.g.*,



These yield halogen and nitro derivatives, which when heated with sulphuric acid give sulphur dioxide and the corresponding *Bz*-substituted coumarins, and when heated with potassium hydroxide solution give the corresponding potassium coumarates. The ethers of coumarinic acid when boiled with sodium hydrogen sulphite solution and then with sodium hydroxide solution give the corresponding ethers of coumaric acid.

Thus coumarin when boiled with aqueous sodium hydrogen sulphite gives *sodium dihydrocoumaric acid*  $\beta$ -sulphonate, colourless plates from water, decomp.  $175\text{--}176^\circ$  (potassium, barium, and calcium salts described). 6-Nitrocoumarin gives *sodium 5-nitrodihydrocoumaric acid*  $\beta$ -sulphonate, whilst 3-chloro- and 3-bromocoumarin both give benzfuran-2-carboxylic acid (cf. Fittig, A., 1883, 474). 3:6-Dinitrocoumarin gives 5-nitrosalicylaldehyde, whilst *o*-coumaric acid behaves like coumarin itself. 3-Acetylcoumarin gives *sodium  $\alpha$ -acetyldihydrocoumaric acid*  $\beta$ -sulphonate, white crystals, m. p.  $163^\circ$  (decomp.). Sodium dihydrocoumaric acid  $\beta$ -sulphonate when treated in aqueous solution with chlorine gives *sodium 3:5-dichlorodihydrocoumaric acid*  $\beta$ -sulphonate (colourless needles), which on heating alone or with sulphuric acid gives sulphur dioxide and 6:8-dichlorocoumarin, crystalline nodules, m. p.  $160^\circ$ , subliming at  $130\text{--}135^\circ$  in colourless needles. Bromine similarly gives *sodium 3:5-dibromodihydrocoumaric acid*  $\beta$ -sulphonate (plates), which on heating gives 6:8-dibromocoumarin, needles, m. p.  $176^\circ$ . Iodine gives *sodium 5-iododihydrocoumaric acid*  $\beta$ -sulphonate, colourless plates, which on heating yields 6-iodocoumarin, needles, m. p.  $165^\circ$ .

Sodium 5-nitrodihydrocoumaric acid  $\beta$ -sulphonate on bromination gives *sodium 3-bromo-5-nitrodihydrocoumaric acid*  $\beta$ -sulphonate, colourless plates, decomp.  $210^\circ$ , on iodination *sodium 3-iodo-5-nitrodihydrocoumaric acid*  $\beta$ -sulphonate, and on treatment with fuming nitric acid gives *sodium 3:5-dinitrodihydrocoumaric acid*  $\beta$ -sulphonate.

8-Bromo-6-nitrocoumarin, colourless needles from acetic acid, m. p.  $200^\circ$ , is obtained by heating the corresponding sodium dihydrocoumaric acid  $\beta$ -sulphonate with sulphuric acid, and on reduction with 5% acetic acid and iron filings gives 8-bromo-6-aminocoumarin, yellow needles, m. p.  $200^\circ$ . The latter gives an *acetyl* derivative, colourless needles, m. p.  $249^\circ$ , a *benzoyl* derivative, needles from acetic acid, m. p.  $217^\circ$ , a *hydrochloride*, colourless prisms, darkening at  $235^\circ$ , m. p.  $246^\circ$  (decomp.), and a *picrate*, yellow needles, m. p.  $180\text{--}181^\circ$  (decomp.). 8-Iodo-6-nitrocoumarin, similarly prepared, colourless needles, m. p.  $249^\circ$  (decomp.), on reduction gives 8-iodo-6-aminocoumarin, orange-yellow needles, m. p.  $210^\circ$ , which yields an *acetyl* derivative, needles, m. p.  $275^\circ$  (decomp.). 6:8-Dinitrocoumarin, similarly prepared, forms yellow needles, m. p.  $158^\circ$ .

The following *o*-coumaric acids were prepared by treating the corresponding sodium dihydrocoumaric acid  $\beta$ -sulphonates with boiling 20% potassium hydroxide solution and then acidifying. The acids on fusion with potassium hydroxide lose carbon dioxide, giving styrene derivatives. 5-Chlorocoumaric acid, needles, m. p.  $228^\circ$  (decomp.); 5-bromocoumaric acid, needles, m. p.  $224^\circ$  (decomp.); 3:5-dichlorocoumaric acid, crystals, m. p.  $242^\circ$  (decomp.), *methyl* ester, colourless needles, m. p.  $176^\circ$ ; 3:5-dibromocoumaric acid, needles, m. p.  $238^\circ$  (decomp.), *methyl* ester, needles, m. p.  $173^\circ$ , *ethyl* ester, spear-shaped crystals, m. p.  $128^\circ$ , *acetyl* derivative, needles, m. p.  $201^\circ$ . 5-Nitrocoumaric acid, colourless needles,



m. p. 247° (decomp.), *silver* salt, insoluble and orange-coloured, *methyl* ester, colourless needles, m. p. 211°, *acetyl* derivative, needles, m. p. 217°, immediately resolidifying, and melting again at 259°. 3-Bromo-5-nitrocoumaric acid, colourless needles, m. p. 234° (decomp.), *methyl* ester, needles, m. p. 212°, *ethyl* ester, fern-shaped crystals, m. p. 184°, *acetyl* derivative, needles, m. p. 186° (decomp.). 5-Nitro-4-methylcoumaric acid, colourless needles, m. p. 219° (decomp.), *silver* salt, deep orange-red, *methyl* ester, needles, m. p. 187°, *ethyl* ester, needles, m. p. 160°; the acid itself, on fusion with potassium hydroxide, gives 5-nitro-2-methoxy-4-methylcinnamic acid, *methyl* ester, needles, m. p. 136°.

The methyl ethers of coumarinic and 5-nitrocoumarinic acids when boiled with 20% sodium sulphite solution were smoothly converted into the ethers of the corresponding coumaric acids.

$\alpha$ -Naphthacoumaric acid, prepared from  $\alpha$ -naphthapyrone, needles, m. p. 167° (decomp.), *silver* salt, pale yellow. 4-Nitro- $\alpha$ -naphthacoumaric acid, prepared from 6-nitronaphthapyrone, small crystals, m. p. 179—180° (decomp.), *silver* salt, orange.

An aqueous solution of  $\alpha$ :1:8-isonaphthoxazone when boiled with sodium sulphite and then with potassium hydroxide, and finally neutralised, gave 6-hydroxyquinoline-5- $\beta$ -acrylic acid,  $\text{OH}\cdot\text{C}_9\text{H}_5\text{N}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , white powder, m. p. 220° (decomp.); *silver* salt, pale yellow. The acid, when heated with sulphuric acid, gave the original isonaphthoxazone. F. G. M.

**Fluorescence.** J. TRÖGER and O. GRÜNTAL (*J. pr. Chem.*, 1923, [ii], 106, 173—202; cf. A., 1923, i, 355).—The authors have prepared a number of arylsulphonearylideneacetonitriles of the type  $\text{R}\cdot\text{CH}:\text{C}(\text{SO}_2\text{R}')\text{CN}$  (cf. A., 1908, i, 798), and recorded the fluorescence (if any) of their solutions in concentrated sulphuric acid, glacial acetic acid, etc.  $\text{R}=2$ -hydroxy-1-naphthyl,  $\text{R}'=\text{Ph}$ , lemon-yellow prisms, m. p. 221° (decomp.): this *nitrile* gives an intense green fluorescence in cold glacial acetic acid; the green fluorescence observed in concentrated sulphuric acid becomes blue on standing, probably owing to the formation of 2-benzenesulphonyl-4:3- $\beta$ -naphthapyrone, which results when the yellow compound is heated with acetic anhydride.  $\text{R}=2$ -hydroxy-1-naphthyl,  $\text{R}'=p$ -tolyl: this *nitrile* [lemon-yellow prisms, m. p. 232° (decomp.)] exhibits fluorescence similar to the last compound and with acetic anhydride affords 2-*p*-toluenesulphonc-*p*-naphthapyrone.  $\text{R}=2$ -hydroxy-1-naphthyl,  $\text{R}'=p$ -chlorophenyl: this *nitrile* [lemon-yellow prisms, m. p. 254° (decomp.)] shows fluorescence as above, and with acetic anhydride gives 2-*p*-chlorobenzenesulphonyl- $\beta$ -naphthapyrone.  $\text{R}=2$ -hydroxy-1-naphthyl,  $\text{R}'=o$ -anisyl: this *nitrile* [sulphur-yellow prisms, m. p. 241° (decomp.)] exhibits fluorescence as above and is converted by acetic anhydride into 2-*o*-anisylsulphone- $\beta$ -naphthapyrone, reddish-yellow prisms, m. p. 280° (decomp.).  $\text{R}=2$ -hydroxy-1-naphthyl,  $\text{R}'=\beta$ -naphthyl: this *nitrile* [yellow prisms, m. p. 198° (decomp.)] exhibits fluorescence as above and with acetic anhydride affords 2- $\beta$ -naphthalenesulphonylnaphthapyrone, yellow prisms, m. p. 234° (decomp.).  $\text{R}=2$ -methoxy-

1-naphthyl,  $R' = \text{Ph}$ : this *nitrile* (prisms, m. p.  $188^\circ$ ) shows the above type of fluorescence.  $R = 2\text{-methoxy-1-naphthyl}$ ,  $R' = p\text{-tolyl}$ : this *nitrile* (yellow prisms, m. p.  $197^\circ$ ) develops fluorescence slowly in the above solvents, as is the case with the *nitrile* (sulphur-yellow prisms, m. p.  $206^\circ$ ) having  $R = 2\text{-methoxy-1-naphthyl}$  and  $R' = p\text{-chlorophenyl}$ .  $R = 2 : 7\text{-dihydroxynaphthyl}$ ,  $R' = p\text{-tolyl}$ : this *nitrile* [yellowish-green prisms, m. p.  $288^\circ$  (decomp.)] shows no fluorescence in sulphuric acid solution, owing to the fact that 9-acetoxy-2-*p*-toluenesulphonyl- $\beta$ -naphthapyrone (m. p.  $251^\circ$ ), which results when it is heated with acetic anhydride, is non-fluorescent under similar conditions. The *nitrile* having  $R = 2 : 7\text{-dihydroxynaphthyl}$  and  $R = \text{Ph}$  forms brownish-green prisms, m. p.  $246^\circ$  (decomp.), and behaves similarly to the tolyl derivative. Other *nitriles* giving non-fluorescent solutions in sulphuric acid are those in which  $R = o\text{-hydroxyphenyl}$ ,  $R' = \text{Ph}$  (white crystals, m. p.  $160^\circ$ ), and  $R = m\text{-acetoxyphenyl}$ ,  $R' = p\text{-tolyl}$  (grey leaflets, m. p.  $134^\circ$ ). The *nitrile* containing  $R = 2 : 5\text{-dihydroxyphenyl}$ ,  $R' = p\text{-tolyl}$  [yellow needles, m. p.  $224^\circ$  (decomp.)], develops very little fluorescence and on boiling in alcoholic solution passes into 3-*p*-toluenesulphonyl-6-hydroxycoumarin, the latter substance possessing very slight fluorescent properties. The *nitriles* (canary-yellow prisms, m. p.  $159^\circ$  and  $150^\circ$ , respectively) containing  $R = 2 : 5\text{-dimethoxyphenyl}$ ,  $R' = \text{Ph}$ , and  $R = 2 : 5\text{-dimethoxyphenyl}$ ,  $R' = p\text{-tolyl}$ , develop fluorescent effects slowly in acid solution. The *nitriles* containing  $R = 3 : 4\text{-dihydroxyphenyl}$ ,  $R' = p\text{-tolyl}$  [yellow prisms, m. p.  $183^\circ$  (decomp.)], and  $R = 3 : 4\text{-methylenedioxy}$ ,  $R' = p\text{-tolyl}$  (pale yellow leaflets, m. p.  $168^\circ$ ) exhibit no fluorescent effects. On the other hand, when  $R = 2 : 4\text{-dihydroxyphenyl}$ ,  $R' = \text{Ph}$  (yellow prisms, m. p.  $237^\circ$ ), marked fluorescence is shown by the *nitrile* in sulphuric acid solution. Moderate fluorescent effects are observed with the *nitrile* having  $R = 2 : 4\text{-dihydroxyphenyl}$ ,  $R' = p\text{-tolyl}$  [yellow prisms, m. p.  $247^\circ$  (decomp.)], this *nitrile* being converted by acetic anhydride into 3-*p*-toluenesulphonyl-7-acetoxycoumarin. Similar properties apply to the *nitrile* in which  $R = 2 : 4\text{-dihydroxyphenyl}$ ,  $R' = p\text{-chlorophenyl}$  [sulphur-yellow prisms, m. p.  $232^\circ$  (decomp.)], this compound passing, in boiling alcoholic solution, into 3-*p*-chlorobenzenesulphonyl-7-hydroxycoumarin (m. p.  $232^\circ$ ). A sulphuric acid solution of the *nitrile* having  $R = 2 : 4\text{-dihydroxyphenyl}$ ,  $R' = o\text{-anisyl}$  (yellow prisms, m. p.  $198^\circ$ ) slowly develops fluorescence. The following *nitriles* show no fluorescence: (1)  $R = 2 : 4\text{-dihydroxyphenyl}$ ,  $R' = \beta\text{-naphthyl}$ , sulphur-yellow prisms, m. p.  $253^\circ$  (decomp.), and (2),  $R = 2 : 4\text{-dimethoxyphenyl}$ ,  $R' = \text{Ph}$ , yellow needles, m. p.  $154^\circ$ .

From the above, it is seen that strongly fluorescent solutions (in concentrated sulphuric acid) are obtained from *nitriles* possessing a hydroxyl group in the ortho-position to the unsaturated side chain. Other theoretical points are discussed, for which the original should be consulted.

E. E. T.

**Attempted Syntheses of *meta*-Related Ring Systems. II.** F. REINDEL and L. SCHUBERTH (*Ber.*, 1924, 57, [B], 369–371; cf. Reindel and Siegel, A., 1923, i, 916).—The action of *m*-xylylene bromide on pyrocatechol, resorcinol, or quinol in alcoholic solution in

the presence of sodium alkoxide yields only mixtures of products which could not be purified satisfactorily. Better results are obtained with the monomethyl ethers, whereby *m*-xylenyl di-*o*-anisyl ether,  $C_6H_4(CH_2 \cdot O \cdot C_6H_4 \cdot OMe)_2$ , colourless needles, m. p.  $115^\circ$ , and *m*-xylenyl di-*p*-anisyl ether, quadratic leaflets, m. p.  $128^\circ$ , are isolated; resorcinol methyl ether gives a compound, b. p.  $121^\circ/10$  mm., which contains halogen. The compounds, however, are not adapted to the production of *meta*-related ring systems, since they cannot be demethylated without extensive decomposition of the molecule. Attempts to replace methyl by more readily eliminable radicals (acetyl, benzoyl, or carbethoxyl) did not lead to the desired result owing to the ready fission of the compounds into their components.

*m*-Dithiolbenzene is converted by *m*-xylylene bromide and sodium ethoxide in the presence of alcohol and benzene into the *meta*-cyclic thioether,  $C_6H_4 \begin{smallmatrix} < S \cdot CH_2 \cdot C_6H_4 \cdot CH_2 \cdot S \\ S \cdot CH_2 \cdot C_6H_4 \cdot CH_2 \cdot S \end{smallmatrix} > C_6H_4$ , colourless needles, m. p.  $235^\circ$ . H. W.

**Formation of Pyrrole Derivatives from Amides of  $\beta$ -Diketonic Esters.** W. KÜSTER and P. SCHLACK [with E. ERFLE and W. HEES] (*Ber.*, 1924, 57, [B], 409—413).—Dicarbonyl derivatives obtained from oxalic esters are not generally suited to the production of pyrrole derivatives by reason of their strongly acidic character. Attempts are described to obtain more successful results from compounds of this type in which the acidity has been diminished by the introduction of groups containing nitrogen.

Acetylpyruvanilide,  $CH_3Ac \cdot CO \cdot CO \cdot NHPh$ , pale yellow needles, m. p.  $140$ — $141$  (cf. Mumm and Bergell, A., 1912, i, 936), is readily converted into the corresponding nitroso derivative,  $C_{11}H_{10}O_4N_2$ , dark yellow prisms, m. p.  $138^\circ$ , which could not be caused to react with ethyl acetoacetate to yield a substituted pyrrole. A negative result was also obtained when the diketone and ethyl nitrosoacetoacetate were employed.

Ethyl oxalate condenses with acetmethylanilide in the presence of sodium ethoxide to give ethoxalylacetmethylanilide,



colourless needles, m. p.  $75^\circ$ , b. p.  $112^\circ/740$  mm. (copper salt,  $C_{26}H_{28}O_5N_2Cu$ , m. p.  $112$ — $115^\circ$ ; and iron salt,  $C_{33}H_{42}O_{12}N_2Fe$ ). Reduction of a mixture of ethyl nitrosoacetoacetate and ethoxalylacetmethylanilide by zinc dust and glacial acetic acid leads to the formation of ethyl 3-carboxyphenylmethylamido-4-methylpyrrole-2 : 5-dicarboxylate,  $\begin{smallmatrix} C(CO \cdot NMePh) : C(CO_2Et) \\ CMe = = = C(CO_2Et) \end{smallmatrix} > NH$ , colourless crystals, m. p.  $82^\circ$ , which is hydrolysed to the corresponding dicarboxylic acid, m. p.  $126^\circ$ .

The acid character of ethyl acetylpyruvate,  $CH_3Ac \cdot CO \cdot CO_2Et$ , is demonstrated by its ability to react with precipitated ferric hydroxide to form the iron salt,  $C_{21}H_{27}O_{12}Fe$ , red, rhombic leaflets. H. W.

**Synthesis of Cryptopyrrolecarboxylic Acid. (The Synthesis of the Acid Scission Products of Blood Pigment. I.)**

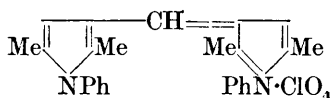
H. FISCHER and B. WEISS (*Ber.*, 1924, **57**, [B], 602—609; cf. A., 1922, i, 759; 1923, i, 707; this vol., i, 201).—Cryptopyrrolecarboxylic acid has been synthesised in the following way: ethyl 2:4-dimethylpyrrole-3-aldehyde-5-carboxylate was condensed with cyanoacetic acid by means of acetic anhydride to give *ethyl 2:4-dimethyl-3-[ω-cyano-ω-carboxyvinyl]pyrrole-5-carboxylate* (yellow needles, m. p. 239°). The latter on reduction gave *ethyl 2:4-dimethyl-3-[ω-cyano-ω-carboxyethyl]pyrrole*, which forms crystals, m. p. 184°; this was then either (i) heated in a vacuum to give *ethyl 2:4-dimethyl-3-ω-cyanoethylpyrrole-5-carboxylate* (m. p. 134°), which was then hydrolysed by concentrated alkali, and after acidification, the crude acid heated with acetic acid and hydriodic acid, the product being cryptopyrrolecarboxylic acid; or (ii) the nitrile-carboxylic acid was (by heating with acetic and hydriodic acids) converted into cryptopyrrolecarboxylic acid. The structure of the acid is thus definitely settled. The following new compounds were also prepared: *ethyl 2:4-dimethyl-3-ω-nitrovinylpyrrole-5-carboxylate*, from the corresponding aldehyde and nitromethane or nitroacetic acid, is yellow and has m. p. 231—232°; *ethyl 2:4-dimethyl-5-ω-nitrovinylpyrrole-3-carboxylate*, m. p. 165°, was prepared from the isomeric aldehyde and nitromethane. *Ethyl 2:4-dimethyl-3-[ω-cyano-ω-carbethoxyvinyl]pyrrole-5-carboxylate* (the ethyl ester of the nitrile-carboxylic acid), m. p. 239°, was prepared from the same aldehyde and ethyl cyanoacetate in presence of methylamine; it forms white needles, m. p. 165°, and on hydrolysis yields *2:4-dimethylpyrrole-3-aldehyde-5-carboxylic acid*, m. p. 230° (decomp.). The following compounds were similarly prepared from cyanoacetic ester and the corresponding aldehyde: *2:4-dimethyl-3-[ω-cyano-ω-carbethoxyvinyl]pyrrole*, crystals, m. p. 121°, giving, when hydrolysed, *2:4-dimethylpyrrole-3-aldehyde*, m. p. 126°; *ethyl 2:4-dimethyl-5-[ω-cyano-ω-carbethoxyvinyl]pyrrole-3-carboxylate*, yellow crystals, m. p. 153°; *3-acetyl-2:4-dimethyl-5-[ω-cyano-ω-carbethoxyvinyl]pyrrole*, yellow crystals, m. p. 174°; *2:4:5-trimethyl-3-[ω-cyano-ω-carbethoxyvinyl]pyrrole*, dark yellow crystals, m. p. 147°; *ethyl 2:4-dimethyl-3-[ω-cyano-ω-carbethoxyethyl]pyrrole-5-carboxylate*, white needles, m. p. 131°; *ethyl 2:4-dimethyl-3-[dicyanovinyl]pyrrole-5-carboxylate*, m. p. 214°, from *2:4-dimethyl-5-carbethoxy-pyrrole-3-aldehyde* and malononitrile in acetic anhydride; *ethyl 4-methyl-3-propionyl-2-ethylpyrrole-5-carboxylate*, from nitrosoacetoacetic ester and dipropionylmethane in glacial acetic acid with the addition of zinc dust, white needles, m. p. 112°; *5-carbethoxy-2:4-dimethyl-3-pyrrylglyoxylic ester*, m. p. 133°, was prepared from *ethyl 2:4-dimethylpyrrole-5-carboxylate* and methyl cyanocarbonate in presence of hydrochloric acid. *Ethyl 2:4-dimethyl-3-[cyanoacetyl]pyrrole-5-carboxylate* reacts with hydrazine hydrate in presence of sodium ethoxide to give an oily substance which shows an intense pyrrole reaction; it forms a *picrate*, and an *azo dye*, m. p. 166°.

F. A. M.

**Synthetic Experiments with the Fission Products of the Blood Pigments and the Formation of Complex Salts from Dipyrromethenes.** II. H. FISCHER and M. SCHUBERT (*Ber.*, 1924, 57, 610—617; cf. preceding abstract).—The synthesis of cryptopyrrole has been modified by heating ethyl 2:4-dimethyl-3-acetylpyrrole-5-carboxylate with hydrazine hydrate and sodium ethoxide at 180°. In the synthesis of cryptopyrrole-aldehyde by the Gattermann hydrocyanic acid method, *cryptopyrrole-aldimine* (isolated as the *picrate*, yellow crystals, m. p. 205°) is formed. Attempts to hydrolyse the intermediate product in the synthesis (dicryptopyrromethylamine) were unsuccessful, the imine, however, readily yielding cryptopyrrole-aldehyde. The amine, with semicarbazide, affords the semicarbazone of the aldehyde. 5-*Chloroacetyl-2:3-dimethyl-4-ethylpyrrole*, from hæmopyrrole and chloroacetonitrile, forms colourless needles, m. p. 140°. 5-*Dimethylaminoacetyl-2:3-dimethyl-4-ethylpyrrole hydrochloride* (colourless needles, m. p. 73°) results from chloroacetyl hæmopyrrole and dimethylamine. On submitting hæmopyrrole to the Gattermann synthesis, the product consists of a mixture of *hæmopyrrole-aldimine (picrate)*, m. p. 200°, decomp. 195—200°, and *C-dihæmopyrromethylamine (aminodihæmopyrromethane)*, which forms colourless needles, m. p. 150°. The hæmopyrrole-aldimine, when boiled in aqueous suspension, gives 5-*formyl-2:3-dimethyl-4-ethylpyrrole*, colourless needles, m. p. 85° (*semicarbazone*, colourless crystals, m. p. 195°). The aldehyde, with hot concentrated hydrochloric acid, yields violet-red crystals of bis-[2:3-dimethyl-4-ethylpyrrol]methene hydrochloride, m. p. 215°. From phonopyrrolecarboxylic ester (Gattermann synthesis), *methyl hæmopyrrolecarboxylate aldimine hydrochloride* was obtained as colourless needles, m. p. 173°. In a similar manner, cryptopyrrolecarboxylic acid yielded *cryptopyrrolecarboxylic acid aldimine hydrochloride* as colourless needles, m. p. 208°, which on hydrolysis yielded 5-*formyl-2:4-dimethylpyrrole-3-propionic acid*, yellowish-brown needles, m. p. 151° (*semicarbazone*, m. p. 223°). The cryptopyrrolecarboxyaldehyde, on heating with dilute hydrochloric acid, yields red needles of bis-[2:4-dimethyl-3-carboxyethylpyrrol]methene hydrochloride, m. p. 235°. Cryptopyrrolecarboxy-aldehyde condenses with cryptopyrrole in presence of hydrochloric acid to give reddish-brown needles of [2:4-dimethyl-3-carboxyethylpyrrol]-[2:4-dimethyl-3-ethylpyrrol]methene hydrochloride, m. p. 215°. The following complex salts of bis-[2:4-dimethyl-3-carbethoxypyrryl]methene were prepared: *copper, nickel, cobalt, and zinc*; the *nickel, cobalt, and zinc* complex salts of bis-[2:4-dimethylpyrrol]methene were also made. F. A. M.

**Di-β-pyrromethenes.** I. H. FISCHER and K. S. SMEYKAL (*Ber.*, 1924, 57, [B], 544—550).—The condensation of ethyl 2:5-dimethylpyrrole-3-carboxylate with formic acid in presence of perchloric acid affords a substance,  $C_{13}H_{17}N_2 \cdot ClO_4$ , orange needles, decomp. 220—230°, and possessing marked sternutatory properties. It appears to be identical with the *perchlorate* of the product obtained by Piloty (*A.*, 1915, i, 461) by condensing 2:5-dimethylpyrrole

with 3-formyl-2 : 5-dimethylpyrrole, which appears to be *di*-3-(2 : 5-dimethylpyrryl)methene. It was obtained also by condensing 2 : 5-dimethylpyrrole with formic acid in presence of perchloric acid. The free *base* forms orange needles charring above 200°. The *hydrochloride* forms long, red needles, the *sulphate*, small, reddish-brown needles. Ethyl 1-phenyl-2 : 5-dimethylpyrrole-3-carboxylate condenses with formic acid in presence of perchloric



acid to give the *perchlorate* of a substance,  $C_{25}H_{25}N_2 \cdot ClO_4$ , presumably *di*-3-(1-phenyl-2 : 5-dimethylpyrryl)methene (annexed formula), which forms reddish-brown leaflets,

m. p. 245° (decomp.).

Diethyl 1-hydroxy-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate condenses with formic acid in presence of perchloric acid to give long, red needles of the perchlorate of a substance, decomposing at 210—215°, of the formula  $C_{13}H_{17}O_6N_2Cl$ , probably the *perchlorate* of *di*-3-(1-hydroxy-2 : 5-dimethylpyrryl)methene. Ethyl 2 : 5-dimethylpyrrole-4-aldehyde-3-carboxylate undergoes auto-condensation when heated with strong hydrochloric acid to give a *hydrochloride*, red needles, m. p. 181°. The perchlorate,  $C_{10}H_{23}N_2 \cdot ClO_4$ , appears to be that of *ethyl* 2 : 5 : 2' : 5'-tetramethyldi- $\beta$ -pyridylmethene-4-carboxylate, the base being a yellow powder charring at 220—230°. The mother-liquors contain a small amount of the base previously obtained from ethyl 2 : 5-dimethylpyrrole-3-carboxylate. F. A. M.

**Catalytic Hydrogenations under Pressure in the Presence of Nickel Salts. VIII. Compounds of the Indole Series.** J. VON BRAUN, O. BAYER, and G. BLESSING (*Ber.*, 1924, 57, [B], 392—403).—An extension of previous work (A., 1923, i, 835; this vol., i, 426). Indole resembles quinoline in that hydrogenation takes place primarily in the heterocyclic nucleus. The presence of substituents in this nucleus increases its resistance to reduction, and causes hydrogenation to occur to a greater or less extent in the benzenoid half of the molecule. As in the quinoline series, this tendency can be balanced by the introduction of substituents into the benzenoid nucleus.

Hydrogenation of the indoles was effected in decahydronaphthalene solution, generally at 220—250°. The reaction usually comes to an end before the calculated volume of hydrogen has been absorbed and, when this is the case, ammonia is also formed.

The pyrrole ring is not completely stable under the conditions of hydrogenation and yields fully hydrogenated indoles (see below) and *o*-alkylanilines, among which, *o*-isopropylaniline, b. p. 95°/13 mm.,  $d_4^{12}$  0.9760 (*hydrochloride*, m. p. 182°; *picrate*, m. p. 160°; *acetyl* derivative, m. p. 70°; *phenylthiocarbamide* compound, m. p. 129—130°), does not appear to have been described previously.

Indole, when hydrogenated at 225° until further absorption of gas does not occur, yields 8% of unchanged material and 66% of basic substances, whereas the remainder suffers more complete degradation accompanied by the production of ammonia. The

bases consist of perhydroindole (octahydroindole), a colourless liquid with an odour of hemlock, b. p. 170—171°/760 mm.,  $d_4^{17}$  0.8845 [Willstätter and Jacquet (A., 1918, i, 392) give b. p. 182—183°/720 mm., 65°/12 mm.,  $d_4^{21}$  0.9947], which yields a chloroplatinate, m. p. 238—239° [Willstätter and Jacquet, m. p. (indefinite) 172—173°]; a *picrate*, m. p. 189—190° (Willstätter and Jacquet, m. p. about 137—138°); a quaternary *iodide*, m. p. 234° (decomp.), and a *benzenesulphonyl* derivative, m. p. 121—122°; also *o*-ethyl-aniline, b. p. 209—210°/760 mm.,  $d_4^{21}$  0.9769 (*hydrochloride*, m. p. 191°; *picrate*, m. p. 194—195°; *acetyl* derivative, needles, m. p. 113°; *benzoyl* derivative, m. p. 146°; *phenylthiocarbamide* compound, needles, m. p. 124°; *benzenesulphonyl* derivative, m. p. 101—102°). 2:3-Dihydroindole can readily be prepared by the partial hydrogenation of indole at 180°.

[In part with G. LEMKE.]—2-Methylindole is converted by hydrogen at 220° into a mixture of 2-methyloctahydroindole and 2-methyl-4:5:6:7-tetrahydroindole. The former compound is a colourless liquid with a pronounced basic odour, b. p. 62°/12 mm.,  $d_4^3$  0.9142; it gives a *picrate*, pale yellow prisms, m. p. 192—193°, and a *benzenesulphonyl* derivative, m. p. 110—112°. The corresponding quaternary *iodide*, m. p. 196°, is decomposed by treatment with silver oxide and subsequent distillation into an apparently homogeneous, unsaturated *base*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_8 \cdot \text{CH} : \text{CHMe}$  or  $\text{C}_6\text{H}_9 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{NMe}_2$ , b. p. 80—81°/13 mm.,  $d_4^{15}$  0.8603, which yields a *picrate*, m. p. 129—130°, and a quaternary *iodide*, m. p. 187—188°. When the latter compound is treated with silver oxide and the product is distilled, *propenyltetrahydrobenzene*,  $\text{C}_6\text{H}_9 \cdot \text{CH} : \text{CHMe}$ , b. p. 161°,  $d_4^{17}$  0.8285,  $n_D^{17.6}$  1.4837, is obtained. 2-Methyl-4:5:6:7-tetrahydropyrrole is a colourless liquid, b. p. 105°/13 mm.,  $d_4^{10}$  0.9871, which gives all the reactions characteristic of pyrroles.

3-Methylindole yields 3-methyl-4:5:6:7-tetrahydroindole, b. p. 105°/12 mm.,  $d_4^{14}$  0.9698, and 3-methyloctahydroindole, a mobile liquid, b. p. 70°/12 mm.,  $d_4^3$  0.8908 [*hydrochloride*, m. p. 260° (decomp.); *picrate*, m. p. 195—196°; *quaternary iodide*,  $\text{C}_{11}\text{H}_{22}\text{NI}$ , m. p. 190°; *benzenesulphonyl* derivative, colourless crystals, m. p. 129—130°].

1:2-Dimethylindole is rapidly hydrogenated at 200° to a mixture of somewhat unstable 1:2-dimethyl-4:5:6:7-tetrahydroindole, b. p. 108°/12 mm.,  $d_4^{20}$  0.9815, and 1:2-dimethyloctahydroindole, a colourless liquid with an odour of hemlock, b. p. 71°/12 mm.,  $d_4^{20}$  0.8822, which suffers partial dehydrogenation when boiled. It yields a methiodide, m. p. 197° (also obtained from 2-methyloctahydroindole), a very hygroscopic *hydrochloride*, a *chloroplatinate*, decomp. 220°, and a *picrate*, m. p. 149—150°.

2:5-Dimethylindole is slowly and incompletely hydrogenated at 250°. It gives small amounts of 2:5-dimethyloctahydroindole, which is characterised as the *benzenesulphonyl* derivative, m. p. 114°, and, preponderatingly, *o*-propyl-*p*-toluidine, a colourless liquid, b. p. 98—99°/13 mm.,  $d_4^{12}$  0.9666. The latter substance gives a *benzenesulphonyl* derivative, m. p. 104°, a *picrate*, m. p. 201°, a *hydrochloride*, m. p. 195°, a *benzoyl* derivative, m. p. 174—175°,

and a *phenylthiocarbamide* compound, m. p.  $146^{\circ}$ ; the amine is converted by boiling its diazotised solution into *o-propyl-p-cresol*, b. p.  $97^{\circ}/13$  mm.,  $d_4^{25}$  1.018.

**2 : 4 : 7-Trimethylindole**, a colourless liquid which rapidly darkens in colour, b. p.  $158-159^{\circ}/13$  mm., is prepared by the condensation of *p*-xylylhydrazine with acetone and treatment of the product with zinc chloride at  $160^{\circ}$ . It is hydrogenated to *2-propyl-3 : 6-dimethylaniline*, b. p.  $107-110^{\circ}/13$  mm.,  $d_4^{21}$  0.9680. The corresponding *picrate*, m. p.  $184^{\circ}$ , the non-crystalline *hydrochloride*, and the brownish-yellow *chloroplatinate*, decomp.  $178^{\circ}$ , are described.

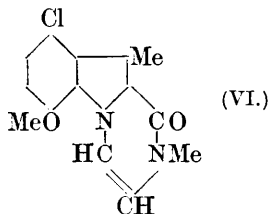
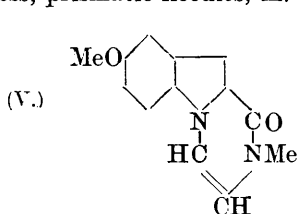
H. W.

**The Methoxyindoles and their Derivatives.** K. G. BLAIR and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1924, **125**, 296—335).—*2-Nitro-5-, -3-, and -6-methoxytoluenes* were condensed with ethyl oxalate in presence of potassium ethoxide to form the corresponding nitromethoxyphenylpyruvic acids. *2-Nitro-5-methoxyphenylpyruvic acid* forms yellow needles, m. p.  $128^{\circ}$ , and gives a *phenylhydrazone*, yellow prisms, m. p.  $151-152^{\circ}$  (decomp.). *2-Nitro-3-methoxyphenylpyruvic acid* crystallises from acetic acid in yellow prisms, m. p.  $118-145^{\circ}$ , containing the solvent, which is lost at  $100^{\circ}$ , leaving the acid as an opaque, pale yellow powder, m. p.  $161-162^{\circ}$ . The *phenylhydrazone* forms yellow needles, m. p.  $159^{\circ}$  (decomp.). *2-Nitro-6-methoxyphenylpyruvic acid* forms yellow, indefinite crystals containing benzene, m. p.  $47-55^{\circ}$ , which retain the solvent after several days in a vacuum. The *phenylhydrazone* forms yellow needles, m. p.  $173-174^{\circ}$  (decomp.). On oxidation with alkaline hydrogen peroxide, the above nitromethoxyphenylpyruvic acids yield, respectively, *2-nitro-5-methoxyphenylacetic acid*, faintly brown needles, m. p.  $176^{\circ}$ ; *2-nitro-3-methoxyphenylacetic acid*, colourless needles, m. p.  $137-138^{\circ}$ ; and *2-nitro-6-methoxyphenylacetic acid*, bright yellow needles, m. p.  $172^{\circ}$ . On reduction with ammoniacal ferrous sulphate, the nitromethoxyphenylpyruvic acids give good yields, respectively, of *5-methoxyindole-2-carboxylic acid*, colourless needles, m. p.  $196-197^{\circ}$  (decomp.) (*ethyl* and *methyl* esters, colourless needles, m. p.  $156^{\circ}$  and  $177^{\circ}$ , respectively); *7-methoxyindole-2-carboxylic acid*, colourless needles, m. p.  $182^{\circ}$  (decomp. at  $220-225^{\circ}$ ) (*ethyl* ester, flat, colourless needles, m. p.  $114^{\circ}$ ; *methyl* ester, colourless plates, m. p.  $129^{\circ}$ ); and *4-methoxyindole-2-carboxylic acid*, colourless needles, m. p.  $234-235^{\circ}$  (decomp.) (*methyl* ester, colourless plates, m. p.  $143.5^{\circ}$ ; *ethyl* ester, colourless needles, m. p.  $161.5^{\circ}$ ). The above acids lose carbon dioxide on heating, with formation, respectively, of 5-, 7-, and 4-methoxyindoles. *5-Methoxyindole* forms colourless needles, m. p.  $55^{\circ}$ , b. p.  $176-178^{\circ}/17$  mm., slightly volatile in steam. It forms a *picrate*,  $C_{15}H_{12}O_8N_4$ , bright red needles, m. p.  $145^{\circ}$ , and a 1-*acetyl* derivative, colourless, prismatic crystals, m. p.  $82^{\circ}$ , b. p.  $210-211^{\circ}/25$  mm. Two *nitro-1-acetyl-5-methoxyindoles* (*a*) light brown, flat needles, m. p.  $149^{\circ}$ , and (*b*) brown plates, m. p.  $213-214^{\circ}$ , are described, and afford, on hydrolysis, *nitro-5-methoxyindoles* (*a*) yellow needles, m. p.  $144^{\circ}$ , (*b*) m. p.  $144^{\circ}$  (mixed m. p.  $112^{\circ}$ ), respectively. Application of the Tiemann-





*oxydimethylacetalylmethylamide* (colourless plates, m. p. 159°) yields about equal proportions of 10-methoxy-3-keto-4-methyl-3:4-dihydro-4-carboline, colourless needles, m. p. 280°, and 10-methoxy-5-keto-4-methyl-4:5-dihydroindolediazine(1:4) (V), colourless, prismatic needles, m. p. 243°.



7-Methoxyindole-2-carboxydimethylacetalylmethylamide, a syrup, yields about 4 parts of 12-methoxy-3-keto-4-methyl-3:4-dihydro-4-carboline, pale yellow plates, m. p. 250°, to 1 part of 12-methoxy-5-keto-4-methyl-4:5-dihydroindolediazine(1:4), four-sided prisms (hydrated), m. p. 135° (anhydrous). 5-Methoxyindole-2-carboxyacetalylmethylamide, colourless prisms, m. p. 151–152°, yields on the same treatment only 10-methoxy-5-keto-4:5-dihydroindolediazine(1:4) microscopic plates, sintering at 265°, m. p. 280°, whilst 5-methoxyindole-2-carboxyacetalylmethylamide, colourless needles, m. p. 127°, yields equal quantities of the above carboline (m. p. 280°) and indolediazine (m. p. 243°). The direction of ring formation is thus dependent on the presence or absence of the methyl group in the acetalylmethylamide chain (cf. T., 1922, 121, 1875). The product derived similarly from 7-methoxyscatole-2-carboxylic acid contained chlorine (apparently introduced in preparing the acid chloride), and was probably 9-chloro-12-methoxy-5-keto-4:7-dimethyl-4:5-dihydroindole-diazine(1:4) (VI), colourless, striated needles, m. p. 109°. It gave no colour reactions with aldehydes.

2-Nitro- $\alpha$ -methoxycinnamic acid, pale yellow clusters of needles, m. p. 164–165°, is obtained by methylation of the condensation product from *o*-nitrotoluene and ethyl oxalate in presence of sodium ethoxide (methyl ester, m. p. 67°). 2-Amino- $\alpha$ -methoxycinnamic acid loses acetic acid of crystallisation at 100°, forming a pale yellow, opaque powder, m. p. 167° (decomp.) (methyl ester, m. p. 60–61°). When treated with cold, concentrated sulphuric acid, boiled with 10% hydrochloric acid, or heated above its m. p., the acid is decomposed into methyl alcohol and indole-2-carboxylic acid. In the same way, by the methylation of metallic derivatives of ethyl nitromethoxyphenylpyruvates, 2-nitro- $\alpha$ :5-dimethoxycinnamic acid, yellow needles, m. p. 198–200° (decomp.) (methyl ester, m. p. 113–114°; ethyl ester, m. p. 74.5°), and 2-nitro- $\alpha$ :3-dimethoxycinnamic acid, colourless needles, m. p. 202° (decomp.) are produced. 2-Amino- $\alpha$ :5-dimethoxycinnamic acid separates from acetic acid in colourless needles containing the solvent, which is lost at 100°, leaving the acid as a pale yellow, opaque powder, m. p. 173–174° (methyl ester, m. p. 81°). 2-Amino- $\alpha$ :3-dimethoxycinnamic acid loses acetic acid of crystallisation on standing in air,

is then yellow, and has m. p.  $139^{\circ}$  (decomp.). Both the above amino-acids decompose on heating into methyl alcohol and the corresponding methoxyindole-2-carboxylic acids. Scatole-2-carboxylic acid can be obtained by a similar synthesis from  $\alpha$ -keto- $\beta$ -*o*-nitrophenylbutyrate, but the corresponding methoxy derivatives could not be isolated.

F. G. W.

**Constitution of Naphtholisatin and its Derivatives.** N. DĂNĂILĂ (*Bul. Soc. Romăna Stiin.*, 1923, **26**, 87—95).—A question of priority in connexion with a paper by Cădea (A., 1923, i, 246; cf. Dănăilă, A., 1916, i, 497, and Dissert., Berlin, 1909).

R. B.

**Oxidation of Carbazole by Silver Oxide.** G. E. K. BRANCH and W. W. HALL (*J. Amer. Chem. Soc.*, 1924, **46**, 438—445).—In continuation of previous work on this subject, the authors have obtained three fractions B, E, and A (cf. A., 1921, i, 56). E,  $C_{36}H_{27}ON_3$  (?), is a white powder, m. p.  $189$ — $197^{\circ}$  (with charring), which reacts with bromine to give a bromide (?), m. p.  $117$ — $125^{\circ}$ . It reacts with nitric oxide, and affords two nitroso derivatives, yellow solids, m. p.  $216^{\circ}$  (decomp.) and  $228^{\circ}$  (decomp.), respectively. Sulphuric acid converts it into an isomeric substance, m. p.  $250^{\circ}$ . A is a yellow powder affording a bromo derivative, m. p.  $85$ — $100^{\circ}$ . E is considered to be an hydroxymonocarbazyldibiphenylenehydrazine in which two or three of the carbazole rings are reduced to diphenylamine nuclei, whilst B (which affords a bromo derivative, m. p.  $230$ — $245^{\circ}$ ) is an intermediate in the formation of E, the latter being formed by the combination of the reduced B radicals and the carbazyl nuclei.

A. B. S.

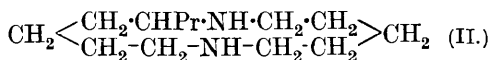
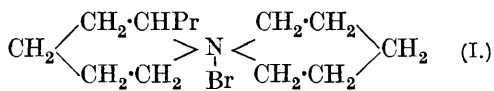
**The Chemistry of Carbazole.** H. LINDEMANN (*Ber.*, 1924, **57**, [B], 555—559).—A method is described for preparing 3-nitrocarbazole from carbazole, using glacial acetic acid, sodium nitrite, and nitric acid. 3-Nitro-9-nitrosocarbazole, first obtained, when hydrolysed with alcoholic 40% potassium hydroxide, gives 3-nitrocarbazole, together with about 4% of an isomeride (1-nitrocarbazole?) (yellow needles, m. p.  $187^{\circ}$ ); the nitro compound (m. p.  $164^{\circ}$ ), hitherto described as the 1-nitro compound, must therefore be either the 2- or 4-nitrocarbazole (cf. A., 1909, i, 961). 3-Nitro-*N*-methylcarbazole (yellow needles, m. p.  $173^{\circ}$ ), and 3-nitro-*N*-ethylcarbazole (yellow needles, m. p.  $128^{\circ}$ ) were prepared by alkylation of the 3-nitro compound. The nitro-*N*-methyl compound when reduced afforded 3-amino-9-methylcarbazole, grey needles, m. p.  $174^{\circ}$ . Its salts with mineral acids are soluble in water and give acetyl and benzoyl derivatives, m. p.  $210^{\circ}$  and  $211^{\circ}$ , respectively. 3-Amino-*N*-ethylcarbazole forms white needles, m. p.  $113$ — $114^{\circ}$  (acetyl derivative, m. p.  $190^{\circ}$ ; benzoyl derivative, m. p.  $180^{\circ}$ ).

3-Nitro-9-ethylcarbazole, m. p.  $128^{\circ}$ , does not agree in its properties with the product obtained by Delétra and Ullmann (A., 1904, i, 272) (cf. also Stevens and Tucker, T., 1923, **123**, 2140) from 2-amino-4-nitro-*N*-ethyldiphenylamine; the latter substance, obtained by reducing the corresponding dinitro compound with sodium sulphide, forms red crystals melting at  $76^{\circ}$ . On treatment

with nitrous acid the corresponding diazonium compound, 2(*phenylmethylamino*)5-nitrophenyldiazonium nitrate, was obtained in the form of very stable yellow needles exploding at about 118°. All attempts to convert it into 3-nitro-*N*-methylcarbazole were unsuccessful.

F. A. M.

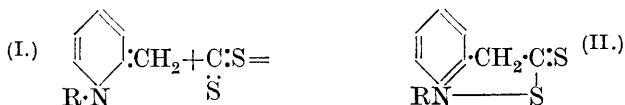
**Cyclic bis-Imines and their Decomposition. IV.** J. von BRAUN and J. POHL (*Ber.*, 1924, **57**, [B], 480—484).—Coniine (2 mols.) and  $\alpha\epsilon$ -dibromopentane interact at water-bath temperatures to give a solid product, probably in accordance with the equation:  $2C_8H_{16} > NH + Br[CH_2]_5Br = C_8H_{16} > N \cdot HBr + C_8H_{16}N[CH_2]_5Br$ . On further warming there results the hygroscopic quaternary bromide,  $C_{13}H_{26}NBr$  (I), m. p. 228°. The latter, when heated with ammonia at 200°, is partly converted into the *bis-imine* (II), a colourless oil, b. p. 145—146°/11 mm.,  $d_4^{25}$  0.89.



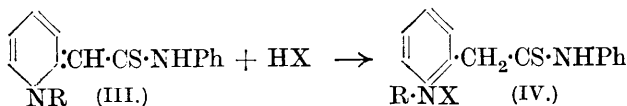
The *picrate*, *hydrochloride*, and *chloroplatinate* are oily. The *dimethiodide* yields a solid *chloroplatinate*, m. p. 248°. A 40-g. frog is completely paralysed by 0.005 g. of the bis-imine in 3—4 minutes, whilst the same dose of coniine requires about 39 minutes to produce paralysis.

F. A. M.

**Reactions of *N*-Alkyl-methylenedihydro-pyridines and -quinolines.** W. SCHNEIDER, K. GAERTNER, and A. JORDAN (*Ber.*, 1924, **57**, [B], 522—532; cf., A. 1921, i, 878).—*N*-Alkyl- $\alpha$ - (or  $\gamma$ -)methylenepyridanes (cf. Decker, A., 1905, i, 667), which are formed on treating quaternary salts of  $\alpha$ - or  $\gamma$ -methylated pyridines or quinolines with alkali, are capable of combining directly with either carbon disulphide, phenylcarbimide, or phenylthiocarbimide to form crystalline products. In the case of  $\alpha$ -picoline alkiodides, it is suggested that the methylene base (I) reacts thus:



so that the product (II) would be the betaine of *N*-alkyl- $\alpha$ -pyridyl-dithioacetic acid; whilst the thiocarbimide additive product of the methylene base would have the structure (III) and its salts the



structure (IV), the carbimide additive compounds having analogous

formulae which would agree with the ready oxidation of both sulphur and oxygen compounds by cold neutral permanganate, whilst in acid solution they are only slowly oxidised.

*N*-Methyl- $\alpha$ -methylenedihydropyridine was prepared by treating  $\alpha$ -picoline methosulphate with alkali and extracting with ether; on treating the yellow ethereal solution with carbon disulphide, yellow leaflets of the *additive* compound,  $C_8H_7NS_2$ , were formed which charred at  $175^\circ$  and had m. p.  $186^\circ$ . The *phenylthiocarbimide* (III) forms dark red crystals, m. p.  $153^\circ$ . It is soluble in dilute acids to give pale yellow solutions of the salts (IV), from which the compound is reprecipitated by alkalis. The *hydriodide* forms colourless needles, m. p.  $160^\circ$ , the *picrate*, yellow needles, m. p.  $156^\circ$ . The *phenylcarbimide* forms yellow needles, m. p.  $172^\circ$  (*picrate*, yellow needles, m. p.  $173^\circ$ ). *N*-Ethyl- $\alpha$ -methylenedihydropyridine gave the following derivatives: *carbon disulphide additive* compound, yellow leaflets, char at  $170^\circ$ , m. p.  $180^\circ$ ; *phenylthiocarbimide*, dark red crystals, m. p.  $143^\circ$ ; *hydriodide*, m. p.  $177^\circ$ , *picrate*, m. p.  $113^\circ$ ; *phenylcarbimide*, needles, m. p.  $172^\circ$ . *N*-Benzyl- $\alpha$ -methylenedihydropyridine (from  $\alpha$ -picoline benzochloride) gave the following derivatives: *phenylthiocarbimide*, red crystals, m. p.  $189^\circ$ ; *picrate*, m. p.  $150^\circ$ ; *phenylcarbimide*, yellow crystals, m. p.  $192^\circ$ ; *picrate*, m. p.  $126^\circ$ . The following are derivatives of *methylene-anhydro bases from s-collidine alkiodides*: (i) *methiodide*: *phenylthiocarbimide*, yellowish-brown crystals, m. p.  $185^\circ$ ; *phenylcarbimide*, yellow, m. p.  $188^\circ$ ; (ii) *ethiodide*: *phenylthiocarbimide* compound, yellowish-brown, m. p.  $190^\circ$ ; *phenylcarbimide*, bright yellow, m. p.  $198^\circ$ . The following derivatives of *N*-methyl- $\gamma$ -methylenedihydropyridine (from  $\gamma$ -picoline methiodide) are described: *phenylthiocarbimide*, brown leaflets, m. p.  $218^\circ$ ; *phenylcarbimide*, yellow needles, m. p.  $196^\circ$ . The *pseudo-bases* from pyridine methiodide and from  $\beta$ -picoline methiodide gave no recognisable crystalline products with either phenylcarbimide or thiocarbimide. *N*-Methyl- $\alpha$ -methylenedihydroquinoline with carbon disulphide gave no definite product but the following are described: *phenylthiocarbimide*, coppery leaflets, m. p.  $170^\circ$ ; *hydriodide*, pale yellow, m. p.  $192^\circ$ ; *perchlorate*, yellowish-brown, m. p.  $188$ – $190^\circ$ ; *picrate*, yellow, m. p.  $168$ – $169^\circ$ ; *phenylcarbimide*, yellow crystals, m. p.  $173^\circ$ ; *hydriodide*, yellow, m. p.  $190$ – $191^\circ$ ; *perchlorate*, colourless, m. p.  $199^\circ$ ; *picrate*, m. p.  $168$ – $169^\circ$ . Derivatives of *N*-ethyl- $\alpha$ -methylenedihydroquinoline are: *phenylthiocarbimide*, reddish-brown crystals, m. p.  $162^\circ$ ; *phenylcarbimide*, yellow needles, m. p.  $167^\circ$ . Derivatives of *methylene-anhydro base from  $\alpha$ : $\gamma$ -dimethylquinoline ethiodide* are: *phenylthiocarbimide*, reddish-brown needles, m. p.  $145^\circ$ ; *phenylcarbimide*, yellow needles, m. p.  $207^\circ$ . Crystalline *additive* compounds were also obtained from the base derived from lepidine ethiodide, but were not examined further. Experiments were carried out also with the *pseudo-bases* derived from 2-ethylquinoline ethiodide, 4-ethylquinoline ethiodide,  $\alpha$ -isopropylquinoline ethiodide, and quinoline ethiodide itself, but no crystalline additive compounds could be obtained.

F. A. M.

**Arylated Pyridines. IV. N-Alkylquinopyridanes.** W. DILTHEY, C. AMMON, and A. EBERT (*J. pr. Chem.*, 1924, [ii], **107**, 7—15; cf. A., 1921, i, 735; 1922, i, 272).—The arylated quinopyridanes obtained by the action of ammonia on the *N*-arylpipridinium salts formed from primary amines and *p*-hydroxylarylpyrylium salts are considered to possess a quinoid structure in the yellowish-red anhydro bases and a benzenoid structure in their bright yellow salts and hydrates. The additive compounds of the bases with benzene are also assigned a quinoid structure. The following individual compounds are described: 1 : 2 : 6-triphenyl-4-*p*-hydroxyphenylpyridinium chloride,  $C_{29}H_{22}ONCl \cdot 0.5HCl$ , bright yellow crystals, m. p.  $335^\circ$ , was obtained from 2 : 6-diphenyl-4-*p*-hydroxyphenylpyrylium chloride and aniline (cf. A., 1922, i, 272), and on heating in a xylene bath this gives the dark yellow, neutral chloride,  $C_{29}H_{22}ONCl$ . The two chlorides behave very differently with alcoholic ammonia. The hydrochloride yields a very stable meriquinoid salt,  $C_{58}H_{43}O_2N_2Cl$ , m. p. about  $295\text{--}300^\circ$ , from which chlorine is removed quantitatively only by boiling with silver hydroxide. The neutral chloride, in the same way, is converted into a dihydrate of the anhydro base, 1 : 2 : 6-triphenyl-4-quinol-1 : 4-dihydropyridine. The dihydrate, yellow plates, darkens at  $120\text{--}130^\circ$ , melting twice between this temperature and  $263^\circ$ . When dehydrated, the dihydrate affords the orange monohydrate, from which the dark red anhydro base (yellow *picrate* and *nitrate*) is obtained, this, when heated, behaving similarly to the dihydrate, melting first at  $175^\circ$  and then, after solidifying, at  $263^\circ$  to a dark red fluid. With benzene, an additive compound,  $C_{29}H_{21}ON, C_6H_6$  is formed, as fine, red needles, these, on heating at  $110^\circ$ , giving the anhydro base. Similarly, 2 : 6-diphenyl-4-*p*-hydroxyphenylpyrylium chloride, on heating with *p*-toluidine, gives 2 : 6-diphenyl-4-*p*-hydroxyphenyl-1-*p*-tolylpyridinium chloride, bright yellow plates ( $+2H_2O$ ; the water is lost at  $100\text{--}130^\circ$ , giving the anhydrous compound, m. p.  $343\text{--}345^\circ$ ). The *nitrate* is yellow, m. p.  $168^\circ$  (decomp.). With alcoholic ammonia, the chloride yields a dihydrate of the anhydro base, yellowish-red needles, which lose their water at  $100\text{--}130^\circ$ , giving the anhydro base, 2 : 6-diphenyl-1-*p*-tolyl-4-quinol-1 : 4-dihydropyridine, reddish-violet, m. p.  $293^\circ$ . The anhydro base forms an insoluble additive compound with benzene,  $C_{30}H_{23}ON, C_6H_6$ . From the reaction product of 4 : 6-diphenyl-2-*p*-hydroxyphenylpyrylium iodide and  $\beta$ -naphthylamine in benzene solution, the *picrate*, yellow, m. p.  $162\text{--}163^\circ$ , and *perchlorate*, yellow, m. p.  $177\text{--}178^\circ$ , of 4 : 6-diphenyl-2-*p*-hydroxyphenyl-1- $\beta$ -naphthylpyridine were isolated.

R. B.

### 5 : 6 : 7 : 8-Tetrahydroquinolines and their Derivatives.

**IV.** J. VON BRAUN, W. GMELIN, and A. PETZOLD (*Ber.*, 1924, **57**, [B], 382—391; cf. von Braun, Gmelin, and Schultheiss, A., 1923, i, 835).—Further examples are cited which confirm the previous conclusion that the presence of alkyl substituents, according to their number and weight, in the pyridine half of the quinoline molecule inhibits to a greater or less extent the introduction of

hydrogen atoms in the presence of nickel into the 1:2:3:4-positions and favours the production of 5:6:7:8-derivatives. The maximum effect is observed in the case of 2:3:4-trimethylquinoline, which, in complete contrast to quinoline itself, is hydrogenated exclusively in the benzenoid nucleus. The introduction of alkyl groups into the 5:6:7:8-positions exerts an opposite effect. The observations are explained by the hypothesis that the quinoline derivatives are equilibrium mixtures of two forms (benzenoid and centric structures alternating in each nucleus); in extreme cases of loading with substituents, only one variety is present.

2-Propylquinoline dissolved in decahydronaphthalene is converted by hydrogen in the presence of nickel at 170° into a mixture of 2-propyl-1:2:3:4-tetrahydroquinoline (65%) and 2-propyl-5:6:7:8-tetrahydroquinoline (35%). The former compound is a colourless liquid, b. p. 140—141°/10 mm. (*hydrochloride*, m. p. 221°; *benzoyl* derivative, microscopic crystals, m. p. 101°), whereas the latter base is a colourless liquid with a pronounced odour of pyridine, b. p. 130—132°/11 mm. (the non-crystalline *hydrochloride*, the *chloroplatinate*, decomp. 62°, and the *picrate*, yellow needles, m. p. 119°, are described). 2-Propyldecahydroquinoline, obtained in almost quantitative yield by the reduction of 2-propyl-5:6:7:8-tetrahydroquinoline with sodium and alcohol, has b. p. 123—125°/20 mm.; it somewhat resembles coniine in physiological activity. It yields a non-crystalline *nitroso* derivative, an extremely hygroscopic *hydrochloride*, and a *picrate*, m. p. 134—135°.

4-Phenyl-2-methylquinoline gives 4-phenyl-2-methyl-1:2:3:4-tetrahydroquinoline, m. p. 66—67° (16%), and 4-phenyl-2-methyl-5:6:7:8-tetrahydroquinoline, a viscous liquid, b. p. 181—183°/13 mm. (84%). The latter compound yields a *picrate*, m. p. 186—187°, a non-crystalline *hydrochloride*, and a yellow *chloroplatinate*, decomp. 145—147°.

2:3:4-Trimethylquinoline, m. p. 92° (65° is recorded in the literature), is prepared in the usual manner from aniline and methylacetylacetone; the *picrate*, m. p. 216°, *hydrochloride*, m. p. 274°, and lemon-yellow *methiodide*, m. p. 260°, are described. When hydrogenated in the presence of nickel at 155—160°, the base yields about 2% of 2:3:4-trimethyl-1:2:3:4-tetrahydroquinoline, which is identified as the *chloroplatinate* of the corresponding *methochloride*,  $C_{25}N_4Cl_2N_6Pt$ , lustrous, orange-coloured needles, m. p. 176°. The main product of the reduction is 2:3:4-trimethyl-5:6:7:8-tetrahydroquinoline, a liquid with an odour resembling that of pyridine, b. p. 145—147°/13 mm., which yields a crystalline *dihydrate*, m. p. 31—32°; the *picrate*, m. p. 147°, *hydrochloride*, m. p. 174°, and *methiodide*, m. p. 125—126°, are described. The base is reduced by sodium and alcohol to 2:3:4-trimethyldecahydroquinoline, a colourless liquid with a pronounced odour of hemlock, b. p. 115°/13 mm.; the non-crystalline *nitroso* derivative, the *hydrochloride*, and the *product*,  $C_{14}H_{25}NI$  (obtained by exhaustive methylation), a crystalline powder, m. p. 227° after softening at 218°, are described.

2:6-Dimethylquinoline readily undergoes catalytic hydrogenation at  $105^{\circ}$ , yielding 2:6-dimethyl-5:6:7:8-tetrahydroquinoline (1.5%) (*picrate*, m. p.  $127^{\circ}$ ; *chloroplatinate*,  $C_{22}H_{32}N_2Cl_6Pt$ , an orange-coloured powder, decomp.  $185^{\circ}$ ), and 2:6-dimethyl-1:3:2:4-tetrahydroquinoline (98.5%), b. p.  $133^{\circ}/12$  mm., m. p.  $32^{\circ}$  (*benzoyl* derivative), m. p.  $103^{\circ}$ .

Acetylacetone and *p*-xylydine readily yield the corresponding *xylylide*,  $C_{13}H_{17}ON$ , b. p. about  $170^{\circ}/12$  mm., m. p.  $41^{\circ}$ , which with concentrated sulphuric acid gives 2:4:5:8-tetramethylquinoline, a pale yellow, crystalline mass, m. p.  $48^{\circ}$ , b. p.  $168-172^{\circ}/12$  mm.; the base exhibits a pronounced, bluish-violet fluorescence in acid solution. The *hydrochloride*, m. p.  $254^{\circ}$  after sintering at  $243^{\circ}$ , and the *picrate*, small needles, m. p.  $161^{\circ}$ , are described; the *methiodide* could not be obtained. The base is hydrogenated at  $160-170^{\circ}$  to a mixture of 2:4:5:8-tetramethyl-5:6:7:8-tetrahydroquinoline (4%), a colourless liquid, b. p.  $135-137^{\circ}/12$  mm. (the non-crystalline *hydrochloride*, the *chloroplatinate*, coarse crystals which blacken above  $196^{\circ}$ , and the *picrate*, m. p.  $131^{\circ}$ , are described), and 2:4:5:8-tetramethyl-1:2:3:4-tetrahydroquinoline (96%), b. p.  $143-145^{\circ}/12$  mm. (the non-crystalline *benzoyl* derivative, the *hydrochloride*, m. p.  $211^{\circ}$ , and the *picrate*, m. p.  $160^{\circ}$ , are described).

[With K. MÜNCKER.]—Tetrahydro- $\alpha$ -naphthylamine reacts readily with acetylacetone to yield the compound  $C_{10}H_{11}N \cdot CMe \cdot CH_2 \cdot Ac$ , a viscous liquid, b. p.  $208^{\circ}/15$  mm., which with concentrated sulphuric acid gives 2:4-dimethyl-7:8:9:10-tetrahydro- $\alpha$ -naphthaquinoline, b. p.  $196-200^{\circ}/15$  mm., m. p.  $49^{\circ}$  (*hydrochloride*, m. p.  $243^{\circ}$ ; *picrate*, m. p.  $201^{\circ}$ ; *methiodide*, m. p.  $254^{\circ}$ ). The catalytic hydrogenation of the base proceeds with unusual difficulty; even at temperatures above  $200^{\circ}$  the action stops prematurely, owing to poisoning of the catalyst. The main product is 2:4-dimethyl-1:2:3:4:7:8:9:10-octahydro- $\alpha$ -naphthaquinoline, a viscous liquid, b. p.  $190^{\circ}/16$  mm. (*benzoyl* derivative, m. p.  $130-131^{\circ}$ ; *nitroso* compound, m. p.  $62^{\circ}$ ; *hydrochloride*, m. p.  $204^{\circ}$ ; *picrate*, m. p.  $130^{\circ}$ ). The portion of the product which does not react with benzoyl chloride appears to have suffered partial hydrogenation in the central nucleus. The catalytic reduction of 2:4-dimethyl- $\alpha$ -naphthaquinoline, m. p.  $52^{\circ}$ , yields a mixture of unchanged base, 2:4-dimethyl-7:8:9:10-tetrahydro- $\alpha$ -naphthaquinoline, and the above octahydro base; the primary change occurs at the extreme benzene nucleus.

H. W.

**Intramolecular Condensation Reactions of Aminoacetals and Aminoaldehydes. I. Synthesis of Dihydroquinoline and certain Homologues.** C. RÄTH (*Ber.*, 1924, 57, [B], 550—555).—If chloro- or bromo-acetal is heated with *o*-toluidine in a closed tube at  $260^{\circ}$ , 1:2-dihydroquinoline (90% yield) is obtained as an almost colourless liquid, b. p.  $226^{\circ}$  (*hydrochloride*, white, crystalline powder, m. p.  $214^{\circ}$ ; *picrate*, yellow, crystalline powder, m. p.  $199-200^{\circ}$ ; *nitroso* derivative, a viscous, yellow oil), and is accompanied by small quantities of the intermediately formed

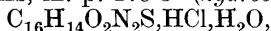


*o*-toluidine-*N*-monoacetal, a viscous substance, b. p. 250—262°. On heating 1:2-dihydroquinoline with ethylene chlorohydrin in benzene solution, 1-( $\beta$ -hydroxyethyl)-1:2-dihydroquinoline is formed as a viscous, pinkish liquid, b. p. 166—168°/11 mm. The *hydrochloride*, *picrate*, and *methiodide* were obtained only as oils.

In a similar way,  $\beta$ -bromopropionacetal condenses with *o*-toluidine to form 1:2-dihydroquinaldine, which is a faintly yellow liquid (b. p. 234—240°) affording an oily *nitroso* derivative; the *hydrochloride*, a white, crystalline powder, has m. p. 197—198°; the *picrate*, yellow crystals, m. p. 189—190°. If methyl-*o*-toluidine be used in place of *o*-toluidine, the product is 1-methyl-1:2-dihydroquinaldine, b. p. 252—260° (Freund, A., 1906, i, 600; 1909, i, 417); the *hydrochloride* is an oil, the *picrate* yellow rosettes, m. p. 148—150°. As a by-product was obtained  $\alpha$ -*o*-tolylmethylaminopropaldehyde,  $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CHMe}\cdot\text{CHO}$ , b. p. 283—288°, which forms a *picrate*, m. p. 152—153°. F. A. M.

**The Reactivity of the Chlorine Atom in the 2-Position in Quinoline and Quinoline Derivatives.** J. TRÖGER and H. MEINECKE (*J. pr. Chem.*, 1923, [ii], 106, 203—225).—2-Chloroquinoline reacts slowly with sodium benzenesulphinate in presence of alcohol to give 2-benzenesulphonylquinoline, colourless needles, m. p. 160°. This compound is unaffected by a short fusion with alkali, prolonged fusion effecting profound decomposition. When heated with dilute hydrochloric acid at 235°, it affords carbostyryl, benzenesulphinic acid, and benzene disulphoxide. It forms no double salts. 2-Chloroquinoline does not react with alkali derivatives of thiophenols, but 2-chloro-3-benzenesulphonylquinoline and the sodium derivative of *p*-thioltoluene afford 3-benzenesulphonylcarbostyryl *p*-tolyl thioether,  $\text{C}_9\text{H}_5\text{N}(\text{SO}_2\text{Ph})(\text{SC}_6\text{H}_4)$ , colourless needles, m. p. 131° with previous sintering. When 2-chloro-3-benzenesulphonylquinoline is heated in alcoholic solution with sodium benzenesulphinate at 130°, 2:3-dibenzenesulphonylquinoline (m. p. 204°) results (cf. A., 1923, i, 368).

2-*Toluenesulphonylquinoline* (colourless prisms, m. p. 127°) was prepared by the above method. 2-Amino-3-*o*-toluenesulphonylquinoline (from *o*-toluenesulphonylacetonitrile and *o*-aminobenzaldehyde), white prisms, m. p. 179.5° (*hydrochloride*,



white crystals), is converted by nitrous acid into 3-*o*-toluenesulphonylcarbostyryl, yellow prisms, m. p. 270°, this substance, with phosphorus pentachloride, affording 2-chloro-3-*o*-toluenesulphonylquinoline, colourless needles, m. p. 161°.

From the last-named chloro compound, 3-*o*-toluenesulphonylcarbostyryl *p*-tolyl thioether (white crystals, m. p. 191°), 3-*o*-toluenesulphonyl-2-benzenesulphonylquinoline (colourless prisms, m. p. 260°), and 3-*o*-toluenesulphonylcarbostyryl phenyl thioether (colourless needles, m. p. 154°) were obtained. The last-named ether, on oxidation, affords 3-*o*-toluenesulphonylcarbostyryl.

Sodium *p*-toluenesulphinate reacts less rapidly than the benzene-sulphinate with 2-chloroquinoline, 2-*p*-toluenesulphonylquinoline

(white crystals, m. p.  $141^{\circ}$ ) resulting. Other compounds in this series are : 3-*p*-toluenesulphonylcarbostyryl *p*-tolyl thioether, colourless crystals, m. p.  $195^{\circ}$ ; 3-*p*-toluenesulphonyl-2-*p*-toluenesulphonylquinoline, colourless needles, m. p.  $184$ — $185^{\circ}$ ; and 3-*p*-toluenesulphonylthiocarbostyryl, lemon-yellow powder, m. p.  $226^{\circ}$ .

2-*p*-Chlorobenzenesulphonylquinoline forms white needles, m. p.  $190^{\circ}$ ; 3-*p*-chlorobenzenesulphonylcarbostyryl phenyl thioether (yellow needles, m. p.  $149^{\circ}$ ) is formed together with some 3-*p*-chlorobenzenesulphonylcarbostyryl when 2-chloro-3-*p*-chlorobenzenesulphonylquinoline reacts with sodium thiophenoxide, and on oxidation affords 3-*p*-chlorobenzenesulphonyl-2-benzenesulphonylquinoline, white crystals, m. p.  $264^{\circ}$  (sintering at  $250^{\circ}$ ).

3-*p*-Chlorobenzenesulphonylcarbostyryl *p*-tolyl thioether, colourless needles, m. p.  $147^{\circ}$ , cannot be oxidised to the corresponding disulphone. 2-*p*-Bromobenzenesulphonylquinoline forms white needles, m. p.  $145^{\circ}$ . 2-Amino-3-*p*-bromobenzenesulphonylquinoline, lemon-yellow needles, m. p.  $223^{\circ}$ , forms a hydrochloride, needles, m. p.  $256^{\circ}$  (decomp.), nitrate, yellow, crystalline powder, m. p. (indef.)  $105$ — $224^{\circ}$ , and chloroplatinate, yellowish-red crystals, and is converted by nitrous acid into 3-*p*-bromobenzenesulphonylcarbostyryl, yellow needles, m. p.  $269^{\circ}$ . The last-named substance is converted by phosphorus pentachloride into 2-chloro-3-*p*-bromobenzenesulphonylquinoline, colourless needles, m. p.  $181.5^{\circ}$ . The following were also prepared : 3-*p*-bromobenzenesulphonylcarbostyryl ethyl ether, colourless needles, m. p.  $156^{\circ}$ ; 3-*p*-bromobenzenesulphonylthiocarbostyryl, yellow crystals, m. p.  $254^{\circ}$ ; and 3-*p*-bromobenzenesulphonylcarbostyryl *p*-tolyl thioether, white needles, m. p.  $159^{\circ}$ .

2- $\beta$ -Naphthalenesulphonylquinoline forms colourless stars, m. p.  $137^{\circ}$ . 2-Amino-3- $\beta$ -naphthalenesulphonylquinoline, yellow needles, has m. p.  $180^{\circ}$  and forms a hydrochloride, yellow needles, m. p.  $250^{\circ}$  (with previous decomp.), and a nitrate, white needles. 3- $\beta$ -Naphthalenesulphonylcarbostyryl forms yellow needles, m. p.  $294^{\circ}$ ; 2-chloro-3- $\beta$ -naphthalenesulphonylquinoline, yellow crystals, has m. p.  $159^{\circ}$ ; 3- $\beta$ -naphthalenesulphonylcarbostyryl ethyl ether forms yellow needles, m. p.  $121^{\circ}$ ; 3- $\beta$ -naphthalenesulphonylcarbostyryl *p*-tolyl thioether, silver crystals, has m. p.  $176^{\circ}$  and oxidises irregularly.

2-*o*-Anisolesulphonylquinoline forms rhombs, m. p.  $134^{\circ}$ . 2-Amino-3-*o*-anisolesulphonylquinoline, colourless crystals, has m. p.  $239^{\circ}$ , and was converted into 3-*o*-anisolesulphonylcarbostyryl, yellow crystals, m. p.  $250^{\circ}$ . 2-Chloro-3-*o*-anisolesulphonylquinoline, quadratic crystals, m. p.  $171^{\circ}$ , was converted into 3-*o*-anisolesulphonylcarbostyryl phenyl thioether, colourless rhombohedra, m. p.  $160^{\circ}$ , and into 3-*o*-anisolesulphonylthiocarbostyryl, yellow crystals, m. p.  $233^{\circ}$  (methyl ether, colourless crystals, m. p.  $150^{\circ}$ ).

2-*p*-Phenetolesulphonylquinoline, white leaflets, has m. p.  $133.5^{\circ}$ . 2-Amino-3-*p*-phenetolesulphonylquinoline forms yellow leaflets, m. p.  $178^{\circ}$  [hydrochloride, needles, m. p.  $233^{\circ}$  (decomp.)], and was converted into 3-*p*-phenetolesulphonylcarbostyryl, yellow needles, m. p.  $241^{\circ}$ . 2-Chloro-3-*p*-phenetolesulphonylquinoline, yellow crystals, m. p.  $162^{\circ}$ , was converted into 3-*p*-phenetolesulphonylcarbostyryl *p*-tolyl thioether, colourless needles, m. p.  $141^{\circ}$ , the last-named substance

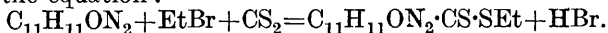
affording, on oxidation, 3-*p*-phenetolesulphonyl-2-*p*-toluenesulphonyl-quinoline, needles, m. p. 249° (sintering at 239°). 3-*p*-Phenetole-sulphonylthiocarbostyryl, yellow needles, has m. p. 142°.

From the above it is seen that in 2-chloroquinoline, the chlorine atom cannot be displaced by the  $\cdot\text{SR}$  radical, whereas the presence of the grouping  $\cdot\text{SO}_2\text{R}$  in position 3 (especially if R is a *p*-tolyl radical) facilitates the displacement. Again, whilst 2-amino- $\beta$ -arylsulphonylquinolines (monoacidic bases) cannot be diazotised, the amino radical can readily be displaced by hydroxyl, using nitrous acid.

E. E. T.

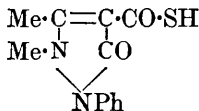
### Carbithionic and Thionic Acid Derivatives of Pyrazolones.

E. BENARY and A. SCHMIDT (*Ber.*, 1924, 57, [B], 517—522).—By the action of chlorocarbonic ester, or ethyl bromide, on antipyrine in carbon disulphide solution, a product is obtained according to the equation:



Since the new substance does not give the typical nitroso reaction of antipyrine, it is assumed that the group  $-\text{CS} \cdot \text{SEt}$  has occupied position 4 and that the substance is *ethyl 1-phenyl-2:3-dimethylpyrazolone-5-carbithionate* (cf. Houben, A., 1906, i, 847). It forms orange leaflets, m. p. 178.5—179°, gives no nitroso compound with nitrous acid, and forms an intense red precipitate with bromine in chloroform solution. When treated with alcoholic potassium

hydroxide, it affords ethyl mercaptan and 1-phenyl-2:3-dimethylpyrazolone-5-thionic acid, sulphur-yellow needles, m. p. 81—82° (annexed formula) (potassium and silver salts described). The methyl ester, yellow needles (+1.5H<sub>2</sub>O) has m. p. 95° (anhydrous ester, m. p. 113—114°). The following were made in a similar manner from the appropriate substance, ethyl bromide, and aluminium chloride in carbon disulphide solution.



*Ethyl 1-phenyl-3-methyl-5-pyrazolone-4-carbithionate*, from 1-methyl-3-phenyl-5-pyrazolone, forms greenish-yellow prisms, m. p. 81—82°. *Ethyl 3-methyl-5-pyrazolone-4-carbithionate*, orange prisms or needles, m. p. 186°, which with alkali yields 3-methyl-5-pyrazolone; on treating the alkaline solution from the hydrolysis with methyl sulphate, white or pale yellow needles (m. p. 115.5°) are formed, of *methyl 1:2:3-(or 1:2:5)-trimethyl-5-pyrazolone-4-carbithionate*. *Ethyl 5-pyrazolone-4-carbithionate*, from 5-pyrazolone, forms reddish-brown prisms, m. p. 184—185°. *Ethyl 1-phenyl-5-methyl-3-pyrazolone-4-carbithionate* forms orange-yellow leaflets, m. p. 114°. From thiopyrine a yellow, crystalline substance, m. p. 166°, probably the corresponding carbithionic acid, was obtained.

F. A. M.

**Dipyridyls from Pyridine.** C. R. SMITH (*J. Amer. Chem. Soc.*, 1924, 46, 414—419).—The author describes the preparation and separation of 2:2-, 3:3-, 3:4-, and 4:4-dipyridyls. 3:4-Dipyridyl (plates, m. p. 61°, b. p. 297°) forms a *dihydrochloride*,

*mercurichloride*, and *chloroplatinate* and is distinguished from its isomerides by certain colour reactions. On oxidation with potassium permanganate, it affords nicotinic and isonicotinic acids. In the interaction of sodium and pyridine in presence of dry oxygen, the proportions of the various isomerides produced depend on the time, temperature, and pressure conditions. A. B. S.

**The Constitution of the Products arising from the Condensation of *o*-Aminoazo Compounds with Aldehydes. II.**

OTTO FISCHER (*J. pr. Chem.*, 1924, [ii], 107, 16—49; cf. A., 1922, i, 956).—A further series of *N*-substituted iminazoles, some already known, has been obtained by the condensation of *o*-aminoazo compounds with aldehydes, and the reduction of these with hydriodic acid is described, the products being a benziminazole and an amine. The condensation products of chrysoidine and aldehydes are shown to be derivatives of 1-anilino-2-phenyl-5-aminobenziminazole. The action of benzyl chloride on *o*-aminoazo compounds did not give the expected *N*-aryldihydrobenziminazoles, but their decomposition products, *e.g.*, aniline and 2-phenylnaphthiminazole. If the benzyl group is introduced into the amine prior to coupling, the azo dyes formed easily decompose in a similar way.

[With E. THIEL].—From benzeneazo- $\beta$ -naphthylamine, the following compounds have been prepared. With acetaldehyde, 1-anilino-2-methylnaphthiminazole [yellow *picrate*, m. p. 234°; yellow *nitrosoamine*, decomp. 124°; *acetyl* compound, m. p. 230° (decomp.)]. With methyl iodide in benzene solution it gives a *methyl* base, lustrous, colourless plates, m. p. 195° (*hydrochloride*, m. p. 250°), which does not form a nitrosoamine. With *o*-chlorbenzaldehyde, 1-anilino-2-*o*-chlorphenylnaphthiminazole, colourless, tufted needles, m. p. 231° [*picrate*, m. p. 192° (decomp.)]. With salicylaldehyde, 1-*o*-hydroxyanilino-2-phenylnaphthiminazole [golden-yellow *nitrosoamine*, *diacetyl* compound, m. p. 169° (decomp.)], an intermediate compound, violet-tinged needles,  $C_{23}H_{17}ON_3$ , being isolated which goes over into the colourless iminazole at 100—110°. With *p*-hydroxybenzaldehyde, 1-anilino-2-*p*-hydroxyphenylnaphthiminazole, colourless crystals, m. p. 233° (decomp.) (*nitrosoamine*, decomp. 200°, *diacetyl* compound, prisms, m. p. 224°).

[With F. STAUBER and W. HILD].—When heated with hydriodic acid (*d* 1.7) under pressure, the *N*-arylbenziminazoles and naphthiminazoles are converted into the corresponding primary amine and iminazole. The iminazoles are not further decomposed even at 180—200°. The following compounds have been prepared.

From *o*-aminoazo-*p*-toluene and benzaldehyde, 1-*p*-toluidino-2-phenyl-5-methylbenziminazole, which on reduction yields *p*-toluidine and 2-phenyl-5-methylbenziminazole, dense white crystals, m. p. 240°. Similarly, *o*-chlorobenzaldehyde yields 1-*p*-toluidino-2-*o*-chlorophenyl-5-methylbenziminazole, white, monoclinic needles, m. p. 178—179°, *nitrosoamine*, decomp. 124°, which is reduced to *p*-toluidine and 2-*o*-chlorophenyl-5-methylbenziminazole, white needles, m. p. 160° (*picrate*, decomp. 189°). From *m*-nitrobenzaldehyde is similarly obtained 1-*p*-toluidino-2-*m*-nitrophenyl-5-

methylbenziminazole, greyish-yellow needles, decomp. 224—225° (*picrate*, decomp. 174°; *nitrosoamine*, decomp. 120°), and on reduction, *p*-toluidine and 2-*m*-aminophenyl-5-methylbenziminazole, white, crystalline plates, m. p. 236°. With *o*-nitrobenzaldehyde, 1-*p*-toluidino-2-*o*-nitrophenyl-5-methylbenziminazole (*picrate*, decomp. 182°; *nitrosoamine*, decomp. 130°) and 2-*o*-aminophenyl-5-methylbenziminazole, white needles, m. p. 190°; and with *p*-nitrobenzaldehyde, 1-*p*-toluidino-2-*p*-nitrophenyl-5-methylbenziminazole and 2-*p*-aminophenyl-5-methylbenziminazole, white plates, m. p. 124°, containing water of crystallisation. This base, when diazotised and coupled with  $\beta$ -naphthol in alcohol-pyridine solution, gives a reddish-brown azo dye, m. p. 330°. From *o*-aminoazo-*p*-toluene and *p*-dimethylaminobenzaldehyde, 1-*p*-toluidino-2-dimethylaminophenyl-5-methylbenziminazole, white needles, m. p. 249° (*picrate*, m. p. 177°; *nitrosoamine*, decomp. 85°), is obtained, which on reduction yields *p*-toluidine and the iminazole, m. p. 124°, obtained in the reduction of the base from *p*-nitrobenzaldehyde.

Benzeneazo- $\beta$ -naphthylamine and benzaldehyde yield 1-anilino-2-phenylnaphthiminazole, which on reduction yields 2-phenylnaphthiminazole, m. p. 217—218°. The reduction of the condensation products of substituted benzaldehydes and benzeneazo- $\beta$ -naphthylamine yields the same phenylnaphthiminazole. From *p*-hydroxybenzeneazo- $\beta$ -naphthylamine (*diacetyl* derivative, m. p. 184°, *dibenzoyl* derivative, m. p. 199°) the following compounds were obtained: with benzaldehyde in alcoholic solution, 1-*p*-hydroxyanilino-2-phenylnaphthiminazole, white needles, m. p. 183° (*nitrosoamine*, decomp. 135°), which on reduction yields *p*-aminophenol and 2-phenylnaphthiminazole; with *o*-chlorobenzaldehyde, 1-*p*-hydroxyanilino-2-*o*-chlorophenylnaphthiminazole, white needles, m. p. 198° (*nitrosoamine*, decomp. 110°), and on reduction *p*-aminophenol and 2-*o*-chlorophenylnaphthiminazole, white needles, m. p. 214°; with salicylaldehyde in methyl-alcoholic solution, 1-*p*-hydroxyanilino-2-*o*-hydroxyphenylnaphthiminazole, white needles, m. p. 276°, which on reduction yields 2-*o*-hydroxyphenylnaphthiminazole, white needles, m. p. 280°; with furfuraldehyde, 1-*p*-hydroxyanilino-2-furylnaphthiminazole, white needles, m. p. 195° (*picrate*, yellow powder, *nitrosoamine*, yellow, easily decomp.). In contrast to the foregoing substituted iminazoles, which are very stable to most reducing agents, 1-*p*-nitroanilino-2-*o*-chlorophenylnaphthiminazole, bright yellow crystals, m. p. 283° (*nitrosoamine*, decomp. 105—107°), prepared from *p*-nitroanilinoazo- $\beta$ -naphthylamine and *o*-chlorobenzaldehyde in acetic acid solution, yields *p*-phenylenediamine and 2-*o*-chlorophenylnaphthiminazole on reduction with zinc and acetic acid.

[With G. SEUFERT and H. HOJER.]—The azo dye obtained from diazotised anthranilic acid and  $\beta$ -naphthylamine forms crimson-red needles, m. p. 182—183°; it gives, with benzaldehyde, 1-*o*-carboxyanilino-2-phenylnaphthiminazole, colourless, monoclinic prisms, m. p. 263—264°, decomp., which on nitration in acetic acid yields 1-*o*-carboxy-*p*-nitroanilino-2-phenylnaphthiminazole, bright yellow pyramids, m. p. 274°, and this on reduction with hydriodic acid gives

2-phenylnaphthiminazole. With acetaldehyde, the same dye yields 1-*o*-carboxyanilino-2-methylnaphthiminazole, colourless, monoclinic plates, m. p. 283° (after slight decomp. at 260°), which gives 2-methylnaphthiminazole, m. p. 168° (*picrate*, m. p. 242°), on reduction.

1-*m*-Carboxybenzeneazo- $\beta$ -naphthylamine, yellowish-red needles, m. p. 220°, gives condensation products with aldehydes which are distinguished by their insolubility in solvents. The following compounds were prepared. From acetaldehyde, 1-*m*-carboxyanilino-2-methylnaphthiminazole, white, crystalline powder, m. p. 276°; from furfuraldehyde, 1-*m*-carboxyanilino-2-furylnaphthiminazole, m. p. 273—274°; from salicylaldehyde, 1-*m*-carboxyanilino-2-*o*-hydroxyphenylnaphthiminazole, colourless granules, m. p. 232° (*nitrosoamine*, decomp. 110°).

*p*-Carboxybenzeneazo- $\beta$ -naphthylamine crystallises from benzene-alcohol in crimson-red needles, m. p. 263—264°; it condenses with aldehydes in alcoholic solution in the presence of pyridine or acetic acid. The following compounds were obtained. From benzaldehyde, 1-*p*-carboxyanilino-2-phenylnaphthiminazole, colourless prisms, m. p. 255° (decomp.) [*picrate*, m. p. 205° (decomp.), *acetyl* derivative, m. p. 218°, *nitrosoamine*, decomp. 213—214°], which on reduction yields 2-phenylnaphthiminazole and *p*-aminobenzoic acid. On nitration, the original base gives 1(2:4-dinitroanilino)-2-phenylnaphthiminazole, small, yellow plates, decomp. 270—272°. The dinitro compound with hydriodic acid gives 2-phenylnaphthiminazole and 1:2:4-triaminobenzene. With acetaldehyde, the azo dye gives 1-*p*-carboxyanilino-2-methylnaphthiminazole, white plates, m. p. 287° (*dinitro* derivative, m. p. 235°, yielding 2-methylnaphthiminazole on reduction). With furfuraldehyde, 1-*p*-carboxyanilino-2-furylnaphthiminazole, colourless prisms, m. p. 251° (greenish-yellow *nitrosoamine*).

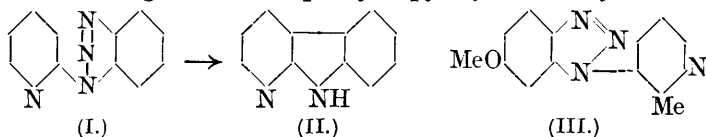
[With F. VON MANN-SIECHLER.]—The base,  $C_{19}H_{16}N_4$ , colourless, white plates, m. p. 228°, obtained by the action of benzaldehyde on chrysoidine (cf. A., 1898, i, 155) gives a *diacetyl* derivative, m. p. 105° (decomp.), a *picrate*, decomp. 204°, a *picrolonate*, decomp. 186°, and with aldehydes stable, well-crystallised benzylidene derivatives, which can be prepared directly from chrysoidine and aldehyde (2 mols.). Thus benzaldehyde and chrysoidine afford the compound  $C_{26}M_{20}N_4$ , bright yellow plates, m. p. 242° (*nitrosoamine*, decomp. 110°), which with 10% sulphuric acid affords benzaldehyde and 1-anilino-2-phenylaminobenziminazole, white flocks, m. p. 229°. Similarly, chrysoidine and salicylaldehyde give the compound  $C_{26}H_{20}O_2N_4$ , bright yellow plates, m. p. 242° (*nitrosoamine*, decomp. 125°), from which dilute sulphuric acid splits off 1 mol. of salicylaldehyde. By diazotisation in alcoholic solution and treatment with 95% alcohol, the base  $C_{19}H_{16}N_4$  was converted into 1-anilino-2-phenylbenziminazole, snow-white prisms, m. p. 211° (*picrate*, decomp. 199°; *picronolate*, decomp. 220°; *nitrosoamine*, decomp. 137°), and this on reduction with hydriodic acid gives the known 2-phenylbenziminazole.

[With F. ELFLIN and K. MÜLLER.]—The action of benzyl chloride on benzeneazo- $\beta$ -naphthylamine, either alone or in acetic acid solu-

tion, gives aniline and 2-phenylnaphthiminazole. Similar results were obtained with *p*-tolueneazo- $\beta$ -naphthylamine, *o*- and *m*-nitrobenzeneazo- $\beta$ -naphthylamine, and *p*-anisoleazo- $\beta$ -naphthylamine. Similarly, benzeneazo- $\beta$ -benzyl-naphthylamine (shining, light red needles, m. p. 136—138°), obtained by coupling benzyl- $\beta$ -naphthylamine with benzene diazonium chloride in alcoholic solution, on boiling with alcoholic hydrochloric acid decomposes into aniline and 2-phenylnaphthiminazole. Similar results were obtained with *p*-tolueneazo-benzyl- $\beta$ -naphthylamine and nitrobenzeneazo-benzyl- $\beta$ -naphthylamine.

R. B.

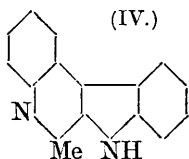
**Harmine and Harmaline. VII. Synthesis of *apo*Harmine and of certain Carboline and Copyrine Derivatives.** W. LAWSON, W. H. PERKIN, jun., and R. ROBINSON (*J. Chem. Soc.*, 1924, **125**, 626—657).—2-Chloropyridine and *o*-phenylenediamine condense to give *o*-aminophenyl-2-pyridylamine hydrochloride,



which, when treated with nitrous acid, yields 1- $\alpha$ -pyridylbenzotriazole (I), colourless needles, m. p. 110—111°. The latter, when heated in small quantities with zinc chloride, gives 3-carboline (II), colourless needles, m. p. 210°; *hydrochloride*, needles from dilute hydrochloric acid; *mercurichloride*, needles; *hydrogen oxalate*, needles from dilute oxalic acid solution; *picrate*, canary-yellow needles, m. p. 260—264°. 2-Chloroquinoline and *o*-phenylenediamine similarly give 1- $\alpha$ -quinolylbenzotriazole, colourless prisms or needles, m. p. 145°, which, when heated, gives quinindoline, identical with that of Gabriel and Eschenbach (*A.*, 1898, i, 199). The triazole (III) cannot be prepared by this method owing to the inactivity of  $\beta$ -halogen substituents in the pyridine molecule, and alternatively the preparation of 3-aminoquinoline and 3-amino-2-methylpyridine was undertaken for condensation with the requisite halogen derivatives. 2-Methylquinoline-3:4-dicarboxylic acid (cf. Pfizinger, *A.*, 1898, i, 207), when strongly heated, gives the *anhydride*, colourless prisms, m. p. 218°, and when heated with carbamide at 230° gives the *imide*, pale yellow needles from ethyl acetate, m. p. 257°. The imide, when treated with bromine and potassium hydroxide, gives 3-amino-2-methylquinoline-4-carboxylic acid, pale yellow needles, m. p. 221—222° (decomp.), which, when heated at 225°, is smoothly converted into 3-amino-2-methylquinoline, m. p. 160—160.5°, identical with that prepared by Stark (*A.*, 1907, i, 973). The condensation of this aminoquinoline with various chlorobenzene derivatives could not be carried out, and is still under investigation.

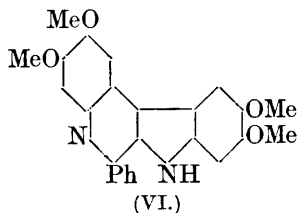
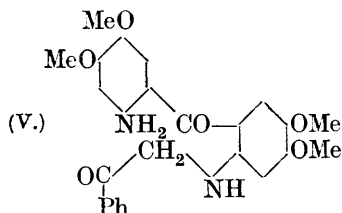
Ethyl  $\beta$ -aminocrotonate and ethyl cinnamoylpyruvate condense to give *ethyl styrylmethylpyridinedicarboxylate*, which is isolated as a *picrate*, yellow needles, m. p. 147.5—148°. These, on treatment with ammonia and subsequent hydrolysis, give *styrylmethylpyridine*.

*dicarboxylic acid*, pale yellow prisms, m. p. 220—221°. This acid cannot be 4-styryl-2-methylpyridine-3 : 6-dicarboxylic acid, since, when boiled with aniline, it gives a *phenylimide*, which was isolated in two forms, (a), bright yellow needles, m. p. 228—230°, (b), yellow needles, m. p. 203—204°; *a* and *b* may be geometrical stereoisomerides, although *a* on recrystallisation from xylene gave *b*. The potassium salt of the dicarboxylic acid, on treatment with potassium permanganate, gives 2-methylpyridine-3 : 4 : 6-tricarboxylic acid, which was isolated as the *potassium barium* salt, colourless crystals, and also gives a *monopotassium* salt, colourless prisms, a characteristic *ferrous* salt, red or orange-brown prisms, and on treatment with an excess of aniline gives the *anilide phenylimide*, pale yellow needles, m. p. 237°, and also the *phenylimide* of 2-methylpyridine-3 : 4-dicarboxylic acid, colourless plates, m. p. 190°. The *tricarboxylic acid* itself crystallises from water in prisms +3H<sub>2</sub>O, which, when anhydrous, darken at 219° and melt at 223° (decomp.), and was found not to be identical with the methylpyridinetri-carboxylic acid obtained by Dobbie and Lauder (T., 1902, **81**, 154) from corydaline, the constitution of which is therefore still in doubt. The tricarboxylic acid in turn gives 2-methylpyridine-3 : 4-dicarboxylic acid, m. p. 252—256°. The synthesis of a



substituted dibenzoapopharmine of the type (IV) was then undertaken in order that subsequent oxidation of the benzene nuclei should furnish apopharmine. Veratrone, the preparation of which from veratric acid has been greatly improved, was converted by nitric acid into 6 : 6'-dinitro-3 : 4 : 3' : 4'-tetramethoxybenzophenone (dinitroveratrone), colourless needles from acetic acid, m. p. 225°, and the latter on reduction gives *diaminoveratrone*, yellow prisms, m. p. 210°. The 6 : 6'-position of the nitroxyl groups in dinitroveratrone is confirmed by converting diaminoveratrone into *diacetyldiaminoveratrone*, pale yellow needles, m. p. 203°, which, on treatment with nitric acid in acetic acid suspension, gives a theoretical yield of 6-nitroacetoveratrylamine (cf. Jones and Robinson, T., 1917, **111**, 914).

Diaminoveratrone, when heated with  $\omega$ -bromoacetophenone in acetic acid, gives the hydrobromide of *N-phenacyldiaminoveratrone*, the *base* itself (V) forming greenish-yellow needles, m. p. 185—186° (decomp.). The base, when treated in alcoholic suspension with

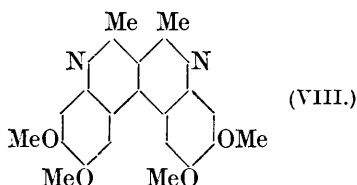
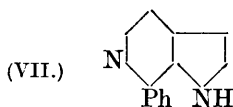


30% aqueous potassium hydroxide, gives *phenyldiveratroharmyrine* (phenyldiveratro-7-pyrindole) (VI), which crystallises from methyl alcohol +1 mol. of solvent, prisms, m. p. 145—148° (decomp.).



Replacement of the  $\omega$ -bromoacetophenone by bromoacetone gave no compound analogous to *N*-phenacyldiaminoveratrone, but *methyldiveratroharmyrine* was obtained, colourless prisms, m. p.  $254^\circ$ , and gave a *methosulphate*, orange-yellow needles. The hydrobromide, on boiling with hydriodic acid, was completely demethylated, giving *methylditetrahydroxydibenzoharmyrine hydriodide*, yellow needles. Methyl- and phenyl-diveratroharmyrine were found on oxidation and subsequent treatment with alkali to give, however, only a minute yield of the corresponding *apoharmine* (VII), owing to almost complete destruction of the base by the oxidising agent.

2:7-Naphthyridine (copyrine) rings may be synthesised also from the 2:2-diaminobenzophenones. Thus diaminoveratrone condenses with acetylacetone to give *dimethyldiveratrocopyrine* (VIII), colourless needles from *n*-butyl alcohol, m. p.  $230\text{--}231^\circ$ ,

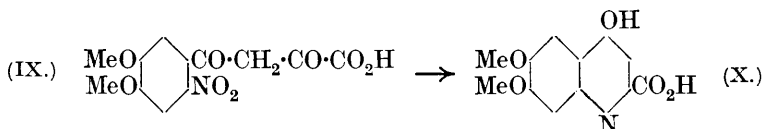


forming a yellow, crystalline *nitrate*, and a *picrate* of composition  $3C_{22}N_{22}O_4N_2 \cdot 5C_6H_3O_7N_3$ , yellow needles, decomp.  $245^\circ$ . Diaminoveratrone with benzoylacetone gives similarly *phenylmethyldiveratrocopyrine*, colourless needles, m. p.  $270^\circ$ ; with dibenzoylmethane gives *diphenyldiveratrocopyrine*, yellow needles, m. p.  $362^\circ$ , and with 1:3-diketohydrindene gives *o*-phenylenediveratrocopyrine, isolated as the *acetate*, yellow needles, the latter being converted by ammonia into the *base*, yellow needles, from nitrobenzene-*n*-butyl alcohol, m. p.  $304^\circ$ . Diaminoveratrone condenses also with ethyl acetoacetate to give *hydroxymethyldiveratrocopyrine*, pale yellow needles from quinoline, m. p.  $320\text{--}330^\circ$ ; with ethyl malonate to give *dihydroxydiveratrocopyrine*, yellow needles from nitrobenzene, m. p.  $300^\circ$  (decomp.); with ethyl cyanoacetate to give *aminohydroxydiveratrocopyrine*, salmon-coloured needles from alcohol-nitrobenzene, decomp.  $280^\circ$ , chars  $280\text{--}290^\circ$ .

Xanthone (*oo'*-dichlorobenzophenone) can be prepared by the dry distillation of calcium *o*-chlorobenzoate. A mixture of ethyl benzoylacetate and ethyl  $\beta$ -aminocrotonate, when boiled in methylalcoholic potassium hydroxide, yields 6-hydroxy-4-phenyl-2-methylpyridine-3-carboxylic acid (cf. Ruhemann, T., 1899, **75**, 412).

The following synthesis of a dimethoxykynurenic acid has been accomplished. Acetoveratrone on nitration does not yield 4:5-dinitroveratrole (Harding, T., 1914, **105**, 2795), but 6-nitroacetoveratrone, pale yellow needles, m. p.  $133\text{--}133.5^\circ$ , in which the 6-position of the nitro group is shown by further nitration, giving 4:5-dinitroveratrole. 6-Nitroacetoveratrone condenses with anisaldehyde to give 6-nitro-3:4-dimethoxyphenyl 4-methoxystyryl ketone, pale yellow prisms from ethyl acetate, m. p.  $170^\circ$ , and also gives a

*piperonylidene* derivative, plates and needles, m. p. 176—177°, re-solidify and then re-melt above 200° (indef.). The 6-nitro compound on reduction gives 6-*aminoacetoveratrone*, colourless prisms, m. p. 133°, and when treated with sodium ethoxide and ethyl oxalate in alcohol yields 6-*nitroveratrolypyruvic acid* (IX), needles, m. p. 163°. The latter, when reduced with ferrous hydroxide,

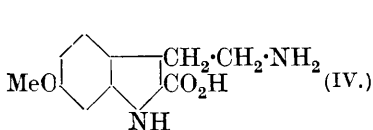
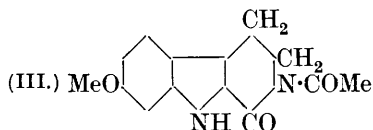
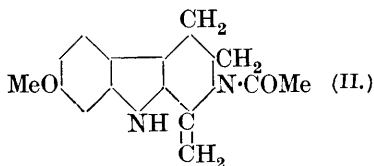
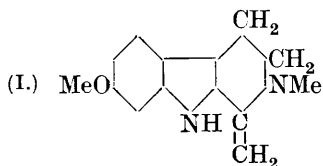


gives 4-*hydroxy*-6 : 7-*dimethoxyquinoline*-2-*carboxylic acid* (dimethoxykynurenic acid) (X), needles, sintering at 260°, m. p. 270° (decomp.). This acid when heated in glycerol solution loses carbon dioxide, giving 4-*hydroxy*-6 : 7-*dimethoxyquinoline*, colourless prisms, softening at 165—170°, re-solidifying and melting at 226°.

5 : 7-Dibromoisatin was converted into 5 : 7-dibromoisatinic acid, and the latter into 6 : 8-*dibromo*-2-*methylquinoline*-4-*carboxylic acid*, colourless needles, m. p. 267° (decomp.). The latter on heating gives 6 : 8-*dibromo*-2-*methylquinoline*, needles, m. p. 100°, *picrate*, orange-yellow needles, m. p. 155°. Attempts made to replace the bromine in the carboxylic acid by hydroxy groups and then by oxidation of the benzene nucleus to obtain 2-methylpyridine-4 : 5 : 6-tricarboxylic acid failed.

F. G. M.

**Harmine and Harmaline. VIII. Constitution of certain Harmaline Derivatives.** H. NISHIKAWA, W. H. PERKIN, jun., and R. ROBINSON (*J. Chem. Soc.*, 1924, 125, 657—663).—Methylharmaline on oxidation with potassium permanganate in acetone solution yields ketoisonormethyltetrahydroharmine; acetylharmaline when thus oxidised yields *acetylketo*tetrahydroharmine (III), colourless prisms, m. p. 207—208°, and when reduced with hydrogen in the presence of palladium gives acetyltetrahydroharmaline.



It follows that methyl- and acetyl-harmaline have the constitution (I) and (II). Harmaline methosulphate on treatment with

potassium cyanide gives *cyanomethyltetrahydroharmine*, colourless leaflets, m. p. 155–156°, whilst harmine methosulphate gives a similar but unstable product, m. p. 141°. Acetylketotetrahydronorharmine on hydrolysis with alcoholic potassium hydroxide yields 6-methoxy-3- $\beta$ -aminoethylindole-2-carboxylic acid (IV), leaflets, decomp. 220–250°, and the corresponding lactam, *ketotetrahydronorharmine*, prisms, m. p. 198°. The lactam could not be hydrolysed to the amino-acid, or the latter dehydrated to the lactam. Hydratoacetylharmaline, which forms a *hydrochloride* (+0.5 aq.), colourless needles, on acetylation gives two isomeric *diacetylhydratoacetylharmalines*, (a) needles, m. p. 134–135°, (b) pale-yellow plates, m. p. 159–160°. The work of O. Fischer (A., 1898, i, 164; 1914, i, 316) is thus confirmed. F. G. M.

**Dyes Derived from Phenanthraquinone. IV. Anilino-flavindulines and Phenanthraquinoneazo-dyes.** A. C. SIRCAR and D. C. ROY (*J. Chem. Soc.*, 1924, 125, 543–547; cf. T., 1913, 103, 295; 1921, 119, 1211; 1922, 121, 1944).—The following phenanthraphenazonium compounds containing an anilino group attached to the benzenoid nucleus did not exhibit the expected property of dyeing in blue shades.

4 : 5-Dibromo-11-anilino*flavinduline chloride*, prepared by reducing nitrosodiphenyl-*m*-phenylenediamine and condensing the product with 4 : 5-dibromophenanthraquinone, green crystals, decomp. 199°, m. p. 245–252°. 2 : 7-Dinitro-11-anilino*flavinduline chloride*, similarly prepared (not crystalline), blackens at 250°, m. p. above 270°. 2-Nitro-11-anilino*flavinduline chloride*, prisms, m. p. above 270°. 2 : 7-Diamino-11-anilino*flavinduline chloride*, bluish-black flocculent precipitate, m. p. above 275°. 4 : 5 : 11-Trianilino-*flavinduline chloride*, prepared from the above 4 : 5-dibromo compound by the action of aniline in the presence of copper powder, is a flocculent precipitate, decomp. 165°, m. p. 205–210°.

The following azo compounds were prepared by coupling the diazotised aminophenanthraquinone with the hydroxy acid in alkaline solution. 1-Hydroxy-2-naphthoic acid with 2-aminophenanthraquinone gives 4-hydroxy-1(2′)-phenanthraquinoneazo-3-naphthoic acid, m. p. not below 275°; with 4-aminophenanthraquinone gives 4-hydroxy-1(4′)-phenanthraquinoneazo-3-naphthoic acid; with 2 : 7-diaminophenanthraquinone gives phenanthraquinone-2 : 7-bis(1-azo-4-hydroxy-3-naphthoic acid), m. p. not below 283°; with 4 : 5-diaminophenanthraquinone gives phenanthraquinone-4 : 5-bis(1-azo-4-hydroxy-3-naphthoic acid), amorphous, m. p. above 275°.

2-Hydroxy-3-naphthoic acid with 2-aminophenanthraquinone gives 2-hydroxy-1(2′)-phenanthraquinoneazo-3-naphthoic acid, blue crystals, decomp. 225°; with 4-aminophenanthraquinone gives 2-hydroxy-1(4′)-phenanthraquinoneazo-3-naphthoic acid, decomp. 250–255°; with 2 : 7-diaminophenanthraquinone gives phenanthraquinone-2 : 7-bis(1-azo-2-hydroxy-3-naphthoic acid), crystals, m. p. not below 283°; with 4 : 5-diaminophenanthraquinone gives phenanthraquinone-4 : 5-bis(1-azo-2-hydroxy-3-naphthoic acid), m. p. not

below 274°. Salicylic acid gives with 4-aminophenanthraquinone *phenanthraquinone-4-azosalicylic acid*, m. p. not below 275°; with 2:7-diaminophenanthraquinone gives *phenanthraquinone-2:7-bis-azosalicylic acid*, m. p. not below 270°; with 4:5-diaminophenanthraquinone gives *phenanthraquinone-4:5-bisazosalicylic acid*, m. p. not below 274°. The dyeing properties on wool of the above compounds and the colours developed in sulphuric acid solution are described.

F. G. M.

**Reaction of Azine and Thiazine Dyes with the Gel of *Chondrus crispus*.** E. JUSTIN-MUELLER (*Bull. Soc. chim.*, 1924, **35**, 390—394).—Azine and thiazine dyes coagulate solutions of the gel obtained from lichen carragheen, *Chondrus crispus*. This property is not possessed by the oxazines, and appears to be characteristic of the “az-azonium” and “az-thionium” groupings.

R. B.

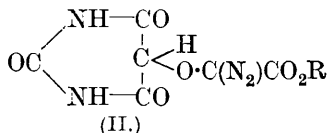
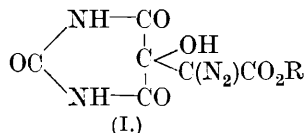
**Catalysis. IV. Behaviour of the Amino Group when Cytosine and Nitrouracil are reduced in the Presence of Colloidal Platinum.** E. B. BROWN and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1924, **46**, 702—708).—Cytosine is reduced by hydrogen in the presence of colloidal platinum with formation of hydro-uracil and ammonia. Partial reduction of 5-nitrouracil with three molecular equivalents of hydrogen forms 5-aminouracil, which compound undergoes partial hydrolysis with the production of 5-hydroxyuracil (*isobarbituric acid*); with four molecular equivalents of hydrogen the hydrolysis proceeds further and a new compound (I) or (II) (?) is obtained. It forms diamond-shaped crystals not



melting at 285°. Yeast-nucleic acid was also submitted to the action of hydrogen in presence of colloidal platinum, and evidence of the formation of ammonia obtained.

C. J. S.

**Interaction of Ethyl Diazoacetate and Alloxan.** H. BILTZ and E. KREMER (*Annalen*, 1924, **436**, 154—173).—Ethyl diazoacetate combines with alloxan to give ethyl dialuryldiazoacetate (I) or (II).



Formula I best explains the results of methylation (to give trimethyl derivative) and the decomposition effected by alkalis, acids, and oxidising agents. Formula II is also possible, since the ester cannot be acetylated, and since among its reduction products are formed dialuric acid and alloxantin.

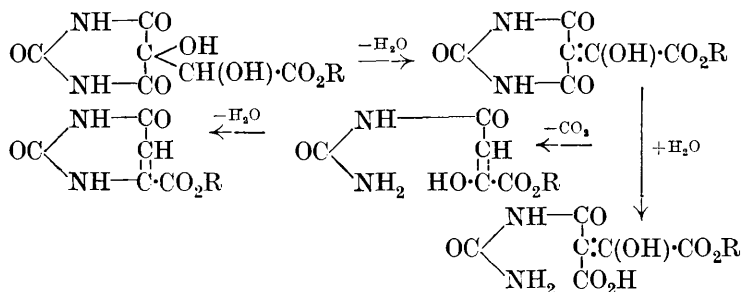
*Ethyl dialuryldiazoacetate* is produced by the interaction of alloxan hydrate (1 mol.) and ethyl diazoacetate (2.5 mols.), when yellow, six-sided plates, decomp. 163—164°, are obtained. The

*disodium* salt,  $C_8H_6O_6N_4Na_2$ , is described. Nitrogen is evolved when the ester is treated with dilute mineral acids or Fehling's solution. *Methyl dialuryldiazoacetate* (from alloxan hydrate and methyl diazoacetate), forms six-sided, yellow needles, decomp.  $153-154^\circ$ .

*Ethyl methyl dialuryldiazoacetate* (from methylalloxan hydrate) forms prisms, decomp.  $136^\circ$ . Methylalloxan will not give a solid derivative with methyl diazoacetate, whilst dimethylalloxan will not react with either ester.

*Methyl 1:3:5-trimethyldialuryldiazoacetate* is produced when ethyl dialuryldiazoacetate and diazomethane react in ethereal solution. It forms clusters of prisms, m. p.  $99-100^\circ$ , and when warmed with dilute sulphuric acid affords two atoms of nitrogen. When oxidised with concentrated nitric acid, dimethylalloxan anhydride and oxalic acid are produced; with hydroxylamine, it gives dimethylvioluric acid.

Ethyl dialuryldiazoacetate, on warming with  $N/2$ -sodium hydroxide, evolves nitrogen, and on acidification, ethyl uracilcarboxylate and carbon dioxide are produced. Uracilcarboxylic acid is also formed in the above reactions, as microscopic needles, m. p. not below  $330^\circ$ , and was characterised as the 5-nitro derivative. The formation of these compounds must take place according to the scheme :



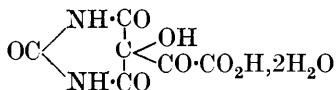
Ethyl dialuryldiazoacetate on hydrolysis with dilute hydrochloric acid yields ethyl glycollate and alloxantin; with concentrated hydrochloric acid, it yields dialuric acid and ethyl glyoxylate.

Another product with either dilute or concentrated hydrochloric acid is ethyl uracilcarboxylate. The methyl ester yields *methyl uracilcarboxylate* (fine needles, m. p.  $230^\circ$ ) on hydrolysis with the concentrated acid.

*Ethyl 5-ethoxyuracil-6-carboxylate* results from the interaction of dialuryldiazoacetate and alcoholic hydrogen chloride, when nitrogen is evolved, and the ester may be obtained as long, colourless needles, m. p.  $203-212^\circ$ . The *ammonium* salt (pale, rose-coloured plates, m. p.  $202-203^\circ$ ) and the *potassium* salt (colourless) are described, and from the latter the free *acid* may be obtained by the action of concentrated hydrochloric acid. It forms colourless prisms, decomposing at  $216-217^\circ$  or on heating at  $190^\circ$ , to give ethyl isobarbiturate.

Oxidation of ethyl 5-ethoxyuracil-6-carboxylate with permanganate yields oxaluric and oxalic acids.

Oxidation of ethyl dialuryldiazoacetate with concentrated nitric acid gives alloxan and oxalic acid, and with milder conditions *dialurylglyoxylic acid* dihydrate [microscopic needles, m. p.  $152^{\circ}$  (decomp.)] may be



isolated (annexed formula). With hydrogen peroxide, oxaluric acid is formed.

Reduction of ethyl dialuryldiazoacetate with hydriodic acid gives alloxantin and ethyl iodoacetate, whereas with stannous chloride, the products are dialuric and glycollic acids. A. E. C.

**Oxidation of Uric Acid.** H. BILTZ and H. SCHAUDER (*J. pr. Chem.*, 1923, [ii], **106**, 108—172).—The oxidation of uric acid in dilute acetic acid suspension at  $0^{\circ}$ , using potassium permanganate (2.6 atoms of oxygen), affords potassium oxalurate and oxalate, carbamide, and oxalyldiureide; when the permanganate used affords 1 atom of oxygen, the same products except the oxalurate are obtained. Oxidation of uric acid with potassium persulphate in presence of potassium acetate is less vigorous than the above and requires water-bath temperatures; when persulphate equivalent to 1 atom of oxygen is used, allantoin results, 2 atoms of oxygen affording potassium oxalurate and oxalyldiureide. Oxidation of uric acid at  $0^{\circ}$  in aqueous suspension using permanganate (=2 atoms O) in presence of a rapid current of carbon dioxide gives the products obtained by using acetic acid, whilst with permanganate equivalent to 1 atom of oxygen, potassium oxalurate and oxalate and carbamide result. No uroxic acid is isolated, probably because its precursor, the hypothetical hydroxyacetylenediureinecarboxylic acid, loses carbon dioxide before passing into uroxic acid.

When uric acid is boiled with aqueous hydrogen peroxide until it is all dissolved, carbonyl dicarbamide is the main product, and is accompanied by a trace of cyanuric acid and a *substance* forming white, hemispherical masses, decomp.  $220^{\circ}$ . The results are unaffected by adding small quantities of acetic acid or of potassium acetate.

Oxidation of uric acid by permanganate (=1 atom O) at the ordinary temperature in presence of sulphuric acid gives alloxan and alloxantin, whilst if the acid is boiled with aqueous potassium persulphate solution (=1 atom O) alloxan is formed in small quantities, the majority of the acid probably passing into alloxanic acid and the latter into 5-hydroxyhydantoin (A., 1921, i, 815). When twice the above proportion of persulphate is used, a little parabanic acid is formed, presumably from alloxan.

Hydrogen peroxide converts uric acid in presence of boiling dilute sulphuric acid into parabanic acid (formed from alloxan). In presence of boiling dilute hydrochloric acid, the oxidation is so satisfactory that the author recommends this as a method of preparing parabanic acid.

Possible intermediate compounds in the oxidation of uric to oxaluric acid are uric acid glycol, alloxan, allantoin, or the hypothetical hydroxyacetylenediureinecarboxylic acid. These compounds require for their formation (from uric acid) 1 atom of oxygen, this amount of oxygen being required to convert them into oxaluric acid. The compounds have therefore been oxidised under different conditions. Uric acid 4 : 5-glycol, when treated with permanganate (=1 atom O) in dilute acetic acid at 0°, is very slowly oxidised and affords impure potassium oxalurate and oxalate. In boiling solution, oxidation is rapid, but the yield of oxalurate is small. The glycol is therefore not the intermediate between uric and oxaluric acids.

9-Methyluric acid 4 : 5-glycol, oxidised with permanganate and acetic acid in the warm, gives methyloxaluric acid (?), m. p. 180—190° (with frothing). 7 : 9-Dimethyluric acid 4 : 5-glycol similarly affords small quantities of dimethylparabanic acid.

Alloxan is very slowly oxidised by cold permanganate and dilute acetic acid to give potassium oxalurate. Oxidation is more rapid in the warm, but alloxan is clearly not the intermediate sought for. Hydrogen peroxide oxidises alloxan at water-bath temperatures to give oxaluric acid.

Allantoin is slowly oxidised by cold and rapidly by warm permanganate, potassium oxalurate and carbamide resulting. Allantoin is ruled out as the intermediate oxidation product, which is evidently the hypothetical hydroxyacetylenediureinecarboxylic acid.

A method is given for the preparation of potassium oxalurate from uric acid and consists in the oxidation of the latter in alkaline solution, and then in acetic acid solution, using permanganate equivalent to one atom of oxygen for each stage. Potassium oxalurate ( $C_3H_3O_4N_3K, H_2O$ ), when treated with hydrochloric acid, affords *oxaluric acid*, decomp. 208—210°. The *ammonium* salt is described. *Methyl oxalurate*, from the acid and diazomethane, forms crystals, m. p. 192° (indef. with frothing). *Oxaluric methylamide*, from the ester and aqueous methylamine, forms needles, decomp. 251—253°. When oxaluric acid is boiled for a short time with water, carbamide oxalate and ammonium tetraoxalate result. The monocarbamide oxalate described by Lubavin (1872) does not exist. If equimolecular quantities of carbamide and oxalic acid are mixed in aqueous solution, carbamide oxalate,  $H_2C_2O_4 \cdot 2CO(NH_2)_2$ , separates, whilst if the solution is boiled for some time, ammonium oxalate is formed.

When 1 : 3-dimethyluric acid is oxidised with alkaline permanganate (=1 atom O), potassium oxalurate and *s*-dimethyloxamide result. Alkaline oxidation (1 atom O) followed by acid oxidation (acetic; 1 atom O) affords potassium oxalurate and dimethylparabanate, together with *s*-dimethyloxamide and oxaluric methylamide. Oxidation (1 atom O) in acetic acid solution gives dimethylparabanic acid and a crystalline *substance* (not examined), oxidation with 2 atoms of oxygen (as permanganate) affording potassium oxalurate and dimethylparabanic acid. Oxidation of 1 : 3-dimethyl-

uric acid with alkaline hydrogen peroxide affords a substance forming needles, m. p.  $215^{\circ}$  (decomp.).

3 : 7-Dimethyluric acid when oxidised by alkaline permanganate (1 atom O) gives 1 : 8-dimethylallantoin together with a potassium salt,  $C_6H_4O_5N_3K$ , plates, m. p.  $275^{\circ}$  (indef. and decomp.) (corresponding with an acid,  $C_6H_5O_5N_3$ , prisms, decomp.  $212^{\circ}$ ). 3 : 7-Dimethyluric acid is converted by alkaline hydrogen peroxide into carbonyl dicarbamide (?), decomp.  $210^{\circ}$ .

No alloxan is formed when chlorine is passed into a suspension of uric acid in aqueous sodium acetate-acetic acid. No alloxans are formed when 9-methyluric acid glycol is heated with hydrochloric acid, the products being carbamide and methylparabanic acid. Similarly treated, 7 : 9-dimethyluric acid glycol affords carbamide and dimethylparabanic acid. The glycol type is therefore not immediately formed when uric acids are oxidised to alloxans.

5-Chloro- and 5-hydroxy- $\psi$ -uric acids are readily converted by hydrochloric acid into alloxan, which is conveniently identified by adding stannous chloride and isolating alloxantin.

The chloraluric acid described by Schiel (1859) is, as stated by Lubavin (*loc. cit.*), a mixture of ammonium chloride and parabanic acid. The stryphnic acid obtained by Gibbs (1869) on treating uric acid with potassium nitrite and mineral acid, is now shown to be a mixture of allantoin with oxaluric and oxalic acids. Similarly, the urinilic acid described by Sokolov (1869) does not exist; nitric oxide has no action on an aqueous suspension of uric acid, whilst nitrogen peroxide has no action on uric acid in absence of water; nitric oxide containing a little nitrogen peroxide converts uric acid, in aqueous suspension, into uric acid glycol, parabanic acid, and alloxan, whilst nitric oxide containing much nitrogen peroxide affords xanthine, parabanic acid, alloxan, and oxalic acid.

The paper contains a useful discussion of the results obtained.

E. E. T.

**Potassium Hydroxyhæmin.** A. HANSIK (*Z. physiol. Chem.*, 1924, **133**, 173—179).—The author has previously (*Spisy lékařské fakulty v Brně*, 1922, **1**, 1A, 5), by extracting the coagulum of blood with alcohol acidified with oxalic acid, obtained a compound  $C_{34}H_{31}O_4N_4Fe$ , small star-like aggregates of crystals, which he named hydroxyhæmin anhydride. By boiling the anhydride with glacial acetic acid and sodium chloride or with alcohol, oxalic acid, and sodium chloride,  $\alpha$ -chlorohæmin was obtained. Potassium hydroxyhæmin,  $C_{34}H_{30}O_4N_4K_2Fe \cdot OH$ , very small spherical, crystalline aggregates, was obtained by treating hydroxyhæmin anhydride or  $\alpha$ -chlorohæmin with alcoholic potassium hydroxide.

S. S. Z.

**A New Type of Cyclic Compound.** E. P. KOHLER (*J. Amer. Chem. Soc.*, 1924, **46**, 503—517; cf. A., 1916, i, 404; 1919, i, 582).—Improved methods are described for the preparation of phenyl  $\gamma$ -nitro- $\beta$ -phenylpropyl ketone and of its  $\alpha$ -bromo derivative, which occurs in two stereoisomeric forms, needles, m. p.  $108^{\circ}$ , and plates



or prisms, m. p. 129°, and is accompanied, in its formation, by the  $\alpha$ -*dibromo* derivative, tablets, m. p. 106°. The  $\alpha$ -bromo derivative, when treated with potassium acetate in methyl-alcoholic solution, affords a mixture of the *cyclopropane* derivative previously described with 2-*hydroxy-3-methoxy-5-benzoyl-4-phenylisoxazolidine* and an unidentified oxazole (?) derivative. If the isoxazolidine (prisms, m. p. 162°) is dissolved in glacial acetic acid and the solution poured into water, 2:3-*dihydroxy-5-benzoyl-4-phenylisoxazolidine*, prisms, m. p. 153°, results (*dibenzoyl* derivative, tablets, m. p. 158—160°). The isoxazolidine (m. p. 162°), when treated with ammonia, affords 3-*amino-2-hydroxy-5-benzoyl-4-phenylisoxazolidine*, needles, m. p. about 162° (decomp.); this substance, when boiled with ethyl alcohol in presence of acetic acid, being converted into 2-*hydroxy-3-ethoxy-5-benzoyl-4-phenylisoxazolidine*, m. p. 168° (decomp.), boiling with methyl alcohol etc. affording the above methoxy compound. The latter, when treated with acetic anhydride, is slowly converted into *phenyl  $\gamma$ -nitro- $\alpha$ -acetoxy- $\beta$ -phenylpropyl ketone* (tablets, m. p. 98°), which with ammonia affords the corresponding  $\alpha$ -*hydroxy* compound (m. p. 142°; *benzoyl* derivative, needles, m. p. 106—107°). The last-named hydroxy compound, when treated with hydrogen chloride in methyl-alcoholic solution, is converted into the methoxyisoxazolidine of m. p. 162°. The formation from the latter of the above ketone (m. p. 98°) takes

CHPh·CHBz place through the intermediate production of 5-*benzoyl-4-phenylisoxazoline oxide*, colourless tablets, m. p. 126° (annexed formula). This compound, which results when the above  $\alpha$ -bromoketone is treated with potassium acetate in isopropyl-alcoholic solution, combines with water, and with primary (but not with secondary) alcohols, in presence of acid, to give isoxazolidines, water, *e.g.*, affording the dihydroxyisoxazolidine mentioned above, whilst ammonia affords the above aminohydroxyisoxazolidine. The isoxazolidines described form sparingly soluble copper salts. The methoxyisoxazolidine, which is converted at its m. p. into methyl alcohol, water, benzonitrile, and a nitrogenous substance, affords a *benzoyl* derivative (colourless plates, m. p. 114°) and a *copper* derivative,  $C_{17}H_{17}O_5NCu$ , and (like the isoxazoline oxide) is converted by alkali into benzonitrile, and formic and phenylacetic acids.

A. B. S.

**Indoxazens and isoOxazoles.** K. VON AUWERS (*Ber.*, 1924, 57, [B], 461—467).—A comparison of the optical properties of indoxazen with those of *isooxazole* and its derivatives confirms the structure,  $C_6H_4 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} N$ , ascribed to the former compound by Conduché (A., 1908, i, 154). The following data, amongst others, are recorded. *isoOxazole*, b. p. 95°,  $d_4^{20}$  1.078,  $n_{He}^{20}$  1.428. 5-Methyl-*isooxazole*, b. p. 122°,  $d_4^{20}$  1.023,  $n_{He}^{20}$  1.439. 3-Methyl-*isooxazole*, b. p. 118°,  $d_4^{20}$  1.022,  $n_{He}^{20}$  1.435. 3:5-Dimethyl-*isooxazole*, b. p. 143°,  $d_4^{20}$  0.983,  $n_{He}^{20}$  1.442. 3:4:5-Trimethyl-*isooxazole*, b. p. 111°/75 mm.,  $d_4^{20}$  0.981,  $n_{He}^{20}$  1.452. 3:4-Tetramethylene-*isooxazole*,

$C_6H_8 \llcorner \begin{smallmatrix} CH \\ N \end{smallmatrix} \gg O$ , b. p.  $93^\circ/15$  mm.,  $d_4^{20}$  1.095,  $n_{He}^{20}$  1.498. Methyltetrahydrobenzo-3:4-*isooxazole*, b. p.  $97^\circ/16$  mm.,  $d_4^{20}$  1.059,  $n_{He}^{20}$  1.491. Methyltetrahydrobenzo-4:5-*isooxazole*, b. p.  $101^\circ/18$  mm.,  $d_4^{20}$  1.062,  $n_{He}^{20}$  1.492.

Indoxazen, b. p.  $84^\circ/11$  mm.,  $d_4^{20}$  1.170,  $n_{He}^{20}$  1.563. 3-Phenylindoxazen,  $C_6H_4 \llcorner \begin{smallmatrix} CPh \\ O \end{smallmatrix} \gg N$ , m. p.  $82-84^\circ$ , b. p.  $181^\circ/13$  mm.,  $d_4^{39.9}$  1.1241,  $n_{He}^{39.9}$  1.59279. Salicylonitrile,  $d_4^{99.6}$  1.1052,  $n_{He}^{99.6}$  1.54359. *o*-Methoxybenzonitrile, b. p.  $146^\circ/20$  mm.,  $d_4^{20}$  1.107,  $n_{He}^{20}$  1.548. *o*-Anisaldoxime methyl ether, b. p.  $235^\circ$ ,  $d_4^{20}$  1.092,  $n_{He}^{20}$  1.554.

Attempts to convert *o*-aminoacetophenone into 3-methylindoxazen gave unexpectedly methylantranil,  $C_6H_4 \llcorner \begin{smallmatrix} CMe \\ N \end{smallmatrix} \gg O$ , b. p.  $121^\circ/17$  mm.,  $d_4^{23.2}$  1.1304,  $n_{He}^{23.2}$  1.57457. H. W.

**Synthesis of Thiobiazolone Derivatives.** C. BÜLOW and F. SEIDEL (*Ber.*, 1924, 57, [B], 357—362).—Thiobiazolone sulphides may be obtained simply by the action of potassium xanthate on the 2:4-dichlorophenylhydrazone of ethyl  $\alpha$ -chloroglyoxylate and analogous substances (cf. Bülow and Neber, A., 1913, i, 207, 999; 1916, i, 845).

The 2:4-dichlorophenylhydrazone of ethyl  $\alpha$ -chloroglyoxylate,  $C_6H_3Cl_2 \cdot NH \cdot N : CCl \cdot CO_2Et$ , is converted by potassium xanthate in warm alcoholic solution into *ethyl 5-thio-4-op-dichlorophenylthiobiazolone-2-carboxylate*,  $\begin{smallmatrix} N(C_6H_3Cl_2) \cdot CS \\ N = C(CO_2Et) \end{smallmatrix} \gg S$ , small, colourless

needles, m. p.  $122^\circ$ , which is transformed by an alcoholic solution of ammonia into the corresponding *amide*,  $C_9H_5ON_3S_2Cl_2$ , colourless needles, m. p.  $235^\circ$ ; the hydrolysis of the ester or amide to the acid could not be effected. A substance,  $C_{21}H_{16}O_4N_4Cl_4S_2$ , m. p.  $158-160^\circ$  or  $173^\circ$  (when crystallised from alcohol or acetic acid, respectively) is obtained as by-product of the preparation of the ester. The latter compound is converted by

prolonged treatment with an excess of hydrazine hydrate in boiling alcoholic solution into the *triazole* derivative,

$\begin{smallmatrix} N = CH \\ N(C_6H_3Cl_2) \cdot CS \end{smallmatrix} \gg N \cdot NH_2$ , colourless needles, m. p.  $153^\circ$ ; under somewhat different conditions, a *product*,  $C_9H_6ON_6Cl_2S$ , colourless needles, m. p.  $196-197^\circ$  (decomp.) after softening at  $191-192^\circ$ , is obtained, to which the annexed constitution is ascribed.

When acetone is used as solvent in place of alcohol, the action between potassium xanthate and the 2:4-dichlorophenylhydrazone of ethyl  $\alpha$ -chloroglyoxylate follows a different course and leads to the production of the *sulphide*,  $S[C(CO_2Et) \cdot N \cdot NH \cdot C_6H_3Cl_2]_2$ , hygroscopic crystals, m. p.  $175-176^\circ$ , which can also be obtained by the action of ammonium sulphide on the chloro ester.

2:4-Dichlorophenylhydrazonopyruvyl chloride does not appear

to be convertible by potassium xanthate into a thiobiazolone; it is transformed by potassium xanthate or colourless ammonium sulphide in the presence of acetone into the *sulphide*,



a yellow substance, m. p. 220—222° (decomp.) after becoming black at about 180°. H. W.

***o*-Hydroxyazoxy Compounds.** D. BIGIAVI and R. POGGI (*Gazzetta*, 1924, **54**, 114—131).—The authors have investigated the pairs of isomeric azoxy compounds obtained from benzeneazo-*p*-cresol and its derivatives when these are oxidised by means of peracetic acid. That *p*-hydroxyazo compounds exhibit the hydroxylic and not the quinonephenylhydrazonic structure was shown by McPherson (A., 1896, i, 27; 1900, i, 123) and by Willstätter and Veraguth (A., 1907, i, 453), who found that the acyl derivatives of benzeneazophenol are different from the compounds resulting from benzoquinone and the *as*-acylphenylhydrazines. For the corresponding ortho compounds no such difference has been encountered, and their tardy solubility in alkali, their failure to react with ammonia in an anhydrous solvent, and various other physico-chemical considerations incline certain authors (cf. Farmer and Hantzsch, A., 1900, i, 122; Puxeddu and Gennari, A., 1922, i, 587) to prefer the quinonoid to the hydroxyazoic structure for *o*-hydroxyazo derivatives.

The assumption of different constitutions for *o*- and *p*-hydroxyazo compounds seems, however, unwarranted, and, indeed, in many reactions benzeneazo-*p*-cresol behaves similarly to *p*-hydroxyazobenzene. Thus, its ready formation of two isomeric azoxy compounds is not easy to explain on the basis of the quinonoid structure. Moreover, the similarity is borne out by (1) the formation of unstable hydrazophenols when the *o*-hydroxyazo compounds are reduced by either aluminium amalgam in ethereal solution or zinc and ammonium chloride, (2) the formation, by the action of nitrous acid, of a nitro derivative containing the nitro group in the cresol nucleus, and the formation of bisbenzeneazo-*p*-cresol (cf. Puxeddu and Maccioni, A., 1907, i, 798) by the action of a normal diazotate.

The structures of the two benzeneazoxycresols are determined as follows. When treated with bromine, the one, m. p. 125°, yields a dibromo derivative with a bromine atom in each nucleus, since it gives *p*-bromoaniline and 3-bromo-6-amino-*p*-cresol on reduction; the other, m. p. 74°, gives a monobromo derivative and then a polybromo derivative which has bromine in only the cresol nucleus, as the only base volatile in a current of steam formed on reduction is aniline. It may be assumed, therefore, that the former isomeride contains the residue  $\text{NPh}_2$  and is the  $\beta$ -compound, and the latter,  $\text{O}:\text{NPh}_2$ , and is the  $\alpha$ -compound. The following observations, confirmatory of these conclusions, have been made.

Nitrous acid does not react with  $\beta$ -benzeneazoxycresol, but with the  $\alpha$ -isomeride readily forms a nitro derivative which has the

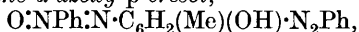
nitro group in the cresol nucleus and in the ortho-position towards the hydroxyl group, as it reacts with diazonium salts to form an azoazoxy derivative. Benzene- $\alpha$ -azoxycresol is readily oxidised by permanganate to isodiazobenzene and, probably, to *o*-nitrocresol; with the  $\beta$ -isomeride, the oxidation is extremely slow, although Bamberger gave this reaction as a means of recognising azoxyphenols. The pale yellow  $\alpha$ -compound changes moderately rapidly to chestnut-yellow under the influence of light, but the  $\beta$ -isomeride retains its colour almost unaltered. Etherification of the hydroxyl proceeds normally with the  $\alpha$ -, but with great difficulty with the  $\beta$ -form. The structure attributed by Baudisch (A., 1917, i, 356) to the  $\beta$ -*o*-hydroxyazoxybenzenes is regarded as unauthorised.

The *nitro* derivative of benzeneazocresol ( $\text{N}_2 : \text{OH} : \text{NO}_2 : \text{Me} = 1 : 2 : 3 : 5$ ) crystallises in dark red, lustrous, plush-like needles, m. p.  $130^\circ$ , and is oxidised with difficulty by peracetic acid, yielding a mixture, m. p.  $110^\circ$ , of the two nitroazoxy compounds.

*Benzene- $\alpha$ -azoxycresol*,  $\text{O}:\text{NPh}:\text{N}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$ , forms transparent, orange prisms, m. p.  $73\text{--}74^\circ$ , and gives a deep, blood-red coloration with concentrated sulphuric acid. Its *acetyl* derivative separates in yellow needles or transparent, prismatic crystals, m. p.  $78\text{--}79^\circ$ , and yields acetylhydrazocresol when reduced by means of aluminium amalgam in ethereal solution. Its *benzoyl* derivative forms pale yellow prisms, m. p.  $97\text{--}101^\circ$ .

*Benzene- $\alpha$ -azoxy-m-nitro-p-cresol*,  $\text{O}:\text{NPh}:\text{N}\cdot\text{C}_6\text{H}_2(\text{Me})(\text{OH})\text{NO}_2$ , crystallises in yellow, silky needles, m. p.  $121\text{--}122^\circ$ , and dissolves in alkali hydroxide or carbonate solution to a blood-red solution.

*Benzeneazobenzene- $\alpha$ -azoxy-p-cresol*,



forms long, silky needles, m. p.  $148\text{--}149^\circ$ , which are almost black when moistened with benzene, but brilliant chestnut-yellow when dry. With concentrated sulphuric acid, it gives a reddish-brown coloration, and with sodium hydroxide solution containing a few drops of alcohol an intense violet coloration turning to reddish-violet when the liquid is diluted.

*Benzene- $\alpha$ -azoxy-m-bromo-p-cresol* crystallises in lustrous, sulphur-yellow needles, m. p.  $143\text{--}144^\circ$ , and dissolves in sodium hydroxide solution to a bright red solution. When brominated further, it yields the *polybromo* derivative,  $\text{C}_{13}\text{H}_7\text{O}_2\text{N}_2\text{Br}_5$ , which crystallises in silky, yellow needles, m. p.  $164\text{--}165^\circ$ .

*Benzene- $\beta$ -azoxycresol*,  $\text{NPh}:\text{NO}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$ , crystallises in lustrous, yellow needles, m. p.  $70\text{--}72^\circ$ ; its yellow *benzoyl* derivative has m. p. about  $56^\circ$ , and its *acetyl* derivative was obtained only as a dense, non-crystallising oil.

*Benzene- $\beta$ -azoxy-nitrocresol*,  $\text{NPh}:\text{NO}\cdot\text{C}_6\text{H}_2\text{Me}(\text{OH})\cdot\text{NO}_2$ , forms yellow, acicular prisms, m. p.  $117\text{--}119^\circ$ , and yields aniline when reduced with tin and hydrochloric acid.

*Benzene- $\beta$ -azoxybromocresol*,  $\text{NPh}:\text{NO}\cdot\text{C}_6\text{H}_2\text{MeBr}\cdot\text{OH}$ , forms chestnut-yellow, silky needles, m. p.  $117^\circ$ .

*p-Bromobenzene- $\beta$ -azoxybromocresol*,  $\text{C}_6\text{H}_4\text{Br}:\text{N}:\text{NO}\cdot\text{C}_6\text{H}_2\text{MeBr}\cdot\text{OH}$ , crystallises in golden-yellow, silky needles, m. p.  $166\text{--}167^\circ$ , is turned scarlet and dissolved by alkali hydroxide solution, and

yields bromoaniline and bromoaminocresol (cf. Thiele and Eichwede, A., 1900, i, 501) on reduction.

T. H. P.

**NN'-Dimethylenesulphurous Acid-3:3'-diamino-4:4'-dihydroxyazobenzene.** W. G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1924, **46**, 497—503).—NN'-Dimethylenesulphurous acid-3:3'-diamino-4:4'-dihydroxyazobenzene,  $C_{14}H_{16}O_8N_4S_2$ , was isolated by the addition of formaldehyde and sodium bisulphite to the solution of the dihydrochloride of the 3:3'-diamino-4:4'-dihydroxyazobenzene prepared by the reduction of the corresponding nitro compound in an atmosphere of carbon dioxide. The sodium, magnesium, and barium salts are described. Contrary to expectations, the substance was physiologically inactive.

A. B. S.

**Absorption Spectra of certain Derivatives of *p*-Cymene.** W. C. HOLMES (*J. Amer. Chem. Soc.*, 1924, **46**, 631—635).—The general effect of introducing methyl and isopropyl groups into a number of azo dyes of the benzene series is to shift the absorption band towards a region of longer wave-length, the displacement of the maximum being about 10  $\mu\mu$ .

Introduction of the isopropyl group into Victoria green (malachite green) in the non-aminated nucleus in the *p*-position to the methane carbon atom produces a converging displacement of the two absorption bands in the visible spectrum. Both bands gradually disappear in sulphuric acid solution, and give rise to a new band, that of the di-acid salt, in the same spectral region as the second band of the neutral solution. The absorption bands of phenol-sulphonaphthalein and the homologue containing the isopropyl group in the sulphonated residue are practically identical, and absorption measurements in buffered solutions show that as  $p_H$  is lowered the transition between the absorption forms characteristic of alkaline and neutral solutions occurs more rapidly with the higher homologue than with the parent substance.

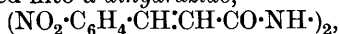
S. K. T.

**Azo Dyes from *m*-Methylethylbenzene.** A. MAILHE (*Bull. Soc. chim.*, 1924, **35**, 382—383).—The following dyes have been prepared from 6-amino-1-methyl-3-ethylbenzene (cf. A., 1921, i, 661): 2-methyl-4-ethyl-4'-hydroxyazobenzene, a brown powder; 1-methyl-3-ethylbenzene-6-azo- $\beta$ -naphthol, a red powder; 1-methyl-3-ethylbenzene-6-azo- $\beta$ -naphthylamine, a maroon powder; 1-methyl-3-ethylbenzene-6-azo- $\alpha$ -naphthylamine, a greenish mass; 1-methyl-3-ethylbenzene-6-azodimethylaniline, a brown powder; from Schäffer salt, 1-methyl-3-ethylbenzene-6-azo- $\beta$ -naphthol-6-sulphonic acid, dark brown, dyeing maroon on silk; from R-salt, 1-methyl-3-ethylbenzene-6-azo- $\beta$ -naphthol-3:6-disulphonic acid, a red powder, dyeing silk a fast ponceau; from crocein acid, 1-methyl-3-ethylbenzene-6-azo- $\beta$ -naphthol-8-sulphonic acid, a maroon powder, giving maroon shades on silk. From G-salt, 1-methyl-3-ethylbenzene-6-azo- $\beta$ -naphthol-6:8-disulphonic acid, dark yellow powder, dyeing maroon shades on silk; and from H-acid, 1-methyl-3-ethylbenzene-6-azo-8-amino- $\alpha$ -naphthol-3:5-disulphonic acid, reddish-scarlet, giving fast reddish-ponceau shades on silk.

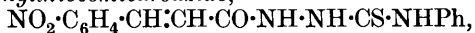
R. B.

**Colour and Constitution. I. Effect of Isomerism on the Colour of certain Azo Dyes.** M. L. CROSSLEY and P. V. RESENVELT (*Ind. Eng. Chem.*, 1924, **16**, 271—273).—Sodium benzeneazo- $\beta$ -naphthol-6-sulphonate is a reddish-orange dye. If the sulphonic group passes to positions 7 and 8, the colour becomes progressively more yellow. The 3:6-disulphonic acid salt is more red, the 6:8-disulphonic acid salt more yellow than any of the mono-sulphonates. Further systematic colour modifications are caused by substitution within the benzene ring. There is also a great difference between the reactivities of the two  $\beta$ -naphtholdisulphonic acids, the presence of the sulphonic group in position 8 appearing to reduce the reactivity of the hydrogen in position 1, by neutralising the effect of the adjacent hydroxyl group. These facts are discussed in terms of the "force-field" and additive theories of chemical reactions. The relation between the effect on colour and the effect on reactivity of the position of the sulphonic group is held to be significant. [Cf. *B.*, 1924, 368.] C. I.

***m*-Nitrocinnamic Acid Hydrazide and its Behaviour with Nitrous Acid.** T. CURTIUS and P. A. BLEICHER (*J. pr. Chem.*, 1924, [ii], **107**, 86—98; cf. *A.*, 1909, i, 838; 1911, i, 682, 814).—The action of hydrazine hydrate on ethyl *m*-nitrocinnamate gives, in addition to the main product of the reaction, *m*-nitrocinnamic acid hydrazide,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$  (bright yellow, anisotropic plates, m. p. 139°), an isomeric substance, bright yellow needles, m. p. 198°, which with nitrous acid yields a true azide (see following abstract). *m*-Nitrocinnamic acid hydrazide when treated with iodine and sodium hydrogen carbonate in alcoholic solution is converted into a dihydrazide,



pale yellow, prismatic needles, m. p. 279° (decomp.). The hydrochloride, tablets, m. p. 212° (decomp.), with benzaldehyde gives benzylidene-*m*-nitrocinnamic acid hydrazide, minute needles, m. p. 206.5°, whilst benzoyl chloride yields benzoyl-*m*-nitrocinnamic acid hydrazide,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHBz}$ , prisms, m. p. 185.5°. With ethyl acetoacetate, *m*-nitrocinnamic acid hydrazide yields the compound,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CO}_2\text{Et}$ , white, fibrous needles, m. p. 67.5°, and with phenylthiocarbimide *m*-nitrocinnamylphenylthiosemicarbazide,



pale yellow plates, m. p. 147°. Sodium nitrite readily converts the hydrochloride into 1-nitroso-5-*m*-nitrophenyl-3-pyrazolidine, yellow, prismatic plates, m. p. 108° (ammonium, silver, and barium salts described). The silver salt on treatment with ethereal ethyl iodide gives 1-nitroso-2-ethyl-5-*m*-nitrophenyl-3-pyrazolidine, greyish plates, m. p. 168°. The ammonium salt of 1-nitroso-5-*m*-nitrophenyl-3-pyrazolidine gives a picrate, m. p. 107—108°. The action of bromine on 1-nitroso-5-*m*-nitrophenyl-3-pyrazolidine in acetic acid solution gives 4-bromo-3-*m*-nitrophenyl-5-pyrazoline, yellow plates, m. p. 188°, only one bromine atom entering the ring, whereas the action of bromine on 1-nitroso-5-phenyl-3-pyrazolidine

gives 4:4-dibromo-3-phenyl-5-pyrazolone. On boiling with dilute sulphuric acid, the 1-nitroso-5-*m*-nitrophenyl-3-pyrazolidine is converted into 3-*m*-nitrophenyl-4-isonitroso-5-pyrazoline, orange, silky needles, m. p. 217°.

The isomeric *m*-nitrocinnamic acid hydrazide, of m. p. 198°, gives a *benzylidene* derivative, m. p. 184°, and a *hydrochloride*, m. p. 256° (decomp.). R. B.

***m*-Nitrocinnamic Acid Azide.** T. CURTIUS and E. KENNGOTT (*J. pr. Chem.*, 1924, [ii], 107, 99—102).—The isomeric *m*-nitrocinnamic acid hydrazide of m. p. 198° formed as a by-product in the action of hydrazine hydrate on *m*-nitrocinnamic ester (see preceding abstract) on treatment with nitrous acid gives *m*-nitrocinnamic acid azide,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{N}_3$ , colourless, rhombic crystals (m. p. 117—118°, with evolution of gas), which are converted into *m*-nitrocinnamic acid when warmed with alkali. When warmed with *p*-toluidine in alcoholic solution, the azide gives *p*-tolyl *m*-nitrostyrylcarbamide,

$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{HN}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$ ,  
bright yellow needles, m. p. 213—214°. Boiling with water converts the azide into nitrogen, carbon dioxide, and a colourless carbamide (?), m. p. 186°. Boiling with methyl alcohol gives the known methyl *m*-nitrostyrylcarbamate,

$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{NH}\cdot\text{CO}\cdot\text{OMe}$ ,  
yellow needles, m. p. 140°, which when boiled with dilute sulphuric acid give *m*-nitrophenylacetaldehyde. The interconversion of *m*-nitrocinnamic acid hydrazide, m. p. 139°, and the isomeric compound, m. p. 198°, can be effected either by heating above the melting point or by warming in alcoholic solution or under pressure. R. B.

**Salts with *para*-, *ortho*-, and *meta*-Quinonoid Structure.**  
V. R. CIUSA and G. RASTELLI (*Gazzetta*, 1924, 54, 72—78; cf. A., 1922, i, 1073).—*p*-Nitrophenylmethylhydrazones,

$\text{CHR}:\text{N}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ ,  
of the following aldehydes have been prepared: *Formaldehyde*, dark yellow crystals, m. p. 153°, separating even from solutions containing the aldehyde in the proportion 1:10,000; *acetaldehyde*, yellow needles, m. p. 91°; *butyraldehyde*, yellow crystals, m. p. 05° (?); *p*-tolualdehyde, yellow, tabular crystals, m. p. 150°; *o*-nitrobenzaldehyde, orange-yellow, acicular crystals, m. p. 211—212°; *m*-nitrobenzaldehyde, lemon-yellow crystals, m. p. 250°; *p*-nitrobenzaldehyde, orange-yellow crystals, m. p. 249—250°; *cumin-aldehyde*, yellow crystals with violet reflection, m. p. 112°; *dimethylaminobenzaldehyde*, bright red needles, m. p. 193°; *cinnamaldehyde*, dark yellow needles, m. p. 153—154°; *salicylaldehyde*, dark yellow needles, m. p. 150°; *p*-hydroxybenzaldehyde, red crystals, m. p. 204°; *anisaldehyde*, small, yellow crystals, m. p. 155—156°; *protocatechualdehyde*, bright red crystals, m. p. 218°; *vanillin*, m. p. 182°, existing in yellow and red chromoisomeric modifications; *piperonaldehyde*, yellow crystals, m. p. 190—191°; 2:4-dihydroxybenzaldehyde, deep red crystals, m. p. 265°; 2-hydroxy-4-methoxy-

*benzaldehyde*, lustrous, yellow needles, m. p.  $148^{\circ}$ , existing also in a red modification; *furfuraldehyde*, orange-yellow, crystalline plates, m. p.  $171^{\circ}$ ; *pyrrolealdehyde*, bright red, acicular crystals, m. p.  $177^{\circ}$ ; *acetone*, silky, yellow needles, m. p.  $54^{\circ}$ ; *cyclohexanone*, yellow crystals, m. p.  $186^{\circ}$ . The *mono-p-nitrophenylmethylhydrazone* of *diacetyl* forms brownish-yellow needles, m. p.  $154^{\circ}$ , that of *acetylacetone*, lustrous, orange needles, m. p.  $128^{\circ}$ , and that of *acetonylacetone*, yellow needles, m. p.  $130^{\circ}$ .

*Benzaldehyde-p-nitrophenylethylhydrazone*,  
 $\text{CHPh}\cdot\text{N}\cdot\text{NEt}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ ,

obtained by the action of ethyl iodide on the potassium salt of *benzaldehyde-p-nitrophenylhydrazone*, forms large, yellow crystals, m. p.  $134^{\circ}$ . When boiled with hydrochloric acid it yields *as-p-nitrophenylethylhydrazine*,  $\text{NH}_2\cdot\text{NEt}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , which crystallises in lustrous, yellow leaflets, m. p.  $74^{\circ}$ , and energetically reduces Fehling's and ammoniacal silver solutions. *p-Nitrobenzaldehyde-p-nitrophenylethylhydrazone* crystallises in yellow needles, m. p.  $267^{\circ}$ .

*Benzaldehyde-p-nitrophenylbenzylhydrazone*,  $\text{C}_{20}\text{H}_{17}\text{O}_2\text{N}_3$ , prepared from benzyl chloride and the potassium derivative of *benzaldehyde-p-nitrophenylhydrazone*, forms lustrous, yellow, laminar crystals, m. p.  $158^{\circ}$ , and *as-p-nitrophenylbenzylhydrazine*,  $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}_3$ , which reduces Fehling's solution and ammoniacal silver solution, yellow needles, m. p.  $121^{\circ}$ .

T. H. P.

[**Aromatic Arsenious Acids.**] A. ALBERT (U.S. Pat. 1472778).—Nitroaminohydroxyacetophenone, when diazotised and treated in alkaline solution with sodium arsenite, yields nitrohydroxyacetylphenylarsinic acid,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)\cdot\text{AsO}_3\text{H}_2$ , needles, m. p. about  $200^{\circ}$ . Similarly, *p*-aminobenzophenone yields benzoylphenylarsinic acid, m. p.  $195$ — $197^{\circ}$ , diaminobenzophenone yields the diarsinic acid compound, m. p.  $260^{\circ}$ , and *p*-aminobenzaldehyde yields *p*-aldehydophenylarsinic acid.

CHEMICAL ABSTRACTS.

**Tin Dicyclohexyl, Hexacyclohexyldistannane, and other cycloHexyl Compounds of Tin.** E. KRAUSE and R. POHLAND (*Ber.*, 1924, **57**, [B], 532—544).—An extension of the work on the organo-metallic derivatives of tin (Krause and Becker, A., 1920, i, 340) to the *cyclohexyl* series. The *cyclohexyl* bromide used had b. p.  $52.5^{\circ}/13.5$  mm.,  $d_4^{16.8}$  (vac.) 1.3348,  $n_D^{16.8}$  1.49758, whereas *cyclohexyl* chloride had b. p.  $141^{\circ}/760$  mm.,  $d_4^{20.3}$  1.0000,  $n_D^{20.3}$  1.46264.

Tin tetracyclohexyl,  $\text{Sn}(\text{C}_6\text{H}_{11})_4$  (cf. Grüttner, A., 1915, i, 335) is prepared by the gradual addition of a solution of stannic chloride in benzene to a solution of magnesium *cyclohexyl* bromide or chloride in a mixture of ether and benzene. The product is a mixture of tin tetracyclohexyl, hexacyclohexyldistannane, and halogenated substances which cannot be separated into its components by crystallisation except with great loss of material; it is therefore converted into the monobromide (see later), which is readily purified and subsequently transformed by magnesium *cyclohexyl* bromide into the tetra derivative, which crystallises in



colourless, quadratic platelets, m. p. 263—264° after slight previous softening (Grüttner gives m. p. 248°).

*Tin dicyclohexyl*,  $\text{Sn}(\text{C}_6\text{H}_{11})_2$ , prepared from stannous chloride and magnesium *cyclohexyl* bromide, is an intensely yellow, voluminous powder, melting to a red liquid at 176—178° after darkening at 130°. It is stable in an atmosphere of nitrogen, but gradually oxidises in air, particularly under the influence of light. It is converted by *cyclohexyl* bromide at 140° into tin *dicyclohexyl* dibromide. Attempts to convert it into hexacyclohexyldistannane by means of magnesium *cyclohexyl* bromide (cf. A., 1920, i, 341) were unsuccessful.

*Hexacyclohexyldistannane*,  $(\text{C}_6\text{H}_{11})_3\text{Sn}\cdot\text{Sn}(\text{C}_6\text{H}_{11})_3$ , is prepared by the action of sodium on a solution of tin *tricyclohexyl* bromide in boiling xylene. It forms colourless, hexagonal platelets, stable towards light and air, decomp. slightly above 300°. Its molecular weight in concentrated solution corresponds with the formula  $[\text{Sn}(\text{C}_6\text{H}_{11})_3]_2$ , whereas the simpler molecular form appears to be present in more dilute solution.

*Tin tricyclohexyl bromide*,  $(\text{C}_6\text{H}_{11})_3\text{SnBr}$ , prepared from the crude product of the action of magnesium *cyclohexyl* halide on stannic chloride (see above) by means of bromine in the presence of chloroform or carbon tetrachloride, crystallises in long, colourless prisms, m. p. 77°, decomp. about 280°. The corresponding *iodide* forms colourless, hexagonal plates, m. p. 65°, decomp. about 290°. The *fluoride* forms hexagonal prisms, decomp. about 305°. *Tin tricyclohexyl hydroxide*, colourless, hexagonal crystals, m. p. 220—222°, is prepared by shaking an ethereal solution of the bromide with an excess of potassium hydroxide solution (15%); when dehydrated, it yields the oxide,  $(\text{C}_6\text{H}_{11})_3\text{Sn}\cdot\text{O}\cdot\text{Sn}(\text{C}_6\text{H}_{11})_3$ . (Tin triphenyl hydroxide, long, hexagonal prisms, m. p. 119—120°, appears to be dehydrated similarly to the *oxide*,  $\text{Ph}_3\text{Sn}\cdot\text{O}\cdot\text{SnPh}_3$ ; there is no evidence of the formation of different hydrates.) *Tin tricyclohexyl chloride*, obtained from the hydroxide and dilute hydrochloric acid, forms long, prismatic rodlets, m. p. 129—130°, decomp. about 286°; with ammonia it appears to yield the *compound*,  $(\text{C}_6\text{H}_{11})_3\text{SnCl}\cdot 2\text{NH}_3$ , m. p. 128° (decomp.).

Tin *dicyclohexyl* dibromide, m. p. 58° (cf. Grüttner, *loc. cit.*), is hydrolysed to the corresponding *dihydroxide* (or *oxide*), a colourless, amorphous powder, m. p. 291° (decomp.) after darkening at 280° and softening at 287°. The corresponding *dichloride*, colourless, asbestos-like needles, m. p. 88—89°, decomp. about 220°, the *difluoride*, a colourless, microcrystalline powder, m. p. 278° after previous softening, and the di-iodide, a colourless, crystalline powder, m. p. 42° (Grüttner, *loc. cit.*, gives m. p. 145°), are described.

The following compounds are prepared by the action of a large excess of the requisite Grignard compound on tin *tricyclohexyl* bromide in ethereal solution: *Tin tricyclohexylmethyl*,  $(\text{C}_6\text{H}_{11})_3\text{SnMe}$ , a colourless, viscous liquid, b. p. 221°/15 mm.,  $d_4^{20.7}$  (vac.) 1.1949,  $n_D^{15.7}$  1.53979. *Tin tricyclohexylethyl*, a very viscous liquid, b. p. 227—228°/15 mm. (partial decomp.),  $d_4^{15.9}$  (vac.) 1.1875,  $n_D^{15.9}$  1.53953. *Tin phenyltricyclohexyl*, colourless, microscopic crystals, m. p. 191—

192°; 0.65 g. dissolves in 100 g. of ethyl alcohol at 30.4°. *Tin p-tolyltricyclohexyl*, prismatic rodlets, m. p. 111°, which dissolves in ethyl alcohol to the extent of 0.70 g. in 100 g. at 30.4°. *Tin triphenylcyclohexyl*, colourless needles, m. p. 131—132°, is obtained from tin triphenyl chloride and magnesium *cyclohexyl* bromide.

H. W.

**Peptisation of Gelatin by Mixed Liquids.** E. W. J. MARDLES (*Biochem. J.*, 1924, **18**, 215—230).—The peptisation of gelatin in mixtures of various solvents has been studied. The solubility of gelatin is greater in mixed liquids than the average value, and under some conditions the solvent power of water can be increased, or not appreciably diminished, by the addition of a non-solvent such as pyridine, glycerol, alcohol, etc. The theory of this phenomenon is discussed.

S. S. Z.

**Constitution of Proteins.** N. TROENSEGAARD and I. SCHMIDT (*Z. physiol. Chem.*, 1924, **133**, 116—125).—The authors bring forward evidence which they claim lends further support to the view that the protein molecule consists mostly of pyrrole derivatives containing oxygen. Acetylated gliadin, gelatin, and proteolic acid from gliadin were degraded by reduction into various fractions which showed properties characteristic of heterocyclic compounds.

S. S. Z.

**Proteins of Oats.** H. LÜERS and M. SIEGERT.—(See i, 597.)

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## Biochemistry.

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**Influence of Intravenous Injection of Protein on the Respiratory Exchange.** E. AMSTAD (*Biochem. Z.*, 1924, 145, 168—177).—In dogs, the average normal output of carbon dioxide per kilogram per minute is 9·5585 c.c. and the oxygen intake is 12·94 c.c. Intravenous injection of Ringer solution has a very slight effect in increasing the respiratory exchange; injection of foreign serum (horse) protein first lowers the exchange by 30% of its normal value, but later it rises above normal to the same extent, whilst injection of the serum-proteins of the dog itself produces the same effect as Ringer solution. J. P.

**Physiology of Glands. LVIII. Possible Presence of Toxic Substances in the Sera of Thyroid- and Parathyroid-ectomised Animals in Relation to the Respiratory Exchange.** L. ASHER and K. JINO (*Biochem. Z.*, 1924, 145, 105—115).—Intraperitoneal injection into rats of 1 to 2 c.c. of the sera of normal or thyroidectomised dogs increases the respiratory exchange, whilst sera from parathyroidectomised dogs with tetany lowers the respiratory exchange. It is concluded that whilst toxic substances are absent in the former case they may be present in the latter. J. P.

**Physiology of Glands. LX. Respiratory Exchange of Normal and Splenectomised Rats.** L. ASHER and Y. TAKAHASHI (*Biochem. Z.*, 1924, **145**, 130—153).—In general, removal of the spleen from rats diminishes the respiratory exchange, and increases the nitrogen excretion and the response to thyroid feeding as compared with the normal animals. The presence or absence of iron in the dietary has no influence on the respiratory exchange effect. Rats from which the spleen has been removed show a greater susceptibility to lack of oxygen than that shown by normal rats. The results are interpreted in favour of the view that the spleen and the thyroid are mutually antagonistic. J. P.

**Physiology of Glands. LXI. Comparison of the Oxygen Consumption of Surviving Excised Mammalian Organs in the Normal Condition and after Thyroid Feeding.** L. ASHER and A. ROHRER (*Biochem. Z.*, 1924, **145**, 154—167).—The isolated surviving liver, kidney, and muscle of mice which had been fed on thyroid consumed more oxygen than the same organs from normal animals. The respective figures found for 1 g. of each tissue per hour are : 639 and 784 c.mm., 818 and 941 c.mm., 791 and 985 c.mm. J. P.

**Collection and Preservation of Blood Samples for Determination of Carbon Monoxide.** R. R. SAYERS, H. R. O'BRIEN, G. W. JONES, and W. P. YANT (*U.S. Public Health Repts.*, 1923, 2005—2011. Reprint No. 863).—A modified Keidel tube method is described for the collection, transport, and storage of samples of 10—15 c.c. of blood in cases of carbon monoxide poisoning. A small vial, well-stoppered with a cork, will serve satisfactorily in emergency. For the inhibition of coagulation, sodium citrate (0.4 to 0.8 %) proved inefficient, sodium or potassium oxalate (0.2%) caused some change in the blood with a slight alteration in the carbon monoxide content, whilst sodium fluoride (0.3%) is recommended as being free from these objections. E. M. C.

**Elimination of Carbon Monoxide from Blood by Treatment with Air, with Oxygen, and with a Mixture of Carbon Dioxide and Oxygen.** R. R. SAYERS and W. P. YANT (*U.S. Public Health Repts.*, 1923, 2053—2074. Reprint No. 865).—Analyses of blood samples, made in carefully controlled experiments on three subjects, showed that the elimination of carbon monoxide depends on the percentage of oxygen in the air breathed and also on the rate and depth of respiration. Pure oxygen was about four times as efficient as ordinary air, whilst a mixture of oxygen containing 8 to 10% of carbon dioxide was about five to six times as efficient. E. M. C.

**Seasonal Changes in the Gases and Sugar of the Blood, and the Nitrogen Distribution in the Blood and Urine of the Alligator.** A. HOPPING (*Amer. J. Physiol.*, 1923, **66**, 145—163).—The oxygen capacity of the blood is highest (15.3) in March, and lowest (9.5) in May and June; the oxygen content of the venous

blood is lowest (1.8) in May and June and highest (11.0) in January and February. The carbon dioxide capacity and content are higher in spring than in summer or winter. Blood-sugar is high (0.095%) in spring and very low (0.0296%) in late autumn. The main nitrogenous constituent of the urine is ammonia; uric acid is present in the blood and urine in small amounts only.

CHEMICAL ABSTRACTS.

**Influence of Oxygen Content on the Hydrogen-ion Concentration of the Blood.** J. HOLLÓ and S. WEISS (*Biochem. Z.*, 1924, **145**, 10—13).—The  $p_H$  of human oxalated venous blood kept at a constant carbon dioxide content and oxygenated, is lowered by 0.03—0.06. J. P.

**Experimental Tetany. III. Alkalosis and Acidosis. IV. Hydrogen-ion Concentration of the Blood. V. Alveolar Carbon Dioxide Tension.** E. W. H. CRUICKSHANK (*Biochem. J.*, 1924, **18**, 47—62).—A change in the acid-base balance in parathyroid tetany, with the production of a condition of alkalosis, is observed in the primary or quiescent stage and is due to  $CO_2$  deficit. With the development of acute tetany, this condition is changed into one of acidosis by the continuous loss of  $BHCO_3$  and increase in  $H_2CO_3$ . The reaction of the blood as determined from  $CO_2$  dissociation curves changes very slightly, the  $p_H$  increasing above normal for the animal by an average of 0.154 during the stage of alkalosis and falling with the introduction of the stage of acidosis. The alveolar  $CO_2$  may fall as low as 1.975%, but with the continued loss of base there is a tendency for it to return towards the normal. S. S. Z.

**Chemical Pathology of Pyloric Occlusion in Relation to Tetany. Chloride, Carbon Dioxide, and Urea Concentrations in the Blood.** H. A. MURRAY, jun. (*Arch. Surgery*, 1923, **7**, 166—196).—With stenosis of the pylorus, hydrogen chloride cannot pass into the intestines and be absorbed. It is expelled by vomiting or by gastric lavage. The result is a disturbance in the acid-base balance of the blood and tissues. The blood shows increased carbon dioxide and urea, and decreased chlorine. The most abnormal values found were:  $CO_2$ , 107% by vol.; Cl, 2.5 g. per l., and urea, 334 mg. per 100 c.c. of blood. There is a relation between these changes and the tetany which develops in severe cases. It is highly probable that nerve irritation is increased by a fall in the hydrogen-ion concentration of the blood or the sodium : calcium ratio.

CHEMICAL ABSTRACTS.

**Nature of the Red Blood-corpuscle.** A. GOUGH (*Biochem. J.*, 1924, **18**, 202—214).—The red corpuscle is a fluid droplet the contents of which form a hydrophile colloidal system. The continuous phase (salts and water) constitutes one-third, the dispersed phase (haemoglobin salts and water) two-thirds of this system. The surface film contains lipoids in a solid state, and all varieties of haemolysis can be explained as due to disintegration of the envelope of the corpuscle. Crenation is due to protrusion through weak areas

in the envelope of the corpuscle. The characteristic shape of the corpuscle is due to tension of liquid surfaces tending to cause a spherical shape and to the repulsive forces between the dispersed particles of the corpuscular contents. S. S. Z.

**Adsorption of Protein Degradation Products by Erythrocytes.** N. GRIASNOV (*Biochem. Z.*, 1924, **145**, 63—65).—Contrary to the results of Sbarsky (A., 1923, i, 1252), biological methods of determining fixation reveal no adsorption of diphtheria toxin by erythrocytes *in vitro*. The disappearance of nitrite observed by Sbarsky and attributed by him to adsorption of protein degradation products is ascribed to oxidation by oxyhæmoglobin derived from hæmolyzed erythrocytes. J. P.

**Hæmoglobin and Methæmoglobin as Oxidative Catalysts.** M. E. ROBINSON.—(See this vol., ii, 320.)

**Lævulose in the Blood of the Human Fœtus.** A. P. ORR (*Biochem. J.*, 1924, **18**, 171—172).—Human fœtal blood gives the Selivanov reaction, which shows the presence of lævulose. This sugar can also be demonstrated in the blood of the kid immediately after birth. S. S. Z.

**Syphilis. V.—VIII. Arsenic Content of the Blood and Spinal Fluid after Neosalvarsan and Salvarsan Treatment.** J. A. FORDYCE, I. ROSEN, and C. N. MYERS (*Amer. J. Syphilis*, 1923, **7**, 444—559).—With neosalvarsan, arsenic was found, in quantities of 0.6—83.6 mg. per 100 g. of dried spinal fluid, at some time during the treatment in 22% of the cases; with salvarsan, after combined intravenous and intraspinal injections, arsenic was present in 88% of the fluids up to 73 mg., whereas after injection and drainage, arsenic was present up to 54.3 mg. in 83% of the specimens. The maximum amount of arsenic is present in the blood immediately after intravenous injection of silver salvarsan, but it quickly becomes localised outside of the circulating blood.

#### CHEMICAL ABSTRACTS.

**Hydrogen-ion Concentration of Gastric Contents of Infants.** F. L. BABBOTT, jun., J. A. JOHNSTON, C. A. HASKINS, and A. T. SHOHL (*Amer. J. Diseases Children*, 1923, **26**, 475—485).—The normal range of the  $p_H$  of the gastric contents on the milk test meal at the end of an hour is  $p_H$  3.2—5.0, with 76% of the readings between  $p_H$  3.9 and  $p_H$  4.6. The error of determining acidity of gastric contents from samples rather than from the entire contents is  $p_H$  0.4. The acidity increases with increase in time. The previous type of feeding has no effect on the test meal. Acid production and hydrogen-ion concentration increase with increase of age. A fourfold increase of the concentration of the test meal decreases the hydrogen-ion concentration. A twofold increase of the amount of the test meal causes a stimulation of acid secretion, but a lessened acidity. The greater the gastric acidity, the more rapidly the stomach empties.

#### CHEMICAL ABSTRACTS.

**Metabolism of Carbohydrates. III. Absorption of Glucose, Fructose, and Galactose from the Small Intestine.** J. A. HEWETT (*Biochem. J.*, 1924, **18**, 161—170).—Glucose, fructose, and galactose are absorbed from hypotonic solution from the small intestine, the rates of absorption decreasing in the order named. However, when the epithelial lining is destroyed, all three sugars are absorbed at the same rate. The results cannot be explained by osmosis or diffusion only. S. S. Z.

**Production of Hypoglycæmia in Experimental Derangements of the Liver.** M. BODANSKY (*Amer. J. Physiol.*, 1923, **66**, 375—379).—Hyperglycæmia is the initial effect of severe liver damage (severe chloroform or phosphorus poisoning). Subsequently this effect disappears and the blood-sugar falls to subnormal levels. Chloroform and phosphorus are general protoplasmic poisons, and death resulting from such acute poisoning is not due entirely to functional damage of the liver. CHEMICAL ABSTRACTS.

**Physiology of Glands. LIX. Influence of Compensation on the Glycosuric Action of Subcutaneous Adrenaline Injections.** L. ASHER and R. TSUKAMOTO (*Biochem. Z.*, 1924, **145**, 116—129).—The adrenaline glycosuria of thyroid-fed dogs which react strongly to the treatment, is, in some cases, more rapid but less intense than that of normal animals, but in others the glycosuria may be more intense than that of the normals. The results are explained on the basis of a double functioning of the thyroid hormone. Removal of blood or transfusion of a Ringer gelatin solution after bleeding produces a diminution in the response to adrenaline. J. P.

**Preparation of Insulin. Alkaline Extraction of Pancreas.** H. W. DUDLEY and W. W. STARLING (*Biochem. J.*, 1924, **18**, 147—150).—By the addition of sodium bicarbonate to the mixture of minced pancreas and alcohol the yield of insulin is increased nearly fivefold. An improved technique for the preparation of insulin hydrochloride through the picrate is also described, whereby at least 90% of the impurities in crude insulin can be removed. 0.2 Mg. of this preparation was found to be a "rabbit unit." S. S. Z.

**Mode of Oxidation of Fatty Acids with Branched Chains. III. The Fate in the Body of  $\alpha$ -Methylcinnamic Acid,  $\beta$ -Phenylisobutyric Acid, and  $\gamma$ -Phenylisovaleric Acid.** H. D. KAY and H. S. RAPER (*Biochem. J.*, 1924, **18**, 153—160).— $\beta$ -Phenylisobutyric acid on oxidation in the body yields benzoic acid. The yield was 77% of the theoretical, assuming that  $\beta$ -oxidation alone had taken place.  $\alpha$ -Methylcinnamic acid, which has been isolated as an intermediate product, also yields benzoic acid, but only to the extent of 33% of the amount expected if  $\beta$ -oxidation alone had taken place. No intermediate product could be isolated in this case. No difference was observed in the ease of oxidation in the body of the two isomorphous forms of  $\alpha$ -methylcinnamic acid.  $\gamma$ -Phenylisovaleric acid gives rise to phenylacetic acid on oxidation

in the body; the yield was not more than 50% of the amount expected if  $\beta$ -oxidation alone had taken place. S. S. Z.

**Odd-carbon Fats in the Treatment of Diabetic Ketosis.** M. KAHN (*Amer. J. Med. Sci.*, 1923, **166**, 826—833).—An odd-carbon fatty acid has been synthesised (the acid group of stearic acid is replaced by an organic radical and on oxidation the  $C_{17}$  acid is produced, which is united with glycerol) which is absorbed to about 90% and is catabolised without the production of ketones.

CHEMICAL ABSTRACTS.

**Metabolism of Milch Cows suffering from Acetonæmia.** B. SJOLLEMA and J. E. VAN DER ZANDE (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 666—668).—Analyses of blood, urine, and milk from cows suffering from acetonæmia show that waste of body fat takes place on a large scale, often about 1 kg. per diem. Lipæmia, glucosuria, and hyperglycæmia do not occur. The total quantity of acetone compounds in the urine may amount to about 120 g. per day. The cholesterol content of the blood is 50% to 100% higher than normal; sometimes it is even higher. The alkali reserve decreases. J. F. S.

**Possibility of Influencing Decomposition of Albumin in the Body by Feeding Individual Amino-acids.** R. W. SEUFERT (*Z. Biol.*, 1924, **80**, 381—404).—Experiments on dogs receiving a diet containing insufficient protein show that whilst the feeding of individual amino-acids of the simplest type or an incomplete mixture of such acids never leads to an increase of body nitrogen or even to nitrogen equilibrium, an appreciable reduction in the daily loss of nitrogen from the body can be achieved by this means, which cannot be accounted for as merely the result of the additional calories brought to the diet by the amino-acids added. These results are checked and confirmed by a consideration of the daily loss of sulphur from the body with and without the addition of amino-acids to the diet. H. C. R.

**Choline as a Precursor of Guanidine. Decrease in the Amount of Choline of the Hen's Egg during Incubation.** J. S. SHARPE (*Biochem. J.*, 1924, **18**, 151—152).—There is a decrease in choline content of the hen's egg as incubation proceeds. It has been previously shown by Burns that the guanidine content increases during this period. The author suggests that choline is a possible source of guanidine in the animal body. S. S. Z.

**Synthesis of Hippuric Acid in the Surviving Kidney of Various Animals and of Man.** I. SNAPPER, A. GRÜNBAUM, and J. NEUBERG (*Biochem. Z.*, 1924, **145**, 40—46).—Perfusion of the isolated surviving kidney of the dog, sheep, pig, and man, with blood containing sodium benzoate and glycine, results in the synthesis of hippuric acid. J. P.

**Sulphur Metabolism of the Dog. I. Synthesis of Ethereal Sulphate.** T. S. HELE (*Biochem. J.*, 1924, **18**, 110—119).—Sodium sulphate, sodium hydrogen sulphite, and cystine are partly



excreted as ethereal sulphate by the dog when administered by the mouth together with guaiacol carbonate. The sodium sulphate is utilised as readily as cystine or as sodium hydrogen sulphite.

S. S. Z.

**Calcium Fixation by Animal Tissues.** R. E. LIESEGANG (*Biochem. Z.*, 1924, **145**, 96—97).—A criticism of the conclusions of Freudenberg and György (this vol., i, 242).

J. P.

**Mineral Metabolism of the Lactating and Dry Goat.** C. H. HUNT, A. R. WINTER, J. A. SCHULTZ, and R. C. MILLER (*Amer. J. Physiol.*, 1923, **66**, 349—362).—Balances were determined for sodium, potassium, calcium, magnesium, sulphur, chlorine, phosphorus, and nitrogen in dry and lactating goats on various diets, the mineral metabolism being found, in general, to be similar to that of the cow. The calcium and chlorine content of goat's milk is higher than of cow's milk. There is evidence that the calcium in green plants may be more highly dispersed, and hence better assimilated than that of dried feeds.

CHEMICAL ABSTRACTS.

**Nitrogen and Mineral Salt Metabolism in Avitaminosis.** N. HIRABAYASHI (*Biochem. Z.*, 1924, **145**, 18—31).—In the avitaminosed dog, the body-weight may increase during the first few weeks, usually with increasing nitrogen retention, although towards the end of this period the nitrogen excretion may show an increase. With increasing duration of avitaminosis, the disturbed gastrointestinal functioning is reflected in diminished body-weight and nitrogen excretion, and in the late stages a temporary increase in the nitrogen retention may set in. The nitrogen excretion is not an indication of the breakdown of nitrogen compounds in the body, since the residual nitrogen of the blood progressively increases in avitaminosis. The phosphorus, calcium, and magnesium balances in avitaminosis are parallel to the diminution in protein metabolism.

J. P.

**Properties of certain South African Oils with Respect to Their Content of Vitamin-A.** E. M. DELF (*Biochem. J.*, 1924, **18**, 93—100).—Sesamé, mafurreira, and castor oils are deficient in vitamin-A. Two samples of seal oil have been found to possess considerable growth-promoting properties. Samples of crude whale oil are active inversely to the temperatures used in the extraction. Sperm whale oil obtained from the head is the least active, and that obtained from the blubber is the most active in growth-promoting. When rats are deficient in vitamin-A, the addition of vitamin-C has a more beneficial effect than when the supply of vitamin-A in the diet is adequate.

S. S. Z.

**Relation of Vitamin-A Potency of the Liver Oil to the Sexual Condition and Age of the Cod.** S. S. ZILVA, J. C. DRUMMOND, and M. GRAHAM (*Biochem. J.*, 1924, **18**, 178—181).—The sexual condition and age of the cod do not influence the vitamin-A potency of the liver oil.

S. S. Z.

**Feeding Experiments in Connexion with Vitamin-A and -B. V. Orange Juice as a Source of Vitamin-B. VI. Ophthalmia in Rats affected with Avitaminosis. VII. The Vitamin Content of Cod-liver Oil and Malt Extract.** A. D. STAMMERS (*Biochem. J.*, 1924, 18, 9—15).—A daily dose of 10 c.c. of orange juice does not contain sufficient vitamin-B to promote growth in rats. The susceptibility of rats to keratomalacia varies directly with the amount of vitamin-A in the diet. Adult animals are less susceptible. "Cod-liver oil and malt extract" contains sufficient vitamin-A and -B to provide the necessary stimulus to growth.  
S. S. Z.

**Vitamins. I. L. MARCHLEWSKI and Z. WIEVZCHOWSKI** (*Bull. Soc. Chim. biol.*, 1924, 6, 40—43).—Vitamin-B is better extracted from bran by dilute aqueous hydrochloric acid (0.1%) than by alcohol. From this solution, after neutralisation and filtration, addition of an ammoniacal solution of silver nitrate produces a greenish-brown precipitate containing the vitamin. This is dissolved out by hydrochloric acid, and after evaporating to dryness in a vacuum, and dissolving in water, a solution of great potency is obtained. From this solution, on the addition of picric acid, a yellowish-orange compound is precipitated, which may be recrystallised from acetone. A brownish-yellow solution of the vitamin, which has a characteristic odour, is obtained on decomposition of the picrate by dilute hydrochloric acid, and removal of the picric acid with ether.  
W. O. K.

**The Reaction Proposed by Jendrassik as Characteristic of Vitamin-B, and its Relation with the Phenolic Grouping.** M. N. BEZSSONOFF (*Bull. Soc. Chim. biol.*, 1924, 6, 35—39).—The solution of ferric chloride and potassium ferricyanide, said by Jendrassik (*A.*, 1923, ii, 892) to turn blue in presence of vitamin-B, is turned blue also by *o*- and *p*-phenols. Jendrassik is not justified in his conclusion that vitamin-B does not contain a phenolic group.  
W. O. K.

**Antiscorbutic Fraction of Lemon Juice. I. S. S. ZILVA** (*Biochem. J.*, 1924, 18, 182—185).—A great part of the solids of decitrated lemon juice consists of invert-sugar. It is possible to ferment the sugar and thus reduce the solids without appreciably altering the antiscorbutic activity of the solution. The remaining solids seem to consist of substances mainly of a nitrogenous character. Some chemical characteristics of the active fraction are given.  
S. S. Z.

**Conservation of the Potency of Concentrated Antiscorbutic Preparations. II. S. S. ZILVA** (*Biochem. J.*, 1924, 18, 186—187).—Concentrated decitrated lemon juice retains its antiscorbutic potency for five months if stored in acid solution in ampoules in a vacuum.  
S. S. Z.

**Water- and Fat-soluble Growth Catalysts (D-Vitamins).** H. VON EULER (*Ark. Kemi, Min., Geol.*, 1923, 8, No. 31, 1—10).—From a top pressed yeast and a brewery yeast, by extraction with

water, dialysis through collodion membranes, concentration under a pressure of 1 mm., and precipitation by means of alcohol, the author has obtained preparations which effect very marked accelerations of fermentation either by living yeast or by washed dried yeast. With such preparations, however, there exists no parallelism between the influence on the growth of the yeast and that on the fermentation; moreover, no quantitative relationship is observable between the effects produced on the growth of yeast and of mice. In the light of these results the suggestion is made that the letter *D* be retained for growth factors but that *D<sub>r</sub>* and *D<sub>m</sub>* be used to denote the growth substance for rats or mice and for micro-organisms, respectively.

It is proposed further that the name vitamin be reserved exclusively for the following substances which act against definite vitamin-deficiency diseases: vitamin-*A* against rickets; vitamin-*B* against polyneuritis, and vitamin-*C* against scurvy. Substances which accelerate growth but may have nothing further in common with vitamins other than natural occurrence in low concentrations and certain properties relating to sorption, may be designated biocatalysts or growth-substances. In this way, the necessity of classifying Harden's co-zymase, hormones, etc., as vitamins is avoided.

As regards the effect on the growth of mice produced by cod-liver oil, at least one-fifth of the substances causing this effect is found to be transferable to aqueous-alcoholic or aqueous solution. The growth-substance obtained by extracting yeast with water is, however, removed to only a small extent from its concentrated aqueous solution when the latter is shaken with double its volume of a vitamin-free animal oil.

T. H. P.

**Separation of a Fat Pigment from Accompanying Fat.** A. N. CURRIE (*Biochem. J.*, 1924, **18**, 231—234).—The fat is ground with lime and hydrolysed for 10 hours in an autoclave. The adipochrome goes mainly into the aqueous layer. The fatty acids are extracted with distilled water and the aqueous portions are combined and extracted with ether. The aqueous layer, which consists of pigment, salt, and glycerol, is acidified with 20% hydrogen chloride and extracted with ether. The adipochrome goes into the ether.

S. S. Z.

**Lipochrome of Adipose Tissue in Malignant Disease.** A. N. CURRIE (*Biochem. J.*, 1924, **18**, 235—244).—The pigment is an unsaturated aliphatic hydrocarbon and is not related to carotene, xanthophyll, fucoxanthin, the anthocyanins, or the melanins. It is probably derived from the associated fats. The bearing of the adipochrome on the pathology of malignant disease is discussed.

S. S. Z.

**Hydrolysis of Hexose-diphosphoric Acid by Various Organs.** Y. TAKAHASHI (*Biochem. Z.*, 1924, **145**, 178—181).—Sodium hexose-diphosphate is hydrolysed *in vitro* by the kidneys, spleen, and muscle of the guinea pig, the activity of the organs diminishing in the order given (cf. also Tomita, A., 1922, i, 960).

J. P.

**Determination, in Different Organs, of Polonium Injected into an Organism.** (MME.) J. S. LATTÈS and A. LACASSAGNE (*Compt. rend.*, 1924, **178**, 771—773; cf. this vol., i, 461).—The distribution, in the rabbit, of polonium, after the injection of the latter, whether intravenously, subcutaneously, or intraperitoneally, is approximately the same. The spleen and kidney are richest in polonium, the former retaining it longer than the latter. The liver, lungs, and especially the heart, rapidly lose their initial polonium. When polonium is injected into a pregnant mouse, the placenta is the organ richest in polonium, which is absent from the amniotic fluid and the foetus. E. E. T.

**Bio-radioactivity.** P. BECQUEREL (*Compt. rend.*, 1924, **178**, 795—797).—Nodon's observation of bio-radioactivity (this vol., i, 347; cf. Berthelot, *ibid.*, i, 348) was made by Tommasina in 1904. Radioactive potassium is present in all animal and vegetable protoplasm, and until an improvement in technique enables its detection, the question of bio-radioactivity must remain open. E. E. T.

**Liquid from *Tænia echinococcus*.** O. FLÖSSNER (*Z. Biol.*, 1924, **80**, 255—260).—The presence of considerable amounts of sodium and chlorine and of lesser amounts of potassium, calcium, ammonium, and magnesium in the liquid from *Tænia echinococcus* was confirmed. Carbonic, sulphuric, and phosphoric acids were also present. The presence of glycogen, betaine, succinic acid, lactic acid, and purine bases was also established. The presence of betaine supports the theory of Kutscher and Ackermann that the metabolism of cold-blooded animals is similar to that of plants. The freedom of the liquid from albumin was confirmed. H. C. R.

**Action of Rennet and of Heat on Milk.** N. C. WRIGHT (*Biochem. J.*, 1924, **18**, 245—251).—The action of rennet and heat (up to 120° for  $\frac{1}{2}$  hour) on caseinogen does not alter the racemisation curves, which suggests that no cleavage takes place in the molecule by the above treatments. Any changes brought about must therefore be of a physical nature. The coloration of autoclaved milk is due to the caramelisation of the lactose, a reaction which appears to be catalysed by the presence of a colloid substrate of calcium caseinogate. The colour of caseinogen precipitated from autoclaved milk is due to adsorption of this pigment. S. S. Z.

**Cholesterol Content of Human Milk.** F. W. FOX and J. A. GARDNER (*Biochem. J.*, 1924, **18**, 127—135).—The total cholesterol of 1—12 days' milk is higher than the average of the later period of lactation in the ratios of 1 : 0.59. S. S. Z.

**Acidity of Urine Measured by Physico-chemical Methods.** C. O. GUILLAUMIN (*Bull. Soc. Chim. biol.*, 1924, **6**, 14—25).—Emphasis is laid on the importance in urine analysis of the determination of  $p_H$  in addition to the usual titration methods. If the  $p_H$  is known, the fractions of the acids present that are ionised may be calculated. It is suggested that the ratio,  $\nu/V = \text{c.c. of}$

$N/10$ -hydrochloric acid required to change  $p_H$  from 8.0 to  $4.0 \div c.c.$  required to change  $p_H$  from 8 to 2.7, might be used to indicate the average degree of dissociation of the organic acids present in urine, but in practice this does not appear to give a trustworthy result.

W. O. K.

**Action of Sodium, Potassium, and Calcium Ions and of Uranyl Nitrate on the Spontaneous Rhythmic Movements of the Muscular Skin of the Earth-worm.** P. C. HART (*Arch. Néerl. Physiol.*, 1924, 9, 1—29).—The rhythmic movements which preparations of the muscular skin of the earth-worm execute when suspended in Ringer's solution have been studied. The effects of variations in the composition of the solution are, in general, similar to those obtained with isolated organs of other animals. The potassium chloride in the perfusion fluid may be replaced by uranyl nitrate; normal movements are obtained when 10 mg. of uranyl nitrate replace 100 mg. of potassium chloride (cf. *Annual Reports*, 1919, 16, 148).

E. S.

**Action of some Physical and Chemical Agents on the Mobility of Ciliated Infusoria.** E. and H. BIANCANI (*Compt. rend.*, 1924, 178, 800—802).—Ciliated infusoria become permanently immobile under the influence of powerful ultra-violet radiation, a temporary immobility being produced by weak radiation. Salt solutions also induce immobility, isotonic solutions of different salts effecting the change at the same rate. Carbamide, ammonia, and iodine act similarly, the effect being proportional to the concentration. With all the agents mentioned, the dose-time curve is hyperbolic.

E. E. T.

**Action of Iodoethylurethane and Iodoethyl Allophanate.** B. VON ISSEKUTZ and A. TUKATS (*Biochem. Z.*, 1914, 145, 1—9).—Ethylurethane, iodoethylurethane, and acetyliodoethylurethane ( $CH_3 \cdot CO \cdot NH \cdot CO \cdot OC_2H_4I$ ) are increasingly toxic in the order given, whilst compared with the parent urethane, iodoethyl allophanate ( $NH_2 \cdot CO \cdot NH \cdot CO \cdot OC_2H_4I$ ) shows a diminished toxicity. The latter is absorbed in the intestinal tract to a greater extent than the iodine derivatives of the fatty acids, and is excreted in the urine approximately as rapidly and completely as potassium iodide.

J. P.

**Pharmacology of the Camphor Group. Comparison of an Isomeric Camphor with Japan Camphor.** T. AMAKAWA (*Arch. Exp. Path. Pharm.*, 1924, 101, 100—126).—The pharmacological action of 3-methyl-5-isopropyl- $\Delta^{2,3}$ -cyclohexenone (hexeton) is very similar qualitatively to that of camphor, but is several times stronger.

W. O. K.

**Bactericidal Action of the Tellurium Derivatives of Aliphatic  $\beta$ -Diketones. II.** G. T. MORGAN, E. A. COOPER, and A. W. BURTT (*Biochem. J.*, 1924, 18, 190—201).—These compounds are extremely germicidal for various strains of bacteria, the bactericidal power being determined by the symmetry of the parent  $\beta$ -diketone and by the presence of methyl and ethyl groups in para-

positions within the heterocyclic ring. Tellurium dipropionylmethane, fulfilling both these conditions of chemical structure, is therefore the most active of the series. The bactericidal power of these compounds increases considerably as the homologous series is ascended, until with the presence of an ethyl group and subsequent substitution of one methyl group, a limit is reached, and with further substitution of alkyl groups there is a diminution in efficacy. Position isomerism plays an important part in determining germicidal power. The tellurium compounds lose their strong bactericidal action in the presence of serum, but retain their inhibitory power. In urine, however, their germicidal power is retained. S. S. Z.

**Comparative Germicidal Efficiency of Phenol, Mercuric Chloride, and Potassium Mercuri-iodide.** J. C. CADORA [in part with R. W. LAMSON] (*J. Amer. Pharm. Assoc.*, 1923, **12**, 401—405).—The values without organic matter were 468.7 for mercuric chloride and 1100 for potassium mercuri-iodide. The minimum lethal dose for the three substances is 0.00035 g., 0.000012 g., and 0.000026 g., respectively. Compared with that of phenol as unity, the coagulating power of mercuric chloride is 55; no coagulating effect was observed with potassium mercuri-iodide. CHEMICAL ABSTRACTS.

**Chemotherapeutic Researches in the Series 205 Baeyer. Carbamates of the Aminobenzoylaminonaphthalenesulphonic Acids.** E. FOURNEAU, J. TRÉFOUËL, (MME.) J. TRÉFOUËL, and J. VALLÉE.—(See this vol., i, 382 and 504.)

**Influence of certain Chemicals on the Rate of Reproduction of Yeast in Wort.** N. A. CLARK (*J. Physical Chem.*, 1924, **28**, 221—231; cf. A., 1922, i, 501).—The rate of reproduction of yeast in wort at 25° follows a logarithmic law up to a certain limiting concentration, when the alcohol formed during fermentation begins to have an effect. The influence on this rate of phenol, methyl green, acetone, sodium bicarbonate, and hydrochloric and acetic acids has been studied. In general, the effect is to reduce the rate, which still, however, follows the logarithmic law. With increasing concentration of the poison there is also a resting period of increasing duration before reproduction begins. In every instance, a limiting concentration is reached above which no growth is observed, although it has been shown that this does not necessarily mean that the yeast is killed. When washed free from poison, it is still capable of reproduction. [Cf. B., 1924, 395.] M. S. B.

**Optimum Temperature of the Action of a Ferment or Lysin.** I. BROWNLEE (*Biochem. J.*, 1924, **18**, 16—18).—The subject is treated mathematically. S. S. Z.

**Nature, Constitution, and Mode of Action of Animal Tissue Enzymes.** F. MAIGNON (*Compt. rend.*, 1924, **178**, 806—807; cf. this vol., i, 464).—Tissue and pancreatic enzymes, similar with regard to their content of metals, differ in their content of

acids (silicic, phosphoric, and arsenic in the former case and hydrochloric in the latter). The tissue enzymes may be written in the form,  $(\text{SiO}_4)^{\text{H.H.H.H.}}$ , etc., those of the pancreatic juice as  $\text{Cl}^{\text{H}}$ . The paper contains other (theoretical) matter. E. E. T.

**Inactivation of Invertase by Heavy Metals.** K. MYRBÄCK (*Ark. Kemi, Min., Geol.*, 1923, 8, No. 29, 1—37).—Experiments similar to those described by Euler and Svanberg (*A.*, 1920, i, 689) have now been carried out with purer preparations of invertase. The extent to which the enzyme is inactivated by mercuric chloride varies greatly with the purity of the enzyme preparation, since the protein impurities are able to fix mercury and thus protect the enzyme; even with the most highly purified specimens of invertase, the first small additions of the mercury salt are without inactivating action. The purity of an invertase preparation is indicated by: (1) The absence, from the curve connecting relative activity with the proportion of mercuric chloride present, of the characteristic initial inflection that is shown when mercury-fixing impurities are present, (2) the constancy or gradual increase of the unimolecular reaction coefficient, and (3) the non-occurrence of auto-regeneration of the enzymic preparation.

Within the optimum zone, the inactivation by mercuric chloride is virtually independent of the hydrogen-ion concentration and, moreover, unlike what is the case with poisoning by silver, no acidity is capable of annulling the effect of the mercuric salt. Sucrose itself exerts a marked protective action. The mercury equivalent of invertase (per mol. of Hg) in the supposed compound Hg-invertase is calculated to be 3530, and the values  $6.6 \times 10^{-7}$  and  $1.0 \times 10^{-7}$  are found by two different methods for the dissociation constant of this compound.

With silver salts also, the amount needed to produce inactivation of invertase becomes very small when the enzyme is highly purified. Cysteine combines with very large proportions of silver, the acidity being without appreciable effect in this case. The poisoning action of copper or lead is similar to that of silver.

In view of the facts that the curve connecting the relative activity of the enzyme with the proportion of mercury present is a dissociation curve, that the acidity is without appreciable influence in the optimum zone, and that the poisoning is affected considerably by the concentration of the sucrose, it must be assumed that mercury forms with the enzyme a dissociating compound; in presence of sucrose, the invertase becomes distributed between the sugar and the mercury. With poisoning by silver, copper, or lead, other conditions must prevail, since the poisoning depends greatly on the acidity and is independent of the concentration of the substrate; in these cases, it is supposed that it is the enzyme-substrate compound which forms with the silver ion a very slightly dissociated salt.

Experiments on the influence of sodium acetate on the action of invertase yielded results similar to those obtained by Fales and Nelson (*A.*, 1916, i, 174) with sodium chloride. T. H. P.

**Inactivation of Invertase by Amines.** K. MYRBÄCK (*Ark. Kemi, Min., Geol.*, 1923, 8, No. 32, 1—11).—The inactivation of invertase by *p*-toluidine as a function of the proportion of base present (cf. A., 1923, i, 496) is dependent only in slight degree on the hydrogen-ion concentration of the medium. Assuming that only the free enzyme, and not the enzyme-substrate compound, is able to fix the amine, values are derived for the dissociation constant of the enzyme-amine compound, which are virtually constant for different concentrations of the amine.

The degree of inactivation produced by aniline is not determined solely by the concentration of the base; the more acid solutions cause increased inactivation, which is due to an unknown factor. Ammonia inactivates invertase to as great an extent as do the aromatic amines. T. H. P.

**Blood Enzymes. IV. Maltase of Dog's Serum : Influence on Activity of the Reaction of the Medium and of the State of Digestion.** A. COMPTON (*Biochem. J.*, 1924, 18, 173—177).—The maltase of the blood of the dog, like that of vegetable origin, requires an acid medium for its maximum activity (1.66 c.c. *N*/100 sulphuric acid to 55.5 c.c. of reaction mixture). The activity and the optimum temperature, *i.e.*, 55°, are the same whether the blood is collected during digestion or in the fasting state. S. S. Z.

**Takalactase.** C. NEUBERG and O. ROSENTHAL (*Biochem. Z.*, 1924, 145, 185—188).—Takadiastase preparations contain an enzyme—*takalactase*—which hydrolyses lactose practically completely in 216 hours. Lactose osazone is similarly resolved into galactose and glucosazone. In the presence of yeast and takalactase, lactose gives rise to carbon dioxide. J. P.

**Fructosediphosphatase in Human Organs. I.** E. FORRAI (*Biochem. Z.*, 1924, 145, 48—53).—Many dried human organs are capable of hydrolysing sodium fructosediphosphate, the percentage hydrolysis varying from 66% in the thyroids, to 19% in healthy muscle and 10% in blood-serum. A widespread distribution of fructosediphosphatase is inferred. J. P.

**Differentiation of Human Phosphatases.** E. FORRAI (*Biochem. Z.*, 1924, 145, 54—56).—From comparative studies of the capacities of extracts of various human organs to hydrolyse glycerol-, saccharo-, and fructosediphosphoric acids, it is concluded that the phosphatases concerned are different and specific enzymes. J. P.

**Determination of the Activity of a Laccase.** P. FLEURY (*Compt. rend.*, 1924, 178, 814—816).—The activity of a laccase may be determined by aspirating air through the enzyme preparation in presence of guaiacol, the oxidation of which affords tetraguaiacoquinone. This substance is extracted with chloroform and determined colorimetrically. The lower the concentration of the laccase, the higher is its effectiveness, but, within certain limits, the ordinary linear relation holds between enzyme concentration and amount of substrate decomposed. Between these limits, the above method is accurate. E. E. T.



**Mechanism of Oxidation in the Plant. II. Substances Capable of Behaving as Peroxydases.** P. H. GALLAGHER (*Biochem. J.*, 1924, **18**, 29—38).—It is concluded that peroxydase activity is associated with aliphatic aldehydes, which do not act directly but after preliminary conversion by atmospheric oxygen into a substance of oxide nature. Peroxydase preparations prepared by alcoholic precipitation from the juices of vegetables such as the potato, the horse-radish, and the mangold contain a substance or substances of aldehydic nature. Oxides of some heavy metals induce oxidation of guaiaconic acid and of indophenol mixture by peroxide. The chemical nature of peroxydase action is discussed in the light of these results. S. S. Z.

**Mechanism of Oxidation in the Plant. III. Peroxydase. Thermostability of the Peroxydase of the Mangold.** P. H. GALLAGHER (*Biochem. J.*, 1924, **18**, 39—46).—Peroxydase of the mangold, inactivated by heat, becomes reactivated when the solution is allowed to remain some time in the cold. This reactivation has been studied quantitatively. The active and the inactivated solutions both contained iron and gave several reactions for aldehyde. Traces of iron added to aqueous solutions of aliphatic aldehydes give rise to an increase of peroxydase activity on standing in the cold. The zymogen of the peroxydase is probably an aldehyde which is activated by the catalytic action of iron after the inactivation by heat. S. S. Z.

**Reaction of *Bacillus coli* applied to the Proteolytic Action of Serum (Abderhalden's "Ferments of Defence").** E. WOLLMAN, V. LABERNADIE, (MME.) E. WOLLMAN, and (MLLE.) J. OSTROWSKI (*Ann. Inst. Pasteur*, 1924, **38**, 115—151).—The production of indole from albumin by *Bacillus coli* only occurs after previous proteolysis of the albumin (Wollman, *Compt. rend. Soc. Biol.*, 1919, **82**, 1263). It is thus an indicator of such proteolysis, and may be used instead of the methods of dialysis or optical rotation in carrying out Abderhalden's reaction. The application of this method gave no evidence for the existence of the "ferments of defence" postulated by Abderhalden. W. O. K.

**Extraction of Sap from Living Tissues by means of Compressed Air.** H. H. DIXON and N. G. BAIL (*Sci. Proc. Royal Dublin Soc.*, 1924, **17**, 263—266).—Liquid was forced out of the wood and leaves of branches by enclosing them in a strong cylinder, in such a way that their cut ends protruded, and increasing the pressure in the cylinder to about 20 atmospheres. This liquid was almost completely free from sugars, except when the leaves had been exposed to toluene vapour. The transport of carbohydrates from the leaves to the stem through the wood involves, in addition to a backward flow through the tracheæ, an increased permeability of the leaf cells. E. M. C.

**Physiological Studies on Apples in Storage.** J. R. MAGNESS and H. C. DIEHL (*J. Agric. Res.*, 1924, **27**, 1—38).—The changes in apples after picking are, in the main, a continuation of those

occurring during ripening on the tree. The softening of stored apples is accelerated by increased temperature. The decrease in acidity during storage was practically the same for all varieties of apples, and was independent of the original acidity. Coating the surface of apples with oil or similar material, by reducing the gaseous exchange, retards ripening. So long as anaërobic respiration does not occur, the flavour of the fruit is not detrimentally affected. The higher the temperature of storage, the smaller is the thickness of the coating which will bring about anaërobic respiration and bad flavour. The retardation of ripening appears to be due both to the reduced amount of oxygen and the increased amount of carbon dioxide in the intracellular spaces. Storage of apples in an atmosphere containing up to 10% of carbon dioxide delayed softening, with no apparent loss of quality, but greater proportions caused a bad flavour.

A. G. P.

**Essential Oil of Manuka (*Leptospermum Scoparium*).** R. GARDNER (*J. Soc. Chem. Ind.*, 1924, 43, 34—35r).—The leaves of the New Zealand wild shrub known as "manuka" yield about 0.45% of greenish-yellow essential oil,  $d^{15}_4$  0.921,  $n_D$  1.50, b. p. 160—270°/760 mm. The oil consists approximately of phenols (leptospermol), 2.8%; terpenes, 2.8%; cinnamic esters (calculated as ethyl cinnamate), 4.8%; other esters (calculated as  $\text{CH}_3\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{15}$ ), 12.9%; semi-solid, non-volatile substances, 7.7%; sesquiterpene, 69.0%.

W. P. S.

**Protein and Vitamin-A Content of the English Walnut.** H. L. MIGNON (*Amer. J. Physiol.*, 1923, 66, 215).—Tannins present in the skins of English walnuts interfere with the extraction of the walnut globulin and constitute a growth-limiting factor in the diets of rats and mice. Vitamin-A is present in extremely small amounts. The distribution of nitrogen as amino-acids in walnut globulin, as determined by Van Slyke's method, is: cystine, 0.86; amide, 9.99; humin, 1.84; arginine, 39.13; histidine, 5.74; lysine, 10.61; monoamino-, 30.26; non-amino-, 0.88%.

CHEMICAL ABSTRACTS.

**Relation between the Chemical Structure of Bile Acids and their Phytopharmacological and Zoöpharmacological Reactions.** D. I. MACHT and O. R. HYNDMAN (*J. Pharm. Exp. Ther.*, 1924, 22, 483—490).—The inhibition of the growth of seedlings by taurocholic and glycocholic acids appears to be due to the cholic acid in the molecules, since glycine and taurine have little or no action on the growth of seedlings (*Lupinus albus* or *Vicia faba*) or on the reactions of rats in a circular maze, whilst cholic (and also choloidinic) acid is very active.

W. O. K.

**Saponin of *Panax repens*, Maxim.** I. Y. MURAYAMA and T. ITAGAKI (*J. Pharm. Soc. Japan*, 1923, No. 501, 783—789; cf. Inoue, *ibid.*, 1902, No. 242, 356).—After treatment with ether, crushed *Panax repens*, Maxim, was extracted with hot alcohol; from the extract a saponin (5%) was isolated as a white, amorphous powder (m. p. 180—190°), which has a bitter taste.

When shaken with water, it dissolves slightly with foaming; it gives a clear solution on the addition of sodium carbonate. It behaves as an acid, thus supporting the hypothesis of Asahina and Momotani (*ibid.*, 1914, No. 384, 117). It contains 0.33% of ash. When hydrolysed with 3% hydrochloric acid it gave dextrose and a sapogenin (15%). The latter was obtained as white, lustrous needles (m. p. 303—304°). The sapogenin gives the same colour reactions as the saponin, but has no taste. It gives two diacetyl derivatives: one, plates (m. p. 207—210°), and the other, needles (m. p. 257—260°).  
K. K.

**Isolation and Identification of Rutin from the Flowers of Elder (*Sambucus Canadensis*, L.).** C. E. SANDO and J. U. LLOYD (*J. Biol. Chem.*, 1924, **58**, 737—745).—The yellow pigment "eldrin" from the flowers of the elder (Lloyd, *Eclectic Med. J.*, 1920, **80**, 591) is shown to be identical with rutin from *Eschscholtzia* (Sando and Bartlett, A., 1920, i, 446) in its appearance, composition, products of acid hydrolysis (quercetin, dextrose, and rhamnose), and in its absorption spectrum. The yield of quercetin on hydrolysis is slightly higher than that calculated, owing to the presence of an impurity.  
G. M. B.

**Proteins of Oats.** H. LÜERS and M. SIEGERT (*Biochem. Z.*, 1924, **144**, 467—476).—Various protein fractions prepared from oats by Osborne's methods, and belonging to the alcohol-, salt-, and alkali-soluble groups, were examined for their products of hydrolysis. The results are given in tabular form. The differences between the alcohol-soluble proteins of oats and those of the other cereals lie chiefly in the higher cystine and in the medium histidine content. The globulins of oats contain less arginine and decidedly more non-amino nitrogen than the globulins of other cereals. Avenaline, the protein characteristic of oats, is rich in arginine and histidine. Although there are many points of similarity between the nitrogen distribution of the proteins of oats and of other cereals, there is not a complete agreement. The proteins of oats are therefore to be regarded as a distinct group.  
S. S. Z.

**Influence of Phylogeny on the Constitution of the Alkaloids.** J. GADAMER (*Pharm. Monatsh.*, 1923, **4**, 157—160; from *Chem. Zentr.*, 1924, i, 56).—Certain families of plants yield characteristic alkaloids. From this fact it is possible to draw conclusions as to the constitution of alkaloids from different species of the same family.  
G. W. R.

**Basic Substances from the Juice of the Alfalfa Plant [Lucerne].** C. S. LEAVENWORTH, A. J. WAKEMAN, and T. B. OSBORNE (*J. Biol. Chem.*, 1923, **58**, 209—214).—The filtrate obtained from the press-juice after precipitation by addition of 53% by weight of alcohol (A., 1922, i, 1104) has been hydrolysed by boiling for 12 hours with 25% sulphuric acid and the product examined for basic substances according to Kossel's method. The following substances were isolated: arginine, stachydrin (cf. Steenbock, A., 1917, i, 439), lysine, and a compound which was apparently a purine

derivative. The latter was obtained from the mercuric sulphate fraction and gave a *picrate*, silky needles, m. p. 298°, and a *hydrochloride* (?), long plates, m. p. about 252°, which contained 31.8% of nitrogen. It is not known whether these bases are present in the press-juice in the free state or whether they are liberated during hydrolysis. Van Slyke's method for analysing the hydrolytic products of proteins is not applicable to the water-soluble constituents of forage plants. E. S.

#### **Extraction of Nitrogenous Constituents from Plant Cells.**

W. E. TOTTINGHAM, E. R. SCHULZ, and S. LEPKOVSKY (*J. Amer. Chem. Soc.*, 1924, **46**, 203—208).—The investigation deals with the efficiency of various methods of desiccation and extraction as related to the proportions of total soluble nitrogenous compounds and soluble proteins in leaves of the barberry and sugar beet. The influence of freezing and drying on the distribution of nitrogen in plant cells is discussed. The results obtained indicate the desirability of extracting with water as general usage in fractionating the nitrogenous constituents of plant cells; water extracts the greater part of the proteins exposed by crushing the cells of fresh tissue. Chibnall's method of extraction does not sharply separate non-protein from protein nitrogen. F. A. M.

**Presence of Vernine (Guanosine) in the Green Leaves and Berries of the Coffee Tree (*Coffea Arabica*, L.) and its Relation to the Origin of Caffeine in this Plant.** T. DE A. CAMARGO (*J. Biol. Chem.*, 1924, **58**, 831—834).—A pentoside containing guanine, found in the green leaves and berries of this species, is probably the guanosine previously found in several plants (Schultze, A., 1886, 157, 736) and in nucleic acid (Levene and Jacobs, A., 1909, i, 620). This substance is probably the origin of caffeine in the leaves and berries of the coffee tree. It is transformed by enzymes to guanine, then to xanthine, and finally to caffeine. G. M. B.

**Method for Sterile Cultures of the Higher Plants.** E. BOBKO (*Z. Pflanz. Düng.*, 1924, **A**, 3, 41—44).—The apparatus consists of a wide-necked vessel, to hold the nutrient solution, inside the wide neck of which is a piece of net stretched on a frame. The whole is covered with a dome-shaped cap, having cottonwool-plugged tubulures through which seed and sand may be introduced. The lower vessel has a side tube through which an air current or renewed nutrient solution may be passed. The vessel and solution are first sterilised; the seeds are separately sterilised and then introduced on to the gauze and covered with sterile sand. The cover is then removed. A. G. P.

**Comparison of the Soil Solution by the Displacement Method and the Water Extract of Alkali Soils.** P. L. HIBBARD (*Soil Sci.*, 1923, **16**, 465—471).—When the composition of 1:5 water extracts of nine alkali soils was used as a basis for the calculation of the composition of the soil solution, results were obtained which were at variance with those given by an analysis of the

solution obtained from the same soil by the displacement method (A., 1921, i, 214). Only in the case of chlorides, nitrates, and sodium were the results given by the two methods in approximate agreement. Calcium and magnesium may be either under- or over-estimated by the water extract method. All the other ions were over-estimated to varying degrees. Analysis of 1:5 water extracts of soils is thus liable to give a distorted and, usually, an unfavourable impression as to the composition of the soil solution and the suitability of the soil for plant growth. H. J. P.

**Replacement of Soil Potassium.** S. C. VANDECAVEYE (*Soil Sci.*, 1924, 17, 91—96).—Organic manures (clover hay and dung) increased the amount of replaceable potassium in soil (as determined by neutral salt extraction) proportionally to the amounts added. Evidence is given that this liberation of replaceable potassium is largely a chemical phenomenon, and is not the result of biological activities or the production of carbon dioxide in the soil. A. G. P.

**Reciprocal Repression Exerted by Calcic and Magnesic Additions upon the Solubility of Native Materials in Surface Soil.** W. H. MACINTIRE, W. M. SHAW, and J. B. YOUNG (*Soil Sci.*, 1923, 16, 449—464).—Lysimeter experiments are recorded in which magnesium and calcium compounds were added to the soil in varying quantities and with the supplementary use of sulphur compounds. In all cases, the addition of lime increased the calcium content of the drainage water and depressed that of magnesium. The reverse occurred when magnesia was substituted for lime. Ferrous sulphate, pyrites, and sulphur each increased the drainage losses of calcium and magnesium; but if used in conjunction with lime, the calcium losses were further increased and those of magnesium lessened. Similarly, magnesia, coupled with either of the sulphur compounds, brought about increased leaching of magnesium, and a depression of the loss of calcium normally occasioned by the sulphur compounds alone. Lime and magnesia in soil slowly revert to an insoluble and unavailable condition. Excessive liming may so depress the solubility of magnesium salts, as to cause a chlorotic condition in plants due to deficiency of magnesium. A. G. P.

**Effect of Soil Suspensions on the Solubility of the Sulphate Radical in the System  $\text{Ca}(\text{OH})_2\text{--CaSO}_4\text{--H}_2\text{O}$ .** W. H. MACINTIRE and W. M. SHAW (*Soil Sci.*, 1924, 17, 65—89).—In small amounts lime increased the amount of dissolved sulphate in a ferrous sulphate-soil-water suspension. Larger amounts of lime, however, almost eliminated dissolved sulphates from the suspensions, even when a period was allowed, before adding lime, for the reaction between soil and ferrous sulphate to proceed. If the excess of lime were removed from the soil suspension by the addition of sodium carbonate or by carbon dioxide the depressive effect on the solubility of sulphates disappeared. Here also the same effects were observed when the addition of sodium carbonate

was delayed. The addition of soil to solutions of calcium sulphate caused the removal of considerable amounts of sulphate from solution. Similar experiments are recorded in which calcium carbonate, magnesium oxide, and carbonate were used in conjunction with ferrous sulphate (cf. *Soil Sci.*, 1923, **16**, 159). Soil structure played an important part in sulphate adsorption. Ignited soil contained more soluble sulphate than the fresh sample, but also adsorbed more sulphate from added solutions, and the effects of lime were accentuated. Greater quantities of sulphate were removed by extracting soil with large amounts of water than by rainwater leaching in lysimeters.

A. G. P.

**Factors affecting the Growth of Crops on Acid Soils.** S. D. CONNER (*Ind. Eng. Chem.*, 1924, **16**, 173—175).—The capacity of a soil to neutralise calcium hydroxide, carbonate, or acetate is a measure of the total acidity, both organic and inorganic. Methods depending on the action of a salt of a strong acid and a strong base, such as potassium nitrate, give a measure of the inorganic acid silicates, but not to any great extent of the organic acids. The expression  $(\text{inorganic acidity})^2/(\text{organic acidity})$  gives a better indication of the lime needs of both organic and inorganic soils than that given by any single method of determining acidity. The toxicity of soil acidity may be due to both aluminium ions and hydrogen ions. Some crops, such as maize and radishes, are more sensitive to aluminium ions than to hydrogen ions, whilst others, such as red clover and beets, are more sensitive to hydrogen ions than to aluminium ions. Both phosphates and lime are needed to correct the toxicity of aluminium and hydrogen ions in most acid soils.

H. C. R.

**Behaviour of Lime in the Soil.** O. LEMMERMANN and L. FRESSENIUS (*Z. Pflanz. Düng.*, 1924, **A**, **3**, 1—20).—The relationship between the action of various calcium compounds on soils was determined by shaking together soil and various salt solutions. Calcium, supplied to soil as chloride or bicarbonate, was “fixed” largely by base exchange in accordance with the usually accepted views. If slaked lime was used, the calcium was held by adsorption. Carbon dioxide can partly, but not wholly, remove calcium from this adsorbed condition. The addition of calcium hydroxide to soils accelerated the decomposition of organic matter. This occurred even when the amount of calcium hydroxide added was so adjusted that the whole of it would be adsorbed by the soil colloids. The addition of small amounts of lime to soil suspensions caused increased dispersion of the clay, larger amounts producing the normal flocculation. The permeability to water of soil to which successively increasing amounts of lime were added decreased with the smaller additions, and increased as the proportion of lime was further increased.

A. G. P.

**Determination of Acidity of Soils.** R. M. BARNETTE and others.—(See this vol., ii, 347.)

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## Organic Chemistry.

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**Primary Products of the Combustion of Carbon.** K. KULLGREN (*Gas- u. Wasserfach*, 1924, **67**, 226—229).—Carbon dioxide was the main product formed when air, freed from carbon dioxide, was passed over heated retort coke, at 260—410°, but 20% of its weight of carbon monoxide was always present. Dry air reduced the velocity, but did not affect the course of the oxidation. [Cf. *B.*, 1924, 457.] T. S. W.

**Sulphochromic Oxidation of Organic Substances and Coals in Presence of Catalysts.** D. FLORENTIN (*Bull. Soc. chim.*, 1924, [iv], **35**, 228—230).—The oxidation of the carbon in organic compounds and coals to carbon dioxide by means of the sulphochromic mixture is complete in the presence of a small quantity of a mercury salt. With other catalysts (copper sulphate, silver chromate), or with no catalyst, a certain amount of carbon monoxide is produced also. E. E. T.

**Preparation of *n*-Hexane.** M. FAILLEBIN (*Bull. Soc. chim.*, 1924, [iv], **35**, 160—161).—Pure *n*-hexane is prepared by the action of pulverised sodium on dry *n*-propyl bromide (Würtz reaction). The sodium is freed from sodium hydroxide by fusion under xylene and is then pulverised under the same liquid. E. E. T.

**Conversion of [Solid] Paraffin by Heating under Pressure in the Presence of Hydrogen, Methane, and other Gases.** H. I. WATERMAN and J. N. J. PERQUIN (*Proc. K. Akad. Wetensch.*, 1924, **27**, 132—139).—The results of further experiments are given. [Cf. *B.*, 1924, 500.] T. H. P.

**Constitution of Melene.** J. MARCUSSE and F. BÖTTGER (*Ber.*, 1924, **57**, [B], 633—635).—Melene, found by Pictet and Bouvier (*A.*, 1915, i, 513) in coal, in vacuum-tar, in Galician paraffin, and in the products of distillation of beeswax, was assumed to be a solid naphthene,  $C_{30}H_{60}$ . The authors have now found that Indian paraffin, m. p. 59—60°, consists very largely of melene, which can be readily isolated by crystallisation from benzene and then from light petroleum. It has m. p. 62—63°,  $d^{25}_4$  0.7913;  $d^{25}_D$  0.9037;  $n^{90}_D$  1.4228. Analyses indicate the composition  $C_{30}H_{62}$ ; oxidation with strong hot nitric acid gave a mixture of aliphatic acids, whereas naphthenes under similar conditions gave nitro compounds. Similar differences in behaviour were found on oxidising catalytically with air in presence of manganese dioxide, melene yielding solid fatty acids, whilst naphthenes yielded polynaphthenic acids. Lastly, melene is slowly assimilated at 30° by *Bacterium aliphaticum*, which is incapable of attacking naphthenes. Melene is therefore a paraffin and not a naphthene. F. A. M.

**Constitution of Kerogen.** J. W. MCKINNEY (*J. Amer. Chem. Soc.*, 1924, **46**, 968—979).—A shale from Albert Mines, New Brunswick.

wick, on extraction with acetone yielded 1.36% (calc. on the shale), which is about 4% of the kerogen. The hydrocarbons, amounting to 85% of the extract, on repeated fractionation in a vacuum yielded 15 separate fractions. These, by cooling, were split up into 28 different hydrocarbons consisting of the homologues:  $C_{14}H_{30}$  to  $C_{26}H_{54}$ ,  $C_{12}H_{24}$  to  $C_{24}H_{48}$ ,  $C_{25}H_{48}$ ,  $d^{25}$  0.8877,  $C_{26}H_{50}$ ,  $d^{25}$  0.8964. Of these, the two last do not appear to have been previously obtained. A. C.

**Silver as Catalyst for the Absorption of Ethylene by Sulphuric Acid.** W. LOMMEL and R. ENGELHARDT (*Ber.*, 1924, 57, [B], 848).—The catalytic acceleration of the absorption of ethylene by sulphuric acid by means of silver salts (cf. Gluud and Schneider, this vol., i, 359) has been observed previously (cf. D.R.-P. 393632). The change consists in the successive addition of ethylene to the silver salt and production of ethyl hydrogen sulphate. Addition occurs very rapidly at the atmospheric temperature, whereas the second reaction does not take place with sufficient rapidity below 40°. The absorption of ethylene by aqueous solutions of silver nitrate (10%) and phosphoric acid (4%) may be used for the gas-analytical determination of ethylene; the gas can be removed subsequently by evacuating the solutions with a water-pump. H. W.

**Formation of Metallic Acetylides.** J. F. DURAND (*Bull. Soc. chim.*, 1924, [iv], 35, 161—171).—Acetylene is a very feeble acid (cf. A., 1902, i, 525) and the general methods of preparing salts are now applied to the formation of acetylides. By the action of pure acetylene on solutions of cupric hydroxide in concentrated potassium but not in sodium hydroxide, at 35° a reddish-brown precipitate,  $CuC_2$ , was obtained (cf. A., 1897, i, 309) which, immediately after preparation, yielded acetylene with hydrochloric acid or potassium cyanide, but after standing it polymerised and then gave with these reagents an organic, colloidal substance free from copper. Acetylene did not react with copper hydride, but with boiling solutions of zinc ethyl in light petroleum the white zinc acetylide,  $ZnC_2$ , was precipitated (A., 1923, i, 449), which gave pure acetylene with water and sodium hydroxide solution; it decomposed (without explosion) at 350° (cf. magnesium and alkaline-earth acetylides).

Solutions of acetylene in acetone gave with mercury ethyl a white, crystalline substance, the precipitation of which was reversible. Boiling solutions of mercury ethyl in light petroleum gave with acetylene gas mercury and carbon, the temperature being too high for carbide formation; boiling solutions of mercury and of lead phenyls in the same solvent gave no result, neither did a benzene solution of lead ethyl. Attempts to prepare aluminium acetylide,  $Al_2(C_2)_3$ , by the action of acetylene on aluminium carbide at 400—500° failed. E. E. T.

**Preparation of Alkyl Chlorides.** J. F. NORRIS and H. B. TAYLOR (*J. Amer. Chem. Soc.*, 1924, 46, 753—757; cf. A., 1916, i, 461; 1920, i, 831).—Alcohols are converted into the corresponding



chlorides when heated for 1 hour under a reflux condenser with concentrated hydrochloric acid and zinc chloride. The lower alkyl halides may be purified from higher polymerides by heating gently under a reflux condenser with concentrated sulphuric acid. The best results are obtained when the molecular ratio of alcohol, hydrogen chloride (as concentrated hydrochloric acid), and zinc chloride is 1 : 2 : 2; yields varying from 60—82% were obtained. Alkyl chlorides were produced from the following alcohols: methyl, ethyl, *n*- and *iso*-propyl, *n*- and *sec*-butyl, *iso*-amyl, pentan- $\beta$ -ol, cetyl,  $\beta$ -phenylethyl,  $\gamma$ -phenylpropyl, *m*-nitrobenzyl, and *p*-nitrobenzyl.

C. J. S.

**Preparation of Various Aliphatic Halides and Halohydrin Compounds.** M. T. BOGERT and E. M. SLOCUM (*J. Amer. Chem. Soc.*, 1924, 46, 763—768).—The method described by Adams and Vorhees (*A.*, 1919, i, 306) for the preparation of alkyl iodides by the use of phosphorus and iodine has been modified so as to avoid the employment of special apparatus. Iodides have been obtained from *n*- and *iso*-propyl, *n*- and *iso*-butyl, and *iso*amyl alcohols (molecular ratio of alcohol, phosphorus, and iodine, 3 : 1 : 3). The trihalides of phosphorus may be used instead of the pentahalides for the conversion of propylene glycol into trimethylene bromide or iodide. Trimethylene bromohydrin and iodohydrin were prepared by passing the dry halogen hydride into propylene glycol; by conducting the operation in the presence of anhydrous benzene, a yield of 90% of the bromohydrin was obtained. A 50% yield of propylene glycol monoacetate was obtained by the action of acetyl chloride on propylene glycol.  $\beta$ -Chloroethyl acetate was obtained in very good yield by the action of a large excess of acetyl chloride on ethylene chlorohydrin. This method was applied to the production of  $\gamma$ -bromopropyl acetate, b. p. 88—90°/22 mm., when a yield of 90% was obtained. The best method for the preparation of  $\gamma$ -chloropropyl acetate consists in heating a mixture of propylene glycol, acetyl chloride, and zinc chloride in a sealed vessel for 8 hours at 100°.  $\beta$ -Iodoethyl acetate was obtained in 70% yield from the corresponding chloro compound by the action of excess of potassium iodide in methyl-alcoholic solution;  $\gamma$ -iodopropyl acetate was prepared in 88% yield by passing dry hydrogen iodide into an equimolecular mixture of propylene glycol and glacial acetic acid cooled to 0°. The *methylene ether* of *trimethyl iodohydrin*,  $\text{CH}_2[\text{O}(\text{CH}_2)_3\text{I}]_2$ , b. p. 180—193°/12 mm., was obtained (yield 60%) when a mixture of equimolecular proportions of trimethylene iodohydrin and trioxymethylene was saturated with dry hydrogen chloride, a second molecular proportion of the iodohydrin added, and the reaction completed by warming; it yields formaldehyde and iodopropyl alcohol when boiled with 20% sulphuric acid.

C. J. S.

**Action of Hydrogen Chloride on Methyl Alcohol.** S. R. CARTER and J. A. V. BUTLER (*J. Chem. Soc.*, 1924, 125, 963).—A solution of hydrogen chloride (400 g.) in methyl alcohol (1 litre) on standing at 18° for 4 days becomes saturated with methyl chloride

which is then steadily evolved. The activity of methyl alcohol is thus far greater than that of higher alcohols. F. G. M.

**Toxic Properties of Methyl Alcohol.** S. BODFORSS (*Svensk Kem. Tidskr.*, 1923, 35, 333—335; from *Chem. Zentr.*, 1924, i, 574—575).—Methyl alcohol is toxic even when pure, and may exert a toxic effect when applied externally. G. W. R.

**Determination of Methyl Alcohol.** W. M. FISCHER and A. SCHMIDT.—(See ii, 427.)

**Detection of Methyl Alcohol.** A. KLING and A. LASSIEUR.—(See ii, 428.)

**Unsaponifiable Constituents (Higher Alcohols) of Shark and Ray Liver Oils. III.** Y. TOYAMA (*Chem. Umschau*, 1924, 31, 61—67; cf. A., 1923, i, 979).—Batyl and selachyl alcohols were prepared from the livers of *Chimæra barbouri* (Garman) and *Narcacion tokionis* (Tanaka). The analyses given by these preparations agreed better with formulae containing 21 carbon atoms than with the formulae containing 20 carbon atoms previously assigned to these alcohols. The solid portion of the unsaponifiable matter of these oils contains another alcohol homologous with batyl alcohol which is named *chimyl alcohol* and probably has the formula  $C_{19}H_{40}O_3$ . This alcohol occurs in the liver oils of several sharks and *Chimæra* and also in many cases is present in greater quantity than batyl alcohol. No trace of the unsaturated alcohol corresponding to chimyl alcohol could be found in these oils. Selachyl acetate had b. p. 242—244°/5 mm.,  $n_D^{20}$  1.4550,  $d_4^{20}$  0.9417, iodine value (Wijs) 64.5, saponification value 260.0, molecular refraction 122.8 (calc. 122.0). Selachyl alcohol prepared from the acetate had b. p. 236—239°/5 mm.,  $n_D^{20}$  1.4691,  $d_4^{20}$  0.9180, iodine value (Wijs) 79.5, molecular refraction 103.9 (calc. 103.3). The transformation of selachyl alcohol into batyl alcohol on hydrogenation was confirmed. By oxidising selachyl acetate with potassium permanganate in acetic acid solution nonoic acid and an acid of the formula  $C_{11}H_{21}O(OAc)_2 \cdot CO_2H$  were obtained. The formula



is therefore indicated as representing selachyl alcohol. The principal product obtained on the dry distillation of selachyl acetate is either oleyl alcohol or nonodecyl alcohol. H. C. R.

**Methyl Ethyl Sulphate as an Alkylating Agent.** T. K. THAYER (*J. Amer. Chem. Soc.*, 1924, 46, 1044—1046).—*Methyl ethyl sulphate*, b. p. 198—200°/742 mm., is prepared by adding ethyl chlorosulphonate (1.3 equivalents) to a suspension of sodium methoxide in dry ether. The yield was 19.7% of the theoretical. The alkylating powers of methyl sulphate and methyl ethyl sulphate were compared by alkylating solutions of phenol. Using methyl sulphate, the yield of anisole was 74.2% of the theoretical. With methyl ethyl sulphate, 56.7% of the phenol was converted into anisole and 13.4% into phenetole, which shows that the methyl group has the greater alkylating power. A. C.

**Laboratory Preparation of Ethyl Sulphate.** E. V. LYNN and H. A. SHOEMAKER (*J. Amer. Chem. Soc.*, 1924, **46**, 999—1001).—A mixture of alcohol (50 g.) and concentrated sulphuric acid (104.5 g.) is allowed to drop on to anhydrous sodium sulphate (90 g.) in a flask fitted with a condenser and arranged for vacuum distillation. The flask is kept at 155—165° (optimum temp.) by an oil-bath and the pressure maintained at 20—45 mm. The mixture enters through a capillary tube at about 120—150 drops per minute. The time of distillation for the above quantities is 1 to 1½ hours. The ethyl sulphate is separated from the alcohol in the distillate, washed with dilute sodium carbonate and then with cold water, and dried over anhydrous sodium sulphate. The product (32.6 g.) is almost pure and is neutral to litmus. A. C.

**Action of Mixed Dialkyl Sulphates on Mixed Organo-magnesium Compounds.** L. BERT (*Compt. rend.*, 1924, **178**, 1182—1184).—Methyl, propyl, isopropyl, *n*-butyl, and isoamyl ethyl sulphates were prepared by the action of ethyl chlorosulphonate on the corresponding sodium alkoxide. Bushong's observations (A., 1903, i, 732) on the isopropyl and isoamyl compounds were confirmed and the following constants are given for the methyl compound: b. p. 85°/15 mm.,  $d^{16.5}$  1.228,  $n_D^{16.5}$  1.399. *Ethyl propyl sulphate* is a colourless oil, b. p. 107—108°/18 mm.,  $d^{16.5}$  1.140,  $n_D^{16.5}$  1.411; *ethyl n-butyl sulphate*, a colourless oil, b. p. 117—118°/20 mm.,  $d^{18}$  1.112,  $n_D^{18}$  1.415. Magnesium phenyl bromide reacts with all the above substances, yielding toluene in the case of methyl ethyl sulphate and ethylbenzene with the other four. H. J. E.

**Explosive Decomposition of Glyceryl Trinitrate.** AUDIBERT (*Compt. rend.*, 1924, **178**, 1167—1169).—The decomposition of glyceryl trinitrate on explosion takes place in two stages; the first (explosive reaction) is represented by the equation  $C_3H_5O_9N_3 \rightarrow 2CO + CO_2 + 2.5H_2 + 1.5N_2O + 1.75O_2 + 21 \text{ cal.}$ , whilst the second (residual reaction) gives rise to the final system,  $3CO_2 + 2.5H_2O + 1.5N_2 + 0.25O_2$ , with a further evolution of 319 cal. Neither reaction is instantaneous; completion of the second depends on the conditions of reaction. H. J. E.

**Action of some Halohydrins on Normal Sodium Phosphate in Aqueous Solution and on some Glycerophosphates.** O. BAILLY and J. GAUMÉ (*Compt. rend.*, 1924, **178**, 1191—1193).—Similar results to those obtained with the chlorohydrin of glycerol and normal sodium phosphate (Bailly, A., 1916, i, 113) were observed in the cases of the bromohydrin and the iodohydrin, but the two stages of the reaction were more clearly differentiated. The authors have prepared the *normal glycerophosphates* of sodium, potassium, and strontium and the *acid glycerophosphates* of barium, strontium, and calcium. H. J. E.

**Ease of Oxidation of Organic Substances at the Ordinary Temperature.** M. GOMPÉL, A. MAYER, and R. WURMSER (*Compt. rend.*, 1924, **178**, 1025—1027).—Solutions of formic, acetic, propionic, oxalic, succinic, citric, lactic, and pyruvic acids, glycine,

alanine, and dextrose when shaken with blood charcoal at 40° evolve carbon dioxide. The rate of evolution of the gas is considerably affected by the presence and concentration of hydrogen ions, especially in the case of the acids of greater dissociation constant. The authors point out the biological significance of their observations.

H. J. E.

**Mechanism of Oxidation Processes. VII. H. WIELAND** (*Annalen*, 1924, 436, 229—262).—I. [With A. WINGLER].—**Catalytic Fission and Oxidation of Keto-acids.**—Under the influence of palladium black, vegetable charcoal, and animal tissue, dilute aqueous solutions of keto-acids are hydrolysed with loss of carbon dioxide (cf. A., 1915, i, 354, 1046; 1916, i, 772). In this way, oxalacetic acid yields pyruvic acid, pyruvic acid gives acetic acid, malic acid yields acetic acid, and  $\alpha$ -keto- $\beta$ -phenylpropionic acid gives phenylacetic acid, benzaldehyde, benzoic acid, and oxalic acid. The reaction takes place in an atmosphere of nitrogen, provided that a hydrogen acceptor such as methylene-blue or *p*-benzoquinone is present. Traces of acetaldehyde were detected in experiments with pyruvic acid and washed animal tissue. The mechanism of the action is discussed.

II. [With H. LÖRENSKIÖLD].—**Mode of Reaction of Hydrogen Peroxide. Critical Experiments on Thunberg's Theory of Carbon Dioxide Assimilation** (cf. A., 1923, i, 1271).—On distilling hydrogen peroxide with pure lead carbonate the authors could detect no formaldehyde in the distillate, and Thunberg's results are considered to be due to the presence of traces of acetate in his lead carbonate. Only the slightest traces of formaldehyde were formed when formic acid was distilled with hydrogen peroxide, and the observation of Wislicenus (A., 1918, i, 472) that formic acid is formed in the oxidation of bicarbonates with hydrogen peroxide has been verified under conditions precluding the possibility of formic acid being introduced from atmospheric sources.

The results obtained by Dakin (A., 1908, i, 74) and Neuberg (A., 1915, i, 214, 215) in the oxidation of organic acids with hydrogen peroxide have been confirmed, but it is shown that the presence of ferrous iron is not essential. Comparative experiments with acetic acid and glycollic acid showed that formaldehyde was formed very much more rapidly in the latter case, and the view is expressed (cf. A., 1901, i, 310) that glycollic acid is the first stage in the oxidation of acetic acid with hydrogen peroxide. [Cf. i, 612.]

Glyoxylic acid, on oxidation with the same reagent, yields carbon dioxide and formic acid (cf. A., 1904, i, 474). In the case of butyric, crotonic, and  $\beta$ -hydroxybutyric acids, in addition to the aldehyde, considerable quantities of acetone are formed. Cinnamic acid yields chiefly the aldehyde; the saturated acid yields the aldehyde and ketone in approximately equal amounts. Malic acid, like succinic acid, is oxidised to acetic acid.

III. [With H. RAU].—**Decomposition of Dihydroxyethyl Peroxide with Alkali** (cf. A., 1923, i, 650).—The decomposition of dihydroxyethyl peroxide with sodium hydroxide in the presence

of silver below  $0^\circ$  follows the course:  $\text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{O}\cdot\text{CHMe}\cdot\text{OH} \rightarrow 2\text{Me}\cdot\text{CO}_2\text{H} + \text{H}_2$ , to the extent of 40%, whereas at  $15^\circ$  only 30% of the peroxide decomposes in this way. The alternative decomposition:  $\text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{O}\cdot\text{CHMe}\cdot\text{OH} \rightarrow \text{Me}\cdot\text{CO}_2\text{Na} + \text{CHO}\cdot\text{Me} + 2\text{H}_2\text{O}$ , has therefore the greater temperature coefficient. [Cf. also A., 1920, i, 709.] R. B.

**Purification of Acetic Acid.** K. J. P. ORTON and A. E. BRADFELD (*J. Chem. Soc.*, 1924, **125**, 960—961).—Acetic acid is best purified by distillation with chromium trioxide (2 g. per 100 c.c. of acid); the first 5% is rejected. The main fraction (85—90%), if distilled through an 8-pear still-head, melts at  $16.2$ — $16.4^\circ$ , and is free from impurities which react with bromine. F. G. M.

**Identity of Phocenic and Valeric Acids.** E. ANDRÉ (*Compt. rend.*, 1924, **178**, 1188—1191).—Synthetic and natural valeric acids were found to have boiling points almost identical with those of specimens of phocenic acid obtained from dolphin-head oil and from porpoise fat. Amides of all four specimens exhibited almost identical melting points, which were unchanged on mixing the substances in pairs. The statement that phocenic acid is a mixture of butyric and caproic acids (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," 5th ed., i, 152) is thus regarded as incorrect. H. J. E.

**$\alpha\beta$ -Dihalogenated Amylacrylic Acids.** C. MOUREU and M. H. SCHINDLER (*Bull. Soc. chim.*, 1924, [iv], **35**, 171—178).— $\alpha\beta$ -Dibromoamylacrylic acid [ $\alpha\beta$ -dibromo- $\Delta^a$ -octenoic acid], a colourless liquid which will not crystallise, b. p.  $144^\circ$  (3 mm.),  $d_4^{18}$  1.6444,  $n_D^{19.5}$  1.5320, is prepared by direct addition of bromine in chloroform solution to amylpropionic acid. The *potassium*, *silver*, and two unstable *lead* salts,  $(\text{C}_5\text{H}_{11}\cdot\text{CBr}\cdot\text{CBrCO}_2)_2\text{Pb}$  and  $(\text{C}_5\text{H}_{11}\cdot\text{CBr}\cdot\text{CBrCO}_2)_2\text{Pb}\cdot\text{PbO}$ ,

are described.  $\alpha\beta$ -Di-iodo- $\Delta^a$ -octenoic acid, white needles, m. p.  $47.5$ — $49.5^\circ$ , decomp.  $100^\circ$ , is prepared by direct addition of iodine to amylpropionic acid, excess halogen being removed by sulphur dioxide. The *potassium* and *lead* salts are described; neither is very stable in solution. A basic *lead* salt was also obtained. The dihalogenated amylic acids are less stable than the corresponding halogenated acrylic and crotonic acids. Attempts to separate the acids into isomerides by fractional distillation of the dibromo acid, fractional crystallisation of the di-iodo acid, and fractional crystallisation and precipitation of the salts all failed. The dibromo acid may be a mixture of two isomerides, one being in excess, and the crystals of the di-iodo acid may be a pure form.

E. E. T.

**Action of Carbonyl Chloride on Metallic Derivatives of Monosubstituted Acetylenes.** I. Action of Carbonyl Chloride on Sodium *tert*-Butylacetylide. M. P. IVITZKY (*Bull. Soc. chim.*, 1924, [iv], **35**, 357—360).—The sodium derivative of *tert*-butylacetylene reacts readily with carbonyl chloride in ethereal solution yielding *trimethyltetrollyl chloride* [ $\gamma\gamma$ -dimethyl-

$\Delta^{\alpha}$ -*pentinoyl chloride*],  $\text{CMe}_3\cdot\text{C}:\text{C}\cdot\text{COCl}$ , b. p. 46.5—47.5°/16 mm., which, on hydrolysis, yields  $\gamma\gamma$ -dimethyl- $\Delta^{\alpha}$ -pentinenoic acid, b. p. 106—107°/10 mm., m. p. 48—49°. The acid chloride can also react with a second molecule of the acetylide, and the unsaturated ketone, *bis- $\gamma\gamma$ -dimethyl- $\Delta^{\alpha}$ -butinenyl ketone*,  $(\text{CMe}_3\cdot\text{C}:\text{C})_2\text{CO}$ , colourless crystals, m. p. 66.5°, is obtained as a by-product in the reaction. If the carbonyl chloride is added at once to the sodium *tert.*-butylacetylide, a violent reaction takes place, and after decomposition of the product with water, *tri- $\gamma\gamma$ -dimethyl- $\Delta^{\alpha}$ -butinenyl carbinol*,  $(\text{CMe}_3\cdot\text{C}:\text{C})_3\text{C}\cdot\text{OH}$ , colourless crystals, m. p. 102.5°, is obtained. By the action of sodium *tert.*-butylacetylide on acetone a substance, m. p. 102.5°, was obtained in almost quantitative yield.

R. B.

**Bauer Oil, the Higher-boiling Residue from Molasses Fusel Oil. A Source of Capric [Decoic] Acid.** C. S. MARVEL and F. D. HAGER (*J. Amer. Chem. Soc.*, 1924, **46**, 726—730).—A dark reddish-brown oil, b. p. 130—235°/35 mm., obtained as a residue during the distillation of molasses fusel oil, consisted of the ethyl esters of decoic, lauric, myristic, and palmitic acids, and a little unsaponifiable matter. This forms an additional source for the preparation of decoic acid, which occurs only in small quantities in the common fats. [Cf. *B.*, 1924, 438.]

C. J. S.

**Glycerides of Fats and Oils. XI. Glycerides of Palm Kernel Oil.** A. BÖMER and K. SCHNEIDER (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 61—89).—Five almost pure mixed glycerides were isolated from a sample of palm kernel oil by repeated fractional crystallisation from acetone, and were identified as decoylomyristolein, myristodilaurin, laurodimyristin, palmitodimyristin, and myristodipalmitin. The first two of these glycerides were present in considerable amount, the third only in small amount, and the last two in very small amount, comprising the most difficultly soluble glycerides in the oil. It is very unlikely that stearic acid is present in the glycerides of palm kernel oil, and hexoic acid was not present in the sample investigated. It is uncertain whether decoic acid was present or not.

H. C. R.

**Chemical Composition of Sesamé Oil.** G. S. JAMIESON and W. F. BAUGHMAN (*J. Amer. Chem. Soc.*, 1924, **46**, 775—778).—Sesamé oil having the characteristics  $d_{25}^{25}$  0.9187,  $n_D^{20}$  1.4731, acid value 1.4, iodine value (Hanus) 110.8, saponification value 189.3, unsaponifiable matter 1.73%, acetyl value 9.8, Reichert-Meissl value 0.11, Polenske value 0.15, was found to contain the glycerides of the following acids in the proportions indicated: oleic (48.1%), linolic (36.8%), palmitic (7.7%), stearic (4.6%), arachidic (0.4%), and lignoceric (0.04%).

C. J. S.

**Oils and Fats from the Seeds of Indian Forest Plants. VI. Oil from the Seeds of *Aleurites montana*, Wilson.** R. M. PARKER, M. G. RAU, W. A. ROBERTSON, and J. L. SIMONSEN (*Indian Forest Records*, 1923, **10**, 11—22).—The oil had the following characters:  $d_{15}^{15}$  0.9467,  $n_D^{15}$  1.494, acid value 3.4, saponification

value 203, unsaponifiable matter 0.6%, iodine value 141.4, insoluble fatty acids 94% (solidifying point 54—54.5°). The principal fatty acid present in the oil was  $\beta$ -elæostearic acid (m. p. 73°). The  $\alpha$ -isomeride was apparently completely absent. The  $\beta$ -elæostearic acid was brominated in chloroform solution and an unstable *dibromo* derivative (m. p. 95°) obtained. On bromination in acetic acid solution, a mixture of a solid and a liquid tetrabromo acid was obtained. The solid product, needles, m. p. 115°, was not identical with the tetrabromo acid from linolic acid. The liquid acids present in the oil were identified as oleic and linolic acids; linolenic acid was absent.

H. C. R.

### Oils and Fats from the Seeds of Indian Forest Plants.

**VII. Oil from the Seeds of *Salvia plebeia*, R. Br.** M. G. RAU and J. L. SIMONSEN (*Indian Forest Records*, 1924, **10**, 23—26).—The ground seeds on extraction with cold benzene gave 11% of an oil having the following characters:  $d_{20}^{20}$  0.934,  $n_D^{20}$  1.4832, acid value 6.0, saponification value 195.0, unsaponifiable matter 0.02%, acetyl value nil, iodine value 131.1, Reichert Meissl value 1.3, solidification point of the insoluble fatty acids 10.5—11°. Stearic acid was the only saturated acid present. Linolenic acid, linolic acid, and oleic acid were identified in the oil.

H. C. R.

**Tung Oil.** A. EIBNER, O. MERZ, and H. MUNZERT (*Chem. Umschau*, 1924, **31**, 69—82).—Tung oil contains 75% of glyceryl  $\alpha$ -elæostearate, which changes under the influence of light into the solid geometrical isomeride, glyceryl  $\beta$ -elæostearate. Both the  $\alpha$ - and the  $\beta$ -triglycerides increase in weight at about the same rate when exposed to the air in thin films. After standing for 10 months in a closed brown glass bottle,  $\beta$ -elæostearin became insoluble in acetone and no longer melted, but charred at about 265°. Both  $\alpha$ - and  $\beta$ -elæostearic acids, m. p. 48° and 72°, respectively, were prepared from tung oil which had stood for some time, by extracting with ethyl alcohol and fractionally crystallising the extract from this solvent at about 0°. Another acid (m. p. 106.5°), giving the reaction of azelaic acid with ferric and mercuric chlorides, was obtained from the residue insoluble in cold alcohol, and is presumably a cleavage product obtained from elæostearic acid. The difference in the drying properties of  $\alpha$ - and  $\beta$ -elæostearic acids was investigated by exposing thin layers of the acids to the air. After 8—10 days, the  $\alpha$ -acid was transformed into a clear yellow syrup, whilst the  $\beta$ -acid remained unchanged for 14 days and was only transformed into a clear yellow, viscous syrup after 4 weeks' exposure. Only two of the three possible geometrical isomerides of elæostearic acid have been obtained. It is considered that the  $\alpha$ -acid is probably the *cis-cis* form and the  $\beta$ -acid the *cis-trans* form. Bromination of both  $\alpha$ - and  $\beta$ -acids yields the same tetrabromide (m. p. 114°). The transformation of the  $\alpha$  into the  $\beta$  geometrical isomeride, on treatment with bromine, is considered to be a peculiarity confined to compounds containing two double linkings separated by two methylene groups, a constitution which explains the high reactivity of elæostearic

y\*

acid. Evidence is adduced in favour of the view that the conversion of the  $\alpha$ - and the  $\beta$ -acid plays very little part in the mechanism of the drying of tung oil, which appears to be a colloidal phenomenon involving transformation from the sol to the gel form rather than a case of molecular polymerisation. H. C. R.

**Hydrate of Bismuth Lactate.** E. MOLES and R. PORTILLO (*Anal. Fis. Quím.*, 1924, **22**, 133—143).—Bismuth lactate obtained by the action of lactic acid on bismuth hydroxide contains water of hydration corresponding to the formula  $C_6H_9O_6Bi \cdot 7Aq$ . In solution, it behaves as a non-electrolyte, as is shown by cryoscopic and conductivity determinations. The solution, on keeping, deposits the anhydrous salt which has a smaller solubility than the hydrated salt. The reaction appears to be autocatalytic.

G. W. R.

**Sebacic Acid.** E. BÆDTKER (*J. Pharm. Chim.*, 1924, **29**, 313—319).—Ricinoleic acid, when distilled with an excess of sodium hydroxide, gives sebacic acid, octyl alcohol, methyl hexyl ketone, and a viscous, brown residue. From the latter have now been isolated stearic acid, m. p.  $69.2^\circ$ , an acid, m. p.  $81$ — $82^\circ$ , which is either ricinic acid,  $C_{18}H_{34}O_3$ , or hydroxystearic acid, undecenoic acid,  $C_{11}H_{20}O_2$  (formed by the pyrogenic decomposition of the ricinoleic acid), and finally an asphaltic resin. The maximum yield of sebacic acid (33 g. from 100 g. of ricinoleic acid) is obtained by heating sodium ricinoleate with one equivalent of sodium hydroxide.

F. G. M.

**Resolution of Racemic Malic Acid and the Preparation of *d*-Malic Acid.** E. DARMOIS and J. PERIN (*Bull. Soc. chim.*, 1924, [iv], **35**, 353; cf. A., 1923, i, 299).—The *d*-malic acid obtained from active chlorosuccinic acid by treatment with silver nitrate according to Walden's process is now shown to be partly racemised, about 25% of the product consisting of the *l*-acid. By the addition of ammonium molybdate, it is possible to isolate successively the lævo- and dextro-rotatory forms of the ammonium dimolybdomalate,  $2MoO_3 \cdot C_4H_6O_5 \cdot 2NH_3$ , the lævo-form crystallising first. Racemic ammonium dimolybdomalate does not appear to exist at the experimental temperatures,  $16$ — $20^\circ$ , the crystals obtained when the compound is prepared from *r*-malic acid consisting of the *d*- and *l*-dimolybdomalate in equal proportions. A satisfactory method of converting the dimolybdomalonates into the corresponding malic acids has not yet been found, the product obtained from ammonium *l*-dimolybdomalonate being *l*-malic acid and not the *d*-form as was expected.

R. B.

**Resolution of Inactive Malic Acid into Optically Active Forms.** H. D. DAKIN (*J. Biol. Chem.*, 1924, **59**, 7—12).—From a solution of cinchonine and inactive malic acid in molecular proportions in hot methyl alcohol or acetone, cinchonine *l*-malate separates in very good yield, and may be completely purified by recrystallisation from methyl alcohol, or from water; from the latter solvent it separates in clear, hard prisms, m. p.  $197$ — $198^\circ$ ,



$[\alpha]_D^{19} +146^\circ$  (in water). The methyl alcohol or acetone filtrate from the lævo salt is concentrated and water added occasionally; the residue is allowed to crystallise from water, when *cinchonine d-malate* ( $+2H_2O$ ) is obtained as fine rosettes of clear, silky, prismatic needles, m. p. (hydrated)  $106^\circ$ , (anhydrous)  $125-135^\circ$ ,  $[\alpha]_D^{18} +153^\circ$  (in water). On decomposition of the cinchonine salts with ammonia, *d-malic acid*, m. p.  $99-100^\circ$ ,  $[\alpha]_D^{18} +2.33^\circ$ , and *l-malic acid*, m. p.  $99-100^\circ$ ,  $[\alpha]_D^{18} -2.31^\circ$ , were obtained.

W. O. K.

**Phosphor-Emetic [Potassium Phosphoryl Tartrate].**

I. H. STERNLIEB (*Bull. Acad. Sci. Roumaine*, 1923, 8, 211—214; cf. Costeanu, following abstract).—Crystals of potassium phosphoryl tartrate,  $CO_2K \cdot CH(O \cdot PO) \cdot CH(OH) \cdot CO_2H \cdot 0.5H_2O$ , are prepared by dissolving 2 parts of phosphorus trioxide and 3 parts of potassium hydrogen tartrate in 16 parts of water and, with constant stirring, heating to the boiling point. The sparingly soluble, small, white crystals, having  $[\alpha]_D^{20} +80.62^\circ$ , which separate, lose the water of crystallisation at  $110^\circ$ , and at  $200^\circ$  form a hygroscopic anhydride, m. p.  $242^\circ$ .

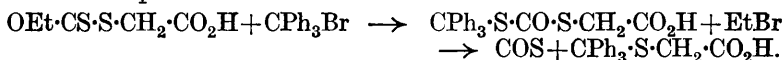
S. K. T.

**Emetics [Cæsium Antimonyl Tartrate].**—N. D. COSTEANU (*Bull. Acad. Sci. Roumaine*, 1923, 8, 215—218; cf. Sternlieb, preceding abstract).—Three methods are given for the preparation of the hitherto unknown *cæsium emetic* (*cæsium antimonyl tartrate*),  $CO_2Cs \cdot CH(O \cdot SbO) \cdot CH(OH) \cdot CO_2H \cdot 0.5H_2O$ . (1) By the action of diantimonyl tartaric acid (prepared by dissolving freshly-precipitated antimony oxide in cold tartaric acid solution and precipitating with alcohol) on normal cæsium tartrate solution, partly precipitating with alcohol, warming the mixture and cooling again. (2) By the interaction of cæsium chloride and silver antimonyl tartrate. (3) By boiling a solution of cæsium hydrogen tartrate with antimony oxide.

Cæsium antimonyl tartrate forms transparent, orthorhombic prisms,  $d$  2.27,  $[\alpha] +79.21^\circ$ , loses its water of crystallisation at  $100^\circ$ , and, at  $200^\circ$ , forms an anhydride. The aqueous solution dissolves iodine, any remaining undissolved assuming a golden colour; it yields precipitates with silver and lead nitrates, ferric chloride, and mineral acids.

S. K. T.

**Action of Triphenylmethyl Chloride on Free Sulphydro Groups.** E. BILMANN and N. V. DUE (*Bull. Soc. chim.*, 1924, [iv], 35, 384—390; cf. A., 1905, i, 625; 1906, i, 625; 1908, i, 142).—The action of triphenylmethyl chloride or bromide on xanthyl-acetic acid proceeds in accordance with the scheme:



The following compounds have been obtained: *Triphenylmethylthiolacetic acid*,  $CPh_3 \cdot S \cdot CH_2 \cdot CO_2H$ , brilliant pointed prisms, m. p.  $162.5-163^\circ$ , which is not decomposed by warm dilute sodium hydroxide, but on treatment with bromine yields dithiolacetic acid and triphenylmethyl bromide;  $\alpha$ -*triphenylmethylthiolpropionic*  $y^* 2$

*acid*, microscopic white crystals, m. p.  $151^{\circ}$ ;  $\beta$ -*triphenylmethylthiolpropionic acid*, white, microscopic crystals, m. p.  $208-209^{\circ}$ ; *triphenylmethylthiolsuccinic acid*, fine octahedra, m. p.  $186-187^{\circ}$  (decomp.).

In a similar way, the action of triphenylmethyl chloride on free xanthic acid in benzene solution yields triphenylmethyl xanthate,  $\text{CPh}_3\cdot\text{S}\cdot\text{CS}\cdot\text{OEt}$ , large, yellow crystals, m. p.  $139^{\circ}$ , in a 97% yield. Free thiobenzoic acid in toluene solution gives triphenylmethyl thiobenzoate,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{S}\cdot\text{CPh}_3$ , m. p.  $187.5-188^{\circ}$ , in 85% yield (cf. A., 1901, i, 636; 1913, i, 1335) and thiocyanic acid in ethereal solution gives an 89% yield of triphenylmethyl thiocyanate,  $\text{NCS}\cdot\text{CPh}_3$ , m. p.  $137.5^{\circ}$ . R. B.

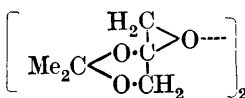
**Alleged Reduction of Carbon Dioxide to Formaldehyde by Hydrogen Peroxide, and the Assimilation Hypothesis of T. Thunberg.** A. BACH and M. MONOSSON (*Ber.*, 1924, 57, [B], 735—738; cf. A., 1923, i, 1271).—The production of traces of formaldehyde on distilling basic lead carbonate with hydrogen peroxide was confirmed. The authors show, however, that the formaldehyde is not produced from the lead carbonate itself, but from the small amounts of organic preservatives (e.g., acetanilide) used to stabilise the hydrogen peroxide, which are catalytically oxidised by the latter in presence of lead. Control experiments using purified materials gave completely negative results, whilst the addition of a little acetanilide led at once to the production of formaldehyde. The addition of barbituric acid, however, gave no trace of formaldehyde. Thunberg's assimilation hypothesis is therefore devoid of foundation. [Cf. i, 606.] F. A. M.

**Electrolytic Oxidation of Formaldehyde.** C. DEL FRESNO (*Anal. Fis. Quím.*, 1924, 22, 121—132; cf. Müller and Hochstetter, A., 1914, ii, 615; Müller, A., 1920, i, 709).—The author has studied the electrolytic oxidation of formaldehyde in solutions of sodium hydroxide with electrodes of platinum, copper, and silver, respectively. Curves are drawn showing the relation between anode potential and current intensity. The results are in agreement with the theories of Müller. In each case where the anode potential exceeds a certain value the current intensity decreases, and at the same time there is a discontinuity in the potential, which becomes more positive. The passage of a current begins at much lower potentials in alkaline solutions containing formaldehyde than in solutions of sodium hydroxide alone. With electrodes of copper and silver, oxidation of formaldehyde occurs accompanied by evolution of hydrogen (dehydroxidation) at low potentials, whilst at high potentials, as is the case also with platinum electrodes, oxidation occurs without evolution of hydrogen. The mechanism of the oxidation is discussed. G. W. R.

**Production of Acetone by the Action of Potassium Acetate on Acetic Anhydride.** E. LUCE (*Bull. Soc. chim.*, 1924, [iv], 35, 179—183).—The amount of acetone produced by refluxing acetic anhydride and potassium acetate for 30 hours at  $170-180^{\circ}$

is not influenced by the presence of acetic acid. The yield of acetone is small, owing to polymerisation and to loss through carrying away by the carbon dioxide produced. The latter is prevented by special apparatus, and the yield then becomes 24% of the theoretical. No carbon monoxide is formed; sodium acetate cannot replace the potassium salt (cf. T., 1886, 49, 317). Since the reaction is slow and at first no carbon dioxide is evolved, elevation of the temperature simply causing acetic anhydride to distil over; it probably follows the course  $\text{Ac}_2\text{O} + \text{Me} \cdot \text{CO}_2\text{K} = (\text{AcO})_2\text{CMe} \cdot \text{OK} = \text{COMe}_2 + \text{CO}_2 + \text{Me} \cdot \text{CO}_2\text{K}$ . When potassium acetate is replaced by the butyrate, acetone and methyl propyl ketone are obtained. E. E. T.

**Dihydroxyacetone.** H. O. L. FISCHER and H. MILDBRAND (*Ber.*, 1924, 57, [B], 707—710).—Dihydroxyacetone has been prepared in the unimolecular form [needles or rhombs, m. p. (indefinite) 65—71°] by the distillation of bimolecular dihydroxyacetone under greatly diminished pressure and immediate cooling of the distillate. It is converted by acetic anhydride and pyridine into the unimolecular diacetate, m. p. 42—45 [Dimroth and Schweizer (*A.*, 1923, i, 745) give m. p. 46—47°]. With acetone in the presence of anhydrous copper sulphate, it yields the corresponding bimolecular *diisopropylidene ether*, needles, m. p. 165.5—167.5°, to which the annexed constitution is ascribed. Freshly distilled dihydroxyacetone is converted by



ethyl orthoformate in alcoholic solution in the presence of ammonium chloride into the corresponding *ethylcycloacetal*,  $\left[ \begin{array}{c} \text{OH} \cdot \text{CH}_2 \cdot \text{C}(\text{OEt}) \cdot \text{O} \cdots \\ | \\ \text{CH}_2 \end{array} \right]_2$ , m. p. 126°. H. W.

**Pennone** [ $\beta\beta\gamma\gamma$ -Tetramethylpentane- $\delta$ -one]. R. LOCQUIN and W. SUNG (*Compt. rend.*, 1924, 178, 1179—1182; cf. A., 1923, i, 433, also Richard, A., 1911, i, 6).—In dehydrating  $\beta\beta\gamma\delta$ -tetramethylpentane- $\gamma\delta$ -diol, only 6—7% of the substance is transformed into hexamethylacetone. The chief product (76%) is  $\beta\beta\gamma\gamma$ -tetramethylpentane- $\delta$ -one,  $\text{C}_9\text{H}_{18}\text{O}$ , m. p. 63—64°, b. p. 167.5°/746 mm. (oxime, m. p. 125°, b. p. 215—220°; semicarbazone, m. p. 207—208°). On reduction by sodium and alcohol, the ketone, which the authors designate as *pennone*, yields the corresponding secondary alcohol, *pennol*, m. p. 50°, b. p. 179—180°. Oxidation of the ketone or alcohol yields  $\alpha\alpha\beta\beta$ -tetramethylbutyric acid, m. p. 200° (ethyl ester, a mobile liquid, b. p. 168—169°/746 mm.). H. J. E.

### Reactions Relating to Carbohydrates and Polysaccharides.

**VIII. Electrolytic Reduction of Carbonyl Derivatives.** H. HIBBERT and R. R. READ (*J. Amer. Chem. Soc.*, 1924, 46, 983—999).—Various ketones and aldehydes were reduced by an electrolytic method in order to compare the activities of the carbonyl group. The carbonyl derivative was added to an electrolyte (usually 2N-sulphuric acid with or without alcohol) in the cathode compartment, and caused a fall in the cathode potential varying with the ease or difficulty with which the substance underwent

reduction. In the case of aldehydes, this depended on (a), whether saturated or unsaturated: the fall was 0.12 volt for *n*-butaldehyde and 0.58 volt for crotonaldehyde; (b) the length of the chain; (c) the spatial relation of the atoms: the values for acetaldehyde, propionaldehyde, isobutaldehyde, and *n*-butaldehyde were 0.30, 0.30, 0.17, 0.12 volt, respectively; (d) character of groups in molecule: substitution of hydrogen by hydroxyl is shown by comparing *n*-butaldehyde 0.12 volt, with acetaldol, 0.25 volt. Ketones brought about a much smaller effect: dimethyl, methyl ethyl, and methyl propyl ketone showed 0.06, 0.06, and 0.04 volt, respectively. To compare the "current efficiencies," which were found to run parallel to the lowering of cathode potentials, the hydrogen absorbed was plotted against the total hydrogen as measured in a coulombmeter in series with the experimental cell. The reduction products of crotonaldehyde were found to be different from those obtained by chemical reduction. The main fraction consisted of 2:3-dimethyl- $\Delta^5$ -cyclopentene-1-aldehyde: 
$$\begin{array}{c} \text{CH}_2\text{---CH} \\ | \qquad | \\ \text{CHMe}\cdot\text{CHMe} \end{array} \text{>C}\cdot\text{CHO}, \text{ b. p.}$$

170—175° (*semicarbazone*, white needles, m. p. 185—187°). Little or no dipropenyl glycol was formed. Dextrose could not be reduced to mannitol. The aldehydes investigated (apart from crotonaldehyde) were in all cases reduced to the corresponding alcohols, acetaldol to a glycol. The ketone reduction products were oily and had a pungent odour; they were not isolated. It is concluded that in the case of carbonyl derivatives such as the carbohydrates, anhydro-sugars, and polysaccharides, the determination of the two factors described results in values lying too close together to be of service as a means of distinguishing between the residual valencies of the carbonyl groups; and, further, that refinements in the measurements of the factors appear of little use owing to the limits imposed by the non-reproducibility of the cathode. A. C.

**Course of the Mutarotation of Dextrose.** H. v. EULER, K. MYRBÄCK, and E. RUDBERG (*Ark. Kemi, Min., Geol.*, 1923, 8, No. 28, 1—9).—According to Euler and Hedelius (A., 1920, i, 712), the reaction constant for this change is  $6 \times 10^{-3}$  in a solution having  $p_H$  5 at 20°, and measurements made by Michaelis give the value  $6.6 \times 10^{-13}$  for the acid dissociation of dextrose at the same temperature. From these results, the concentration of the intermediate product or of the reacting ions is calculated to be  $3.7 \times 10^{-8}$ . Since Michaelis employed dextrose solutions containing  $\alpha$ - and  $\beta$ -dextroses in equilibrium in the known proportions, the authors have carried out experiments to ascertain if  $\alpha$ -dextrose behaves, with respect to salt-formation, differently from  $\beta$ -dextrose or from the equilibrated mixture; no appreciable difference is found in this regard. Further, the degree of hydrolysis of the dextrose-alkali salt varies inconsiderably with the temperature. [Cf. Euler and Rudberg, A., 1923, ii, 840.] T. H. P.

**Action of Guanidine on Dextrose in the Presence and Absence of Oxygen.** E. J. WITZEMANN (*J. Amer. Chem. Soc.*, 1924, 46, 790—794).—Morrell and Bellars (T., 1907, 91, 1010) have shown

that guanidine is comparable with sodium and potassium hydroxides with regard to the velocity of hydrolysis of ethyl acetate. The results now described show that guanidine is also comparable with these bases in its action on dextrose both in the presence and absence of air or hydrogen peroxide. Guanidine causes polymerisation accompanied by yellowing more rapidly than potassium hydroxide, but this action is much less influenced by temperature than in the instance of the latter base. C. J. S.

**Optical Behaviour of  $\beta$ -Anhydroglucose, of  $\beta$ -Anhydrogluconic Acid, and of  $\beta$ -Anhydromannonic Acid.** P. A. LEVENE (*J. Biol. Chem.*, 1924, 59, 135—139).—Stereochemical considerations lead to the expectation that epichitose ( $\beta$ -anhydroglucose) would not be able to form an oxide ring structure, and that it therefore exists in the aldehydic form. It is actually found that it is decolorised very rapidly by permanganate. Chitonic acid and chitaric acid do not exhibit mutarotation, probably because, likewise, lactone formation is not possible. W. O. K.

**Preparation of  $\alpha$ -Mannose. II.** P. A. LEVENE (*J. Biol. Chem.*, 1924, 59, 129—134).—A solution of mannose (100 g.) in water (25 c.c.) is cooled to 0°, and cooled glacial acetic acid (400 c.c.) is added. The crystals of  $\alpha$ -mannose which separate are filtered after 4—5 hours, and subsequently extracted eight times with alcohol (80% by weight, 200 c.c., for each 100 g. of sugar). From optical observations on the mutarotation of  $\alpha$ -mannose it is found that  $K_1 + K_2 = 0.0054$ , in 80% alcohol at 25°, and 0.0029 in water at 1.5°, where  $K_1$  is the rate of conversion of the  $\alpha$ - into the  $\beta$ -form, and  $K_2$  the rate of the reverse reaction. From similar observations on  $\beta$ -mannose,  $K_1 + K_2 = 0.0029$ , in water at 1.5°, and 0.00575 in 80% alcohol at 25°. Measurements of solubility give  $K_1 = 0.00193$  and  $K_2 = 0.00041$ . These results elucidate the discrepancy previously reported (Levene, this vol., i, 15). W. O. K.

**$\alpha$ -Mannose Penta-acetate.** P. A. LEVENE (*J. Biol. Chem.*, 1924, 59, 141—144).—Acetylation of  $\alpha$ -mannose in pyridine with acetic anhydride results in the formation of  $\alpha$ -mannose penta-acetate, m. p. 64°,  $[\alpha]_D^{17} + 57.6^\circ$ , identical with the penta-acetate obtained by Hudson and Dale (A., 1915, i, 502) by the action of zinc chloride on  $\beta$ -mannose penta-acetate. W. O. K.

**Three Isomeric Crystalline Tetra-acetylmethyl-*d*-mannosides.** J. K. DALE (*J. Amer. Chem. Soc.*, 1924, 46, 1046—1051).— $\alpha$ -Tetra-acetylmethyl-*d*-mannoside, m. p. 65°,  $[\alpha]_D^{20} + 49.1^\circ$ , was prepared by acetylating methyl-*d*-mannoside with acetic anhydride and sodium acetate.  $\beta$ -*d*-Mannose penta-acetate dissolved in glacial acetic acid saturated with hydrobromic acid yields a syrupy product containing bromine, which is converted by silver carbonate in the presence of methyl alcohol into  $\gamma$ -tetra-acetylmethyl-*d*-mannoside, m. p. 105°,  $[\alpha]_D^{20} - 26.6^\circ$ . This compound possesses properties not generally characteristic of the acetylated glucosidic derivatives of the sugars. When subjected to alkaline hydrolysis, only three out of the four acetyl groups are removed,

although the whole four are removed by acid hydrolysis. On treating its solution in methyl alcohol with hydrogen chloride, a rapid change in rotation occurs and an apparent equilibrium is reached in a few minutes at  $[\alpha]_D^{20} + 10.4^\circ$ . The solution at this stage was neutralised, and yielded a third isomeride,  $\beta$ -*tetra-acetyl-methyl-d-mannoside*, m. p.  $162^\circ$ ,  $[\alpha]_D^{20} - 47.0^\circ$ . Although the yield was only 7% of the theoretical, attempts to extract further crystalline substances were unsuccessful.

The close parallel in specific rotation and behaviour on hydrolysis between these isomerides and the three crystalline triacetylmethyl-*l*-rhamnosides recently prepared by Fischer, Bergmann, and Rahe (A., 1921, i, 94), is pointed out. A. C.

**Isomeric Diacetone-mannoses [Mannose Diisopropylidene Ethers].** P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1924, 59, 145—149).—Methylation of diacetone-mannose by methyl iodide and silver oxide resulted in the formation of a *methyl diacetone-mannose*, b. p.  $115^\circ/1.2$  mm.,  $[\alpha]_D^{20} + 23^\circ$  (in *s*-tetrachloroethane), which on hydrolysis by alcoholic hydrochloric acid yields mannose. Methylation by sodium and methyl iodide (cf. Freudenberg and Hixon, A., 1923, i, 1179) results in the formation of a *methyl diacetone-mannose*,  $[\alpha]_D^{20} - 42.2^\circ$  (in *s*-tetrachloroethane). These may be more or less pure samples of the  $\alpha$ - and  $\beta$ -forms of  $\alpha$ -methyl- $\beta$ - $\gamma$ - $\epsilon$ -diacetone-mannoside, as from  $\alpha$ -methylmannoside a diacetone- $\alpha$ -methylmannoside, b. p.  $105^\circ/0.5$  mm.,  $[\alpha]_D^{20} + 34.9^\circ$ , was obtained.

W. O. K.

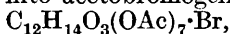
**Specific Rotations of Hexonic and  $\alpha$ -Aminohexonic Acids and of their Salts.** P. A. LEVENE (*J. Biol. Chem.*, 1924, 59, 123—127).—The following specific rotations are given: gluconic acid,  $[\alpha]_D^{20} 0.0^\circ$ ; mannonic acid,  $[\alpha]_D^{20} + 15.6^\circ$ ; gulonic acid,  $[\alpha]_D^{20} + 1.6^\circ$ ; galactonic acid,  $[\alpha]_D^{20} - 8.0^\circ$ ; allonic acid,  $[\alpha]_D^{20} - 10.0^\circ$ ; altronic acid,  $[\alpha]_D^{20} + 8.0^\circ$ ; whilst only sufficient idonic acid was available to ascertain that it is in all probability dextrorotatory. On comparison of these figures with those previously given for their sodium salts, phenylhydrazides, and amides, it appears that the rotation of the free acid is in the opposite sense from that of the derivatives. The following figures are also given: chitos-aminic acid,  $[\alpha]_D^{20} - 1.3^\circ$  in 5% sodium hydroxide solution ( $c = 5.0\%$ ),  $-15^\circ$  in 2.5% hydrochloric acid; epichitosaminic acid,  $[\alpha]_D^{20} - 5.0^\circ$  in 5% sodium hydroxide solution ( $c = 5\%$ ),  $+10^\circ$  in 2.5% hydrochloric acid solution; “dextro-*d*-xylos- $\alpha$ -aminohexonic acid,”  $[\alpha]_D^{20} - 16^\circ$  in 5% sodium hydroxide solution ( $c = 2.5\%$ ),  $+14^\circ$  in 2.5% hydrochloric acid solution; “lævo-*d*-xylos- $\alpha$ -aminohexonic acid,”  $[\alpha]_D^{20} + 2.0^\circ$  in 5% sodium hydroxide solution ( $c = 2.5\%$ ),  $-11^\circ$  in 2.5% hydrochloric acid solution; chondrosaminic acid,  $[\alpha]_D^{20} - 15^\circ$  in 5% sodium hydroxide solution ( $c = 2.5\%$ ),  $-17^\circ$  in 2.5% hydrochloric acid solution; epichondrosaminic acid,  $[\alpha]_D^{20} - 1.8^\circ$  in 5% sodium hydroxide solution ( $c = 2.5\%$ ),  $+8.0^\circ$  in 2.5% hydrochloric acid solution, “dextro-*d*-ribos- $\alpha$ -aminohexonic acid,”  $+2.0^\circ$  in 5% sodium hydroxide solution ( $c = 2.5\%$ ),  $+12.5^\circ$  in 2.5% hydrochloric acid solution; “lævo-*d*-ribos- $\alpha$ -amino-

hexonic acid,"  $-15^{\circ}$  in 5% sodium hydroxide solution ( $c=2.5\%$ ),  $-26.0^{\circ}$  in 2.5% hydrochloric acid solution. W. O. K.

**Relation between Rotatory Power and Structure in the Sugar Group. IV. Two Isomeric Crystalline Hexa-acetates of  $d\text{-}\alpha\text{-Mannoheptose}$ .** C. S. HUDSON and K. P. MONROE (*J. Amer. Chem. Soc.*, 1924, **46**, 979—983).—Acetylation of  $d\text{-}\alpha\text{-mannoheptose}$  by adding the sugar to gently boiling acetic anhydride containing sodium acetate resulted in the isolation of a crystalline *hexa-acetate*, m. p.  $106^{\circ}$ ,  $[\alpha]_D^{20} +24.2^{\circ}$  in chloroform. It was transformed by hot acetic anhydride and zinc chloride into a strongly dextrorotatory syrup from which a second *hexa-acetate*, m. p.  $139\text{--}140^{\circ}$ ,  $[\alpha]_D^{20} -31^{\circ}$  in chloroform, crystallised. From a comparison with the dextrose penta-acetate, it is inferred that the first hexa-acetate is a  $\beta$ -form and that the main (strongly dextrorotatory) amorphous product is the  $\alpha$ -form. Comparison of the hexa-acetates with the galactose penta-acetates (A., 1916, i, 546) indicates that the compound, m. p.  $106^{\circ}$ , and the strongly dextrorotatory amorphous product are probably  $\beta$ - and  $\alpha$ -forms of the butyleneoxide type, whereas the substance, m. p.  $139\text{--}140^{\circ}$ , is a  $\beta$ -form of some other type. A. C.

**Polysaccharides. VIII. Molecular Structure of  $\beta$ -Hexa-amylose.** J. C. IRVINE, H. PRINGSHEIM, and J. MACDONALD (*J. Chem. Soc.*, 1924, **125**, 942—947).—Karrer and Bürklin's statement (A., 1922, i, 435) that triamylose and  $\beta$ -hexa-amylose are identical is disproved by the conversion of the latter on exhaustive methylation into the crystalline  $\beta$ -*hexa(trimethylamylose)*,  $C_{54}H_{96}O_{30}$ , m. p.  $102\text{--}105^{\circ}$ , thus confirming the view of Pringsheim and Dernikos (A., 1922, i, 632).  $\beta$ -Hexa(trimethylamylose) on hydrolysis in methyl-alcoholic solution containing 1% of hydrogen chloride gave an equilibrium mixture of  $\alpha$ - and  $\beta$ -trimethylmethylglucoside, which on further hydrolysis in 8% aqueous hydrochloric acid gave only 2:3:6-( $\beta\gamma\zeta$ -)trimethylglucose. F. G. M.

**Synthesis of Amygdalic Acid from Gentiobiose.** G. ZEMPLÉN (*Ber.*, 1924, **57**, [B], 698—704).—Gentiobiose octa-acetate is converted by successive treatment with methyl-alcoholic sodium methoxide solution, sodium hydroxide, and methyl sulphate, and finally with silver oxide and methyl iodide, into heptamethyl methylgentiobioside, long, colourless needles, m. p.  $109^{\circ}$ ,  $[\alpha]_D^{11} -22.39^{\circ}$  in water,  $[\alpha]_D^{16.5} -20.89^{\circ}$  in alcohol [Haworth and Wylam (T., 1923, **123**, 3124) give m. p.  $106^{\circ}$ ,  $[\alpha]_D -33.9^{\circ}$  in water,  $-29.9^{\circ}$  in alcohol]. On hydrolysis, it yields 2:3:5-trimethyl  $\beta$ -methylglucoside and 2:3:5-trimethylglucose. Gentiobiose octa-acetate is transformed by glacial acetic and hydrobromic acids in the presence of chloroform into acetobromogentiobiose,



m. p.  $131\text{--}133.5^{\circ}$ ,  $[\alpha]_D^{19} +111.8^{\circ}$  in chloroform, which is converted by silver *dl*-mandelate into *hepta-acetylgentiobiosidyl mandelate*,  $C_{12}H_{14}O_{11}Ac_7\cdot CO\cdot CH\cdot PhOH$ , small, colourless needles, m. p.  $209^{\circ}$  (decomp.) after softening at  $205^{\circ}$ ,  $[\alpha]_D^{17.5} -9.73^{\circ}$  in chloro-

form, and hepta-acetylamygdalic acid, m. p. about  $90^{\circ}$ ,  $[\alpha]_D^{15} +6.25^{\circ}$  or  $+10.55^{\circ}$  in chloroform. In its main features, synthetic hepta-acetylamygdalic acid closely resembles the product derived from amygdalin, but an exact comparison is rendered difficult by the amorphous nature of both compounds. A wide discrepancy is observed only in the specific rotation, which is attributed to the incomplete racemisation of the mandelic complex in the conversion of amygdalin into hepta-acetylamygdalic acid and to a partial resolution of silver *dl*-mandelate into its active components during the preparation of the synthetic acid (cf. Karrer and co-workers, A., 1921, i, 260).  
H. W.

**Starch Grains.** L. ROSENTHALER (*Schweiz. Apoth.-Ztg.*, 1923, 61, 654—659; from *Chem. Zentr.*, 1924, i, 451—452).—Starch grains from different plants may in some cases be distinguished by their behaviour towards methylene-blue, naphthylene-blue, and neutral-red, respectively. Observations are also recorded on the behaviour of different kinds of starch grains towards peptising reagents, acids, and alkalis. Whilst the results are of value for analytical purposes, they are nevertheless in many cases influenced strongly by experimental conditions.  
G. W. R.

**Iodo Compounds of Simple  $\alpha\beta$ -cycloAcetals of the Type of Starch Iodide.** M. BERGMANN (*Ber.*, 1924, 57, [B], 753—755).—A solution of acetolmethylcycloacetal,  $(\text{OMe}\cdot\text{CMe} < \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix})_2$ , in methyl alcohol is converted by iodine and potassium iodide below  $0^{\circ}$  into the compound  $\text{C}_8\text{H}_{16}\text{O}_4\text{I}_4\cdot\text{KI}$ , very unstable, bluish-black prisms, m. p.  $50$ — $52^{\circ}$  when rapidly heated. The methylcycloacetal of acetoin gives a similar, but even less stable, compound, dark, steel-blue prisms. The formation of starch iodide is attributed to the presence in starch of similar oxygen rings, which cause addition of iodine and potassium iodide owing to their pronounced residual affinity. The polyamyloses do not behave in this manner.  
H. W.

**Polymerisation of the Cellulose Molecule.** P. BARY (*Compt. rend.*, 1924, 178, 1159—1161).—A theoretical paper in which the two different types of reaction undergone by cellulose involving (a) no depolymerisation and a colloidal resultant, or (b) depolymerisation with a resultant which is less colloidal in its nature than cellulose, are considered. Cellulose is represented, not as  $(\text{C}_6\text{H}_{10}\text{O}_5)_m$ , but as  $(\text{C}_6\text{H}_{10}\text{O}_5)_m\cdot\text{H}_2\text{O}$ , where  $m$  is very large, and the suggestion is put forward that hydrolysis and depolymerisation are effected by hydration of one of the oxygen linkings in the unit structure of the molecule.  
H. J. E.

**Cellulose in Coal.** F. SCHULZ and J. HAMACKOVA (*Bull. Soc. chim.*, 1924, 35, [iv], 183—187).—Cellulose was extracted from various recent lignites by Schorger's method (*J. Ind. Eng. Chem.*, 1917, 9, 556). The maximum content was 12% (referred to the weight of lignite less moisture and ash). The cellulose, a greyish-white mass in the crude state, was recognised by hydrolysis to a



hexose and by conversion to cellobiose octa-acetate. Analyses showed that only in exceptional cases does the cellulose of wood remain unaltered, on the conversion of the latter into coal, up to the tertiary geological age. Other coals and lignites yielded no trace of cellulose.  
E. E. T.

**Effect of 5*N*-Nitric Acid on Cellulose, Dextrose, Natural and Artificial Humic Acids, and Lignin.** H. TROPSCH and A. SCHELLENBERG (*Ges. Abh. Kenntn. Kohle*, 1921, 6, 257—262; from *Chem. Zentr.*, 1924, i, 562).—The action of 5*N*-nitric acid on natural and artificially prepared humic acids and on lignin is similar, nitrophenolic substances occurring amongst the products of reaction. Cellulose and dextrose behave differently. Humic acid artificially prepared from sugar is more readily attacked than natural humic acid and lignin.  
G. W. R.

**[Esterification and Mercerisation of Cellulose.]** R. O. HERZOG and G. LONDBERG (*Ber.*, 1924, 57, [B], 750; cf. this vol., i, 373).—The authors' inability to obtain a monoacetate or monobenzoate of cellulose is due to the fact that further esterification occurs more rapidly in the altered layers than does monoacylation in the deeper layers.  
H. W.

**Acetylation of Lignin.** E. HEUSER and W. ACKERMANN (*Cellulosechemie*, 1924, 5, 13—21; 30—31).—Lignin was obtained by treating resin-free wood meal with 41.2% hydrochloric acid; the product contained 13% of methoxyl and was free from residues of pentosan. This was acetylated by heating with acetic anhydride in the presence of pyridine; the acetyl value increased up to a maximum corresponding with 32.5% of combined acetic acid and then decreased on further heating owing to hydrolysis of the ester. Acetylation with acetyl chloride gave substantially identical results. Acetic anhydride alone gave inferior acetylation values as compared with those obtained in the presence of pyridine; addition of sodium acetate was still less favourable to esterification. Much more rapid esterification was effected by a mixture of acetic anhydride and nitric acid, and the same maximum limit of acetyl value was attained. On further treatment, this acetyl value decreased as before, but subsequently increased up to 42.5% owing to hydrolysis and re-acetylation of groups originally combined as methoxyl. The acetyl-lignin esters obtained were lighter in colour than the original lignin. Natural lignin existing in wood probably contains three hydroxyl groups on Klason's formula; the triacetate,  $C_{41}H_{37}O_{11}(OAc)_3$ , should contain 20.07% of combined acetic acid, as against 17.8% calculated from the authors' equilibrium value duly corrected.  
J. F. B.

**Humic Acids. I. Method of Preparation.** H. TROPSCH and A. SCHELLENBERG (*Ges. Abh. Kenntn. Kohle*, 1921, 6, 191—195; from *Chem. Zentr.*, 1924, i, 600).—Rosenthal coal used for the preparation of humic acids contained 3.7% of material extractable by benzene. The ethyl alcohol extract (18.9%) contained 55% of humic substances. The humic acid used in subsequent

investigations was obtained as follows. The coal was first extracted repeatedly with benzene and ethyl alcohol and the residue treated with 1% hydrochloric acid, after which it was shaken with 2*N*-sodium hydroxide. The alkaline solution was separated by filtration and centrifuging, and the humic acids were precipitated by acidifying with hydrochloric acid. The precipitate was collected and washed with water to the stage of incipient sol formation. The yield of humic acid was 60%, having the composition carbon 54.7%, hydrogen 3.0%, and ash 10.2%. G. W. R.

**Humic Acids. II. Products of Alkali Fusion and Heating under Pressure.** H. TROPSCH and A. SCHELLENBERG (*Ges. Abh. Kenntn. Kohle*, 1921, 6, 196—213; from *Chem. Zentr.*, 1924, i, 600—601; cf. preceding abstract).—Humic acid (40 g.) obtained from bituminous coal was heated with potassium hydroxide (160 g.) and water (100 c.c.) at 240—300°. Humic substances were obtained in 40—50% yield. Steam distillation of the acid solution gave 3% of volatile acids, principally acetic acid together with a little formic acid, and small quantities of neutral reducing compounds. The ethereal extract contained isophthalic acid, and hydroxyisophthalic acid or hydroxyterephthalic acid. Oxalic acid was obtained from the residue after ether extraction. Heating humic acid under pressure with 10*N*-potassium hydroxide for 140 hours at 150° yielded 52% of humic substances soluble in alkali, containing carbon 47.9%, hydrogen 2.6%, and ash 26.7%. From these products, after acidification, acetic acid and formic acid were isolated by steam distillation, and oxalic acid by extraction with ether. *m*-Hydroxybenzoic acid and 5-hydroxyisophthalic acid were also obtained. G. W. R.

**Humic Acids. III. Action of Nitric Acid on Humic Acids.** H. TROPSCH and A. SCHELLENBERG (*Ges. Abh. Kenntn. Kohle*, 1921, 6, 214—234; from *Chem. Zentr.*, 1924, i, 601—602; cf. preceding abstracts).—Humic acid from coal is rapidly attacked by 5*N*-nitric acid at 60°, and by prolonged heating the material goes into solution with the exception of 4—9% of solid, brown residue. Oxalic acid and certain strongly acid substances having the character of nitrophenols are obtained. Reduction of these nitro compounds gives black, humic substances. From the ethereal extract in certain cases, 5% (calculated on the original humic acid) of trinitrodihydroxybenzene is obtained. It forms yellow needles, m. p. 267° (decomp.). On drying in a vacuum, water of crystallisation is lost at 80°, and the composition is then given by the formula  $C_6H_3O_8N_3 \cdot 0.5H_2O$ . A crystalline tin double salt is obtained on reduction with tin and hydrochloric acid; it forms thick, well-formed crystals. On attempting to isolate the amino compound, decomposition takes place with formation of black, humic substances. The products of reaction of humic acid with nitric acid (*d* 1.4) or with 2.5*N*-nitric acid are similar. With nitric acid (*d* 1.5), however, nitrohumic acid is obtained. The action of 5*N*-nitric acid on humic acid prepared from quinol is more energetic than is the case with humic acid prepared from natural products. Oxalic

acid and substances of the character of nitrophenols are obtained. Humic acid from sugar gives, with 5*N*-nitric acid at room temperature, a red, amorphous substance similar to the nitrohumic acid obtained from natural humic acid by the action of nitric acid (*d* 1.5). With nitric acid (*d* 1.5), sugar humic acid yields 20% of substances of the character of nitrophenols. G. W. R.

**Humic Acids. IV. Effect of certain Reagents on Humic Acids.** H. TROPSCH and A. SCHELLENBERG (*Ges. Abh. Kenntn. Kohle*, 1921, 6, 235—247; from *Chem. Zentr.*, 1924, i, 602; cf. preceding abstracts).—Humic acid from coal yields, with 72% sulphuric acid, 87.5% of humic substances, of which 22% is soluble in alcohol; 11.4% of volatile acids, including formic acid and acetic acid, and 1.8% of an orange-red, lacquer-like substance. Hydrochloric acid reacts in a similar manner. By chlorination of humic acid suspended in *s*-tetrachloroethane, substances containing 18 to 30.8% of chlorine are obtained. Among the products of reaction of potassium chlorate and hydrochloric acid on humic acid is hexachloroethane. G. W. R.

**Humic Acids. V. Dry Distillation of Humic Acid and its Alkaline Derivatives.** H. TROPSCH and A. SCHELLENBERG (*Ges. Abh. Kenntn. Kohle*, 1921, 6, 248—256; from *Chem. Zentr.*, 1924, i, 603; cf. preceding abstracts).—Dry distillation of humic acid at 525° and 0.8—5.1 mm. yields 57.5% of carbonaceous residue and gaseous products, including steam, carbon dioxide, and acetic and formic acids. Tarry substances were not obtained in the distillate. Similar products were obtained by distillation at 300° under atmospheric pressure. The humic substance obtained by heating humic acid with 10*N*-potassium hydroxide at 150° under pressure yields similar products on distillation. The substance obtained by heating humic acid with potassium hydroxide at 300° behaves differently on distillation in that it yields a certain amount of tar both at atmospheric and under reduced pressures. From the products of distillation under reduced pressure, a wax-like substance having m. p. 62° is obtained, the composition of which corresponds with a ketone, C<sub>47</sub>H<sub>94</sub>O. Distillation of humic acid with zinc dust gives, in addition to gaseous products and an aqueous distillate, a certain amount of oil having b. p. 80—130°, which by the action of nitric acid yields a heavy oil having the odour of nitrobenzene. Among the products of the distillation of humic acid with zinc dust in a current of hydrogen is an oil having the odour of pyridine and quinoline. G. W. R.

**Electrolytic Reduction of Acid Oximes.** M. ISHIBASHI (*Trans. Amer. Electrochem. Soc.*, 1924, 45, 335).— $\gamma$ -isoNitrosovaleric acid is so easily hydrolysed in acid solution that it cannot be reduced chemically to the corresponding amine. An 84% yield of the latter is, however, obtained by electrolytic reduction, employing a current density of 2 amp. per sq. dm., a temperature of 3—5°, and a sulphuric acid concentration of less than 5%. The amine from  $\alpha$ -isonitrosopropionic acid is obtained

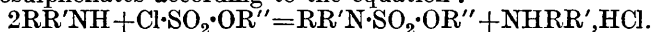
in 95% yield with a current density of 4.5 amp. per sq. dm., a temperature of 7–10°, and an acid concentration of 8%.

W. T. K. B.

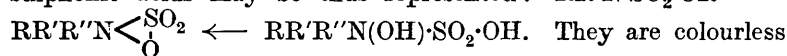
**Trialdehyde Compounds of Primary Amines.** M. BERGMANN and A. MIEKLEY (*Ber.*, 1924, 57, [B], 662–664; cf. Bergmann, Jacobsohn, and Schotte, this vol., i, 19).—Aliphatic aldehydes combine with primary amines to give trialdehyde compounds of the type  $R\cdot CH < \begin{smallmatrix} O\cdot CHR \\ O\cdot CHR \end{smallmatrix} > NR'$ ; the property is not shared by benzaldehyde.

*Triformaldehyde-ethylamine*, ( $R=H$ ;  $R'=Et$ ), b. p. 62–64°/42 mm. (picrate, m. p. 75°), is prepared by the gradual addition of ethylamine to a large excess of well-cooled, aqueous formaldehyde solution (30%). *Triacetaldehyde-ethylamine* is a colourless, unstable liquid, b. p. 59–60°/15 mm. Allylamine and formaldehyde give the relatively stable *triformaldehyde-allylamine*, b. p. 38–40°/1.5 mm., together with compounds richer in aldehyde. *Triacetaldehyde-allylamine* is a colourless, exceedingly unstable liquid, b. p. 48–50°/2.5 mm. Benzaldehyde and allylamine give *benzylidene-allylamine*, b. p. 96°/12 mm., which is transformed by bromine into *benzylidene-βγ-dibromopropylamine*, m. p. 36–37°. H. W.

**Action of Secondary Amines on Alkyl Chlorosulphonates.** M. DÉLÉPINE and R. DEMARS (*Bull. Sci. Pharmacol.*, 1923, 30, 577–599; from *Chem. Zentr.*, 1924, i, 415; cf. A., 1922, i, 634).—Dialkylaminosulphonic acids or their esters might be expected to be formed by the action of secondary amines on alkyl chlorosulphonates according to the equation:



Actually, however, compounds of the betaine type are obtained which may be considered as anhydrides of trialkylammonium hydroxide sulphonic acids. Their formation from dialkylaminosulphonic acids may be thus represented:  $RR'N\cdot SO_2\cdot OR'' \rightarrow$



They are colourless neutral compounds which hydrolyse slowly with alkalis or acids to tertiary amines and sulphuric acid, behaving in this respect like the compounds formed from sulphur dioxide and tertiary amine oxides or hydroxylamines. *Trimethylammonium hydroxide N-sulphonic anhydride*,  $Me_3NSO_3$ , from dimethylamine and methyl chlorosulphonate, forms shining needles, m. p. above 200° (decomp.). It is also formed from sulphur dioxide and trimethylamine oxide. *Dimethylethylammonium hydroxide sulphonic anhydride*,  $Me_2EtNSO_3$ , has m. p. 131–133°, and *methyldipropylammonium hydroxide sulphonic anhydride*, m. p. 120–121°. G. W. R.

**Constitution of Galegine.** G. TANRET (*Bull. Soc. chim.*, 1924, [iv], 35, 404–405; cf. A., 1914, i, 859).—One of the two open-chain structures advanced for galegine by Barger and White (this vol., i, 272) has been suggested previously by the author (Thesis, Paris, 1917). R. B.

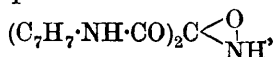
**Catalytic Decomposition of the Formic Amides.** A. MAILHE (*Bull. Soc. chim.*, 1924, [iv], 35, 363—365).—The primary amides of the formic acid series are dehydrated in contact with nickel at 400°, yielding the corresponding nitrile. The water formed in the reaction hydrolyses part of the unchanged amide to ammonia and the carboxylic acid, which in the presence of active nickel is decomposed into gaseous products and carbon.

R. B.

**Preparation of Diethylchloroacetamide.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 209706).—Diethylchloroacetyl chloride, b. p. 93°/70 mm., obtained by chlorinating diethylacetyl chloride at about 100°, is shaken with excess of ammonia or of a compound evolving ammonia (*e.g.*, ammonium carbonate). The diethylchloroacetamide produced forms white flakes, m. p. 58°, and possesses valuable soporific properties.

W. T. K. B.

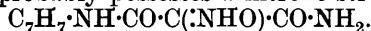
**The Oxime of Mesoxamide (Oximinomalonamide) and some Allied Compounds.** V. Structural- and Stereo-isomerism in the Methyl Ethers of the *p*-Tolyl Derivatives. A. PLOWMAN and M. A. WHITELEY (*J. Chem. Soc.*, 1924, 125, 587—604; cf. *ibid.*, 1922, 121, 2110).—Investigations of the ethers of alkyl- and aryl-substituted derivatives of oximinomalonamide have now been extended to the ethers of the *p*-tolyl derivatives, in which the stable yellow form appears to possess the *N*-ether structure. The yellow tautomeride of oximinomalon-*p*-toluidide, yellow scales, m. p. 170—171°, is obtained from mesox-*p*-toluidide and hydroxylamine under conditions (dilute alcoholic solution) which indicate that it possesses the *isooxime* structure,



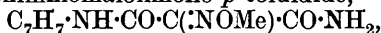
whereas the colourless tautomeride, thin needles, becoming yellow at 150°, m. p. 170—171°, is formed under different conditions (absolute alcoholic solution) pointing to the oxime structure,  $(\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO})_2\text{C}\cdot\text{NOH}$ . Of the two *methyl ethers* of oximinomalon-*p*-toluidide, the colourless stable *isomeride*, m. p. 171° [*hydrate*,  $(\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO})_2\text{C}(\text{OH})\cdot\text{NH}\cdot\text{OH}$ , m. p. 196°] from its formation from the hydrated form of mesox-*p*-toluidide and  $\alpha$ -methylhydroxylamine must be regarded as the *O*-ether, whilst the structure of the yellow *isomeride*, m. p. 182° (decomp.), is established as the *N*-methyl ether by its hydrolysis to  $\beta$ -methylhydroxylamine and mesox-*p*-toluidide, and by its synthesis from the same two compounds. Further work on oximinomalonmono-*p*-tolylamide has led to the isolation of three yellow and two colourless *isomerides*. The original yellow *isomeride* ( $\alpha$ ), m. p. 184°, is converted into a colourless *isomeride* ( $\beta$ ), m. p. 157°, by spontaneous evaporation from alcohol, and into a second colourless *isomeride* ( $\beta'$ ), m. p. 175°, by the action of moist hydrogen chloride in the presence of chloroform; each of these colourless *isomerides* yields a corresponding yellow tautomeride ( $\gamma$  and  $\gamma'$ ) when crystallised from non-hydroxylic solvents, melting at the same temperature as the parent

colourless compound. On treatment with phosphorus pentachloride the  $\beta$ - and  $\gamma$ -isomerides yield *p*-tolylloxamidonitrile,  $C_7H_7 \cdot NH \cdot CO \cdot CN$ , colourless needles, m. p.  $178^\circ$ , together with carbon dioxide, a reaction which indicates that they are the two structural forms of *anti-p*-tolylmesoxamideoxime, the coloured  $\gamma$ -isomeride possessing the isooxime structure,  $C_7H_7 \cdot NH \cdot CO > C < \begin{smallmatrix} NH \\ | \\ O \end{smallmatrix}$ . On treatment

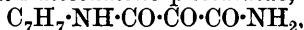
with phosphorus pentachloride the  $\beta'$ - and  $\gamma'$ -tautomerides undergo the normal Beckmann change and yield oxamide, carbon dioxide, and *p*-toluidine. They are therefore regarded as the structural isomerides of *syn-p*-tolylmesoxamideoxime, the true oxime structure,  $NH_2 \cdot CO \cdot C(:NOH) \cdot CO \cdot NH \cdot C_7H_7$ , being assigned to the colourless  $\beta'$ -isomeride. The  $\alpha$ -isomeride is the most stable isomeride and forms the sole product of the action of nitrosyl chloride on malonmono-*p*-toluidide. It yields the same ethers as the  $\beta$ - and  $\gamma$ -forms, and is similarly decomposed by the action of phosphorus pentachloride; it probably possesses a nitron structure,



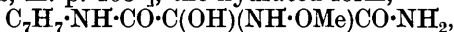
The action of methyl iodide on the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -isomerides in the presence of silver oxide yields an *O*-methyl ether, colourless needles, m. p.  $204^\circ$ , a second colourless ether, flat needles, m. p.  $155^\circ$ , being obtained from the  $\beta'$ - and  $\gamma'$ -isomerides under similar conditions. The structure of these isomeric ethers as the *anti*- and *syn*-forms, respectively, of oximinomalonmono-*p*-toluidide,



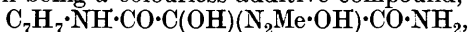
is deduced from the synthesis of the isomeride, m. p.  $204^\circ$ , by the condensation of  $\alpha$ -methylhydroxylamine hydrochloride in aqueous alcoholic solution with mesoxmono-*p*-toluidide,



m. p.  $222^\circ$  (decomp.), [*hydrate*,  $C_7H_7 \cdot NH \cdot CO \cdot C(OH)_2 \cdot CO \cdot NH_2$ , colourless plates, m. p.  $222^\circ$ , decomp., *phenylhydrazone hydrate*, colourless needles, yellow at  $165^\circ$ , m. p.  $193^\circ$ , *phenylhydrazone*, yellow needles, m. p.  $193^\circ$ ], the hydrated form,



colourless needles, m. p.  $179^\circ$  (decomp.), being produced immediately. Methylation with diazomethane converts the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -isomerides of oximinomalonmono-*p*-toluidide into an *N*-methyl ether, bright yellow, felted needles, m. p.  $200^\circ$  (decomp.), the  $\beta'$ - and  $\gamma'$ -isomerides yielding a second yellow isomeride, m. p.  $150^\circ$ , decomp. (*hydrate*, colourless needles). The structure of these yellow isomerides as *N*-methyl ethers of the *anti*- and *syn*-forms, respectively, of oximinomalonmono-*p*-toluidide is indicated by their hydrolysis with moist hydrogen chloride to the hydrated form of the corresponding ketone, mesoxmono-*p*-toluidide, from which a small quantity of the yellow isomeride, m. p.  $200^\circ$ , is formed by the action of  $\beta$ -methylhydroxylamine, the main product of this latter reaction being a colourless additive compound,



flat needles, m. p.  $174^\circ$  (decomp.), which has hitherto resisted dehydration.

Acetylation of the five isomerides of oximinomalonmono-*p*-toluid-

ide yielded one of two colourless *acetyl* derivatives, m. p. 132° and 165°, respectively. The former is obtained from the  $\alpha$ -oximino compound, the latter from the  $\beta'$ - and  $\gamma'$ -isomerides, the  $\beta$ - and  $\gamma$ -isomerides yielding a mixture from which only the *acetyl* derivative, m. p. 165°, could be isolated. On hydrolysis the latter substance yields the  $\beta'$ -oximino compound, whilst the compound melting at 132° yields a mixture of the  $\alpha$ - and  $\beta$ -isomerides. The *acetyl* derivatives are accordingly regarded as acetates of the *syn*- and *anti*-type, respectively.

R. B.

**Thermal Decomposition of Allophanic Esters.** J. GRANDIÈRE (*Bull. Soc. chim.*, 1924, [iv], 35, 187—196).—The following new esters were prepared by Béhal's method (A., 1919, ii, 301): *allophanates* of ethylpropylcarbinol (m. p. 185.5°); ethylbutylcarbinol (m. p. 187°), methyldiethylcarbinol (m. p. 152°), triethylcarbinol (m. p. 156°), methylethylpropylcarbinol (m. p. 148°), methylethylbutylcarbinol (m. p. 130°),  $\Delta^{\alpha}$ -penten- $\gamma$ -ol (m. p. 155°), *o*-methylcyclohexanol (m. p. 177°), furyl alcohol (m. p. 167.5°), *o*-chlorophenol (m. p. 179°), glycol chlorohydrin (m. p. 182.5°).

On heating to 20° or 30° above the melting point most allophanic esters decompose into the alcohol and cyanuric acid, together with a small quantity of cyanic acid which reacts with the alcohol to give the corresponding urethane and allophanate. The esters of tertiary alcohols behave differently; a hydrocarbon of the ethylene series is evolved and allophanic acid probably formed as an intermediate product, but decomposes to carbamide, which immediately loses ammonia, both substances being unstable at the decomposition temperature of the ester. A certain amount of the alcohol and cyanuric acid is also formed.

The allophanates of geraniol, rhodanol, and citronellol decompose at 180—200° into carbon dioxide, ammonia, cyanuric acid, the alcohol, and a hydrocarbon, together with a brown, viscous liquid which, on hydrolysis, yields a small quantity of the corresponding alcohol. The allophanic esters of furyl and cinnamyl alcohols decompose into ammonia and carbon dioxide, leaving a resinous residue.

It is suggested that the behaviour of the allophanates of tertiary alcohols will serve for the detection of these alcohols (cf. A., 1919, ii, 301).

E. E. T.

**Isomeric Modifications of Methyleneaminoacetonitrile and their Biological Significance.** T. B. JOHNSON and H. W. RINEHART (*J. Amer. Chem. Soc.*, 1924, 46, 768—774).—Further investigation of the methyleneaminoacetonitriles, m. p. 129° and 86°, obtained by Klages (A., 1903, i, 469) has shown that they are structural isomerides having the formula  $C_9H_{12}N_6$ . The two compounds have different crystalline forms, behave differently on hydrolysis, and the one cannot be transformed into the other. The compound, m. p. 129°, for which the designation  $\alpha$ -hydroformamine cyanide is proposed, forms orthorhombic crystals;  $\beta$ -hydroformamine cyanide, m. p. 86°, forms monoclinic crystals.

C. J. S.

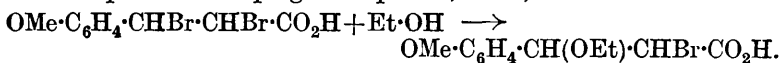
**Deamination. III. Evidence of the Existence of Aliphatic Diazonium Salts from the Formation of Chloro-oximino Compounds.** G. S. SKINNER (*J. Amer. Chem. Soc.*, 1924, **46**, 731—740).—The formation of ethyl chloro-oximinoacetate from the hydrochloride of ethyl aminoacetate and nitrous acid at low temperatures is presented as evidence of the existence of an aliphatic diazonium salt. It is believed to be produced according to the scheme:  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}\cdot\text{HCl} \xrightarrow{+\text{HNO}_2} \text{Cl}\cdot\text{N}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \xrightarrow{+\text{HNO}_2} \text{Cl}\cdot\text{N}_2\cdot\text{CH}(\text{N}\cdot\text{O})\cdot\text{CO}_2\text{Et} \longrightarrow \text{OH}\cdot\text{N}\cdot\text{CCl}\cdot\text{CO}_2\text{Et}$ . A modified method is given for the preparation of ethyl and *n*-butyl diazoacetates. By the action of nitrous anhydride and of nitrosyl chloride on the ethyl diazoacetate a nitrile oxide,  $\text{C}(\text{N}\cdot\text{O})\cdot\text{CO}_2\text{Et}$ , b. p. 132—133°/3 mm.,  $d_4^{20}$  1.2780,  $d_4^{25}$  1.2726, was obtained which is unimolecular in benzene, bimolecular in ethylene dibromide, and intermediate in nitrobenzene; it has also been obtained from ethyl chloroaminoacetate and sodium carbonate. The decomposition of ethyl and *n*-butyl aminoacetates by nitrous acid in the presence of hydrochloric acid leads to the formation of the corresponding chloroacetates. Ethyl pyrazolinetriacrylate, m. p. 98°, has been obtained by treating ethyl aminoacetate hydrochloride with nitrous acid in a manner described in the original and preserving the resulting liquid, b. p. 5—40°/4—5 mm., for several months. The preparation of *chloro-oximinoethane*,  $\text{CCl}(\text{N}\cdot\text{OH})\cdot\text{Me}$ , m. p. 84—85°, by the action of nitrous acid on ethylamine is described.

C. J. S.

### Reactions of certain Aromatic and Aliphatic Derivatives.

A. ANGELI (*Atti R. Accad. Lincei*, 1924, [v], **33**, 109—116).—The author quotes fresh data confirming his rule concerning the analogy of behaviour exhibited between two groups united directly and the same groups occupying ortho- or para-positions in one and the same aromatic nucleus (cf. A., 1923, i, 1003).

With reference to the mobility which the alkoxy groups of an aromatic nucleus impress on the halogen atoms of side chains in the ortho- or para-position to such groups, Werner and Goldschmiedt have shown that, whilst the group  $\text{CHPhCl}(\text{or Br})\cdot$  resists the action of boiling alcohol, the analogous ortho- or para-substituted groups,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHCl}(\text{or Br})\cdot$  and  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CHCl}\cdot$ , are readily converted into  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OEt})\cdot$  and  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}(\text{OEt})\cdot$ . Similarly, simple heating with alcohol produces the changes  $\text{OMe}\cdot\text{CH}_2\text{Cl} \longrightarrow \text{OMe}\cdot\text{CH}_2\cdot\text{OEt}(\text{or Me})$ . Such behaviour is limited to the halogen atom united to the carbon contiguous to the aromatic ring, halogens in other positions keeping their places; thus,



The same holds with aliphatic compounds containing a halogen atom at a distance from the carbon atom united to the alkoxy; thus, the compounds  $\text{OMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}(\text{I})$ ,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\text{I}$ ,  $\text{OMe}\cdot\text{CH}_2\cdot\text{CBr}(\text{NO}_2)_2$ , and  $\text{O}(\text{CH}_2\cdot\text{CH}_2\text{I})_2$  are so stable that some of them resist the actions of sodium, zinc, sodium acetate, and silver



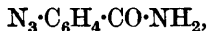
acetate, whereas the compounds  $O[CH_2Cl(\text{or } Br)]_2$  are so unstable that they decompose in moist air.

This varying behaviour of halogen atoms according to their position furnishes explanations for many reactions. The ready elimination of the halogen is regarded by Zincke and Werner as due to the formation of an intermediate oxonium or quinonic compound, thus,  $OMe \cdot C_6H_4 \cdot CHRBr \rightarrow BrMe - O \cdot C_6H_4 \cdot CHR$ , or  $OH \cdot C_6H_4 \cdot CH_2Br \rightarrow O \cdot C_6H_4 \cdot H(CH_2Br) \rightarrow OH \cdot C_6H_4 \cdot CH_2 \cdot OEt$ ; an intermediate oxonium compound is probably formed in the case of the aliphatic derivatives:  $OMe \cdot CH_2Br \rightarrow BrMe - O \cdot CH_2$ . [Cf. Hoering, A., 1904, i, 577.]

Certain groups, such as the nitro and cyano residues, enhance the activity of other groups in the para-position in an aromatic nucleus. Thus, the nitrosoamine,  $NPhMe \cdot NO$ , exhibits indifferent behaviour and gives up the nitroso residue only with difficulty, whereas its *p*-nitro derivative,  $NO_2 \cdot C_6H_4 \cdot NMe \cdot NO$ , immediately yields diazomethane when treated with cold sodium hydroxide. Further, alkyl ethers of phenols yield their alkyl groups only as the result of energetic reactions, but if a nitroso- or an azo-group is introduced in the ortho position to the alkoxy, the alkyl residue is easily removed with formation of the corresponding phenols:  $Ph \cdot N_2 \cdot C_6H_4 \cdot OMe \rightarrow Ph \cdot N_2 \cdot C_6H_4 \cdot OH$ , and  $NO \cdot C_6H_4 \cdot OMe \rightarrow NO \cdot C_6H_4 \cdot OH$ . Recently, Borsche and Exss (this vol., i, 218) have shown that the azo group increases the activity of halogen atoms in the ortho- or para-position, although its effect is less than that of other negative groups, such as the nitro, cyano, carbethoxy groups, etc.

In addition to the numerous examples, given earlier, of the migration of an oxygen atom from nitrogen to carbon, in aliphatic as well as in aromatic compounds, mention is made of the following, which take place under the influence of an alkali: the conversion of nitrocoumarone into an oxime,  $C_6H_4 \langle \begin{smallmatrix} CH \\ O \end{smallmatrix} \rangle C \cdot NO_2 \rightarrow$

$C_6H_4 \langle \begin{smallmatrix} CO \\ O \end{smallmatrix} \rangle C \cdot NOH$ , and the formation of an amide,



from the *o*-azide,  $N_3 \cdot C_6H_4 \cdot CH \cdot NOH$ ; the latter change is the only example of such a transposition taking place in an alkaline medium.

T. H. P.

**Low-temperature Tar obtained from the Zeche Fürst Hardenberg Coal and, in particular, the Content of Benzene, Phenol, and Acetone. Reply to Broche.** F. SCHÜTZ, W. BUSCHMANN, and H. WISSEBACH (*Ber.*, 1924, 57, [B], 619—622; cf. A., 1923, i, 907).—The conflicting results obtained by Broche are due to the fact that the authors dealt with the composition of the so-called "tar benzines" (*i.e.*, the light oils obtained by dehydrating primary tar), whereas Broche mixed the "tar benzines" and the "gas benzines" together before examination. The authors confirm their previous results (cf. A., 1923, i, 195, 452) regarding the content of benzene, phenol, and acetone. H. Lange obtained 30

kg. of pure acetone on working up 120 cubic metres of tar-water; the authors do not accept Broche's suggestion that their "abnormal" results were due to overheating of the retorts. F. A. M.

**Remarks on F. Fischer's Paper, "The Relation between Low-temperature Tar, Coke-oven Tar, and Petroleum."** F. SCHÜTZ (*Ber.*, 1924, 57, [B], 623—627; cf. A., 1923, i, 889).—Facts are quoted, such as the percentage of aromatic hydrocarbons, specific gravities, etc., to prove that Fischer's view as to the similarity between crude petroleum and low-temperature tar cannot be maintained. On the contrary, the products obtained from the low-temperature carbonisation of coal must be regarded as new types of products which cannot be compared with the great majority of natural petroleum but are of great technical importance. [Cf. also preceding abstract.] F. A. M.

**Japanese Petroleum. II.** S. KOMATSU and N. TANAKA (*Mem. Coll. Sci. Kyōtō*, 1924, 7, 143—146; cf. this vol., i, 502).—Petroleum from Nishiyama, Echigo, contains benzene and *n*-hexane.

**Hydrogenation of Aromatic Compounds with the Aid of Platinum. VII. Decahydronaphthalene prepared using Platinum Black.** R. WILLSTÄTTER and F. SEITZ (*Ber.*, 1924, 57, [B], 683—684; cf. A., 1923, i, 771).—According to Hückel (this vol., i, 31), all preparations of decahydronaphthalene are mixtures of the *cis*- and *trans*-forms, the product obtained by the use of platinum black containing about 90% of the *cis*- and 10% of the *trans*-form. The authors have examined various preparations made with the aid of platinum and found all to have the constants (b. p. 193—193.5° corr.;  $d_4^{20}$  0.8938—0.8942;  $n_D^{20}$  1.4796) of the pure *cis*-form, nor could any trace of the *trans*-form be obtained on fractional distillation. Reduction of naphthalene with nickel and hydrogen at 160—162°, however, yielded chiefly the *trans*-form,  $d_4^{20}$  0.8784;  $n_D^{20}$  1.4729. F. A. M.

**Preparation of Tetralin [Tetrahydronaphthalene].** H. INOUE (*J. Chem. Ind. Japan*, 1923, 26, 1316—1329).—For the hydrogenation of naphthalene, electrolytic hydrogen was used, and the nickel catalyst was prepared by electrolysis a 5—10% solution of sodium phthalate containing a slight excess of phthalic acid at 17—25°, using a nickel anode; the nickel hydroxide precipitated in the neighbourhood of the cathode is more active than that obtained by any other process. It is converted into oxide and then to metal at 310—320°. Purified naphthalene containing only 0.04% of sulphur was used and the hydrogenation was conducted in a specially designed autoclave of 7 litres capacity at 30 atm. pressure. The tetralin obtained had, after distillation,  $d$  0.970. Decalin was prepared from tetralin by the same process. K. K.

**Lely's Benzene Theory.** J. D. VAN ROON (*Chem. Weekblad*, 1924, 21, 174).—A reply to Lely's response (this vol., i, 380) to the author's criticism of the theory. S. I. L.

**Electrochemical Oxidation of Aromatic Hydrocarbons.**

F. FICHTER (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 75—95).—A general theoretical discussion of the electrolytic oxidation of benzene derivatives, illustrated mainly by the results of the author and his collaborators. Benzene is oxidised first to phenol, then to quinol and pyrocatechol, eventually to quinone, and is finally completely disrupted. The oxidation process is governed by the following factors: (1) concentration, (2) current density, (3) nature of anode, (4) influence of cathode if no diaphragm be used, (5) nature of the electrolyte, (6) secondary reactions, *i.e.* use of a solution of a salt of a metal having a variable valency, (7) superimposition of alternating on direct current.

When phenols are oxidised, the tendency is for *p*-quinones to be formed; thus anisole gives benzoquinone, *m*-tolyl methyl ether yields toluquinone, and *m*-xylenol *p*-xyloquinone. When phenol itself is appropriately oxidised there are formed, besides the usual products, certain hydroxydiphenyls and diphenyl ethers (Fichter and Brunner, A., 1916, i, 644; Fichter and Ackermann, A., 1919, i, 586). Recent investigation, the results of which remain unpublished, has shown that guaiacol, *p*-tolyl methyl ether, and *m*-xylenol similarly yield 4 : 4'-dihydroxy-3 : 3'-dimethoxydiphenyl, 2-hydroxy-2'-methoxy-4 : 4'-dimethyldiphenyl, and 2 : 2'-dihydroxy-3 : 5 : 3' : 5'-tetramethyldiphenyl respectively. W. A. S.

**Action of Sodium Sulphite on some Trinitro Compounds and on Tetranitromethane. Purification of Tolite [2 : 4 : 6-Trinitrotoluene].** H. MURAOUR (*Bull. Soc. chim.*, 1924, [iv], **35**, 367—379; cf. A., 1922, i, 443, 1006).—Dilute solutions of sodium sulphite (3 to 5%) dissolve 2 : 3 : 4-trinitrotoluene ( $\beta$ ) and 2 : 4 : 5-trinitrotoluene ( $\gamma$ ) in the cold, giving colourless solutions of the corresponding sodium dinitrosulphonates, one of the adjacent ortho-nitro groups being replaced. Thus 2 : 4 : 5-trinitrotoluene is converted into sodium 2 : 4-dinitrotoluene-5-sulphonate. Symmetrical trinitrotoluene, however, only reacts slightly with dilute sodium sulphite, forming an additive product which is only stable in concentrated solutions of the sulphite and from which, on dilution, the greater part of the trinitrotoluene is precipitated. Trinitrobenzene dissolves in cold dilute sodium sulphite giving an intense red solution, from which the trinitrobenzene is precipitated unchanged on acidifying. *s*-Trinitro-*m*-xylene and trinitromesitylene do not react with aqueous sodium sulphite. Tetranitromethane reacts readily; the reaction appears to proceed in two stages, the sodium trinitromethanesulphonate first formed being subsequently hydrolysed to the sodium salt of trinitromethane.

The purification of crude commercial trinitrotoluene by the sodium sulphite process is discussed, and the application of the process to the determination of the unsymmetrical trinitrotoluenes in crude trinitrotoluene is described.

The reaction has also been utilised for the separation and approximate determination of the trinitroxylenes, the trinitro-

derivatives of *o*- and *p*-xylene reacting with dilute sodium sulphite, whilst trinitro-*m*-xylene does not. [Cf. *B.*, 1924, 451.] R. B.

**Sulphonation of *p*-Cymene.** M. PHILLIPS (*J. Amer. Chem. Soc.*, 1924, 46, 686—694).—The proportions of the isomeric monosulphonic acids produced by sulphonation of *p*-cymene have been investigated using a method based on the melting-point curves of the corresponding sulphonamides. The proportion of sulphuric acid used has less effect than temperature. The best yield of the  $\beta$ -acid (*p*-cymene-3-sulphonic acid) is obtained using 1 part of *p*-cymene to 3 parts of sulphuric acid, sulphonating for 4 hours at 100°. Sulphonation at lower temperatures favours formation of the 2-isomeride; thus 15.6% of the 3-sulphonic acid is formed at 100° and 2.5% at 0° (using fuming sulphuric acid containing 20% of anhydride). No disulphonic acid appears to be formed at or below 50°, but increasing amounts are produced at higher temperatures. The proportion of *p*-cymene-2-sulphonic acid is somewhat increased by addition of copper or mercuric sulphate.

C. J. S.

**Synthesis of Higher Homologues of *m*-Methylethylbenzene.** A. MAILHE (*Bull. Soc. chim.*, 1924, [iv], 35, 365—367).—By the action of acid chlorides on *m*-methylethylbenzene in carbon disulphide solution in the presence of aluminium chloride, followed by hydrogenation of the ketone first formed in the presence of nickel according to Darzens' method (A., 1905, i, 66), a number of higher homologues of *m*-methylethylbenzene have been obtained. The new alkyl group enters the benzene ring in the 6-position. 2-Methyl-4-ethylacetophenone has b. p. 239—240° (semicarbazone, m. p. 185°), 1-methyl-3:6-diethylbenzene, b. p. 205—207°; 2-methyl-4-ethylphenyl ethyl ketone, b. p. 250—252°; 1-methyl-3-ethyl-6-propylbenzene, b. p. 213—215°,  $d_4^{25}$  0.8831; 2-methyl-4-ethylphenyl isopropyl ketone, m. p. 132°, b. p. 258—259°,  $d_4^{25}$  0.9557; 1-methyl-3-ethyl-6-isobutylbenzene, b. p. 228—229°,  $d_4^{25}$  0.8863; 2-methyl-4-ethylphenyl propyl ketone, b. p. 265—266°; 1-methyl-3-ethyl-6-butylbenzene, b. p. 236—237°,  $d_4^{25}$  0.6882 (?); 2-methyl-4-ethylphenyl isobutyl ketone, b. p. 274°; 1-methyl-3-ethyl-6-isoamylbenzene, b. p. 245—246°,  $d_4^{25}$  0.8801. By the action of benzoyl chloride on *m*-methylethylbenzene in the presence of aluminium chloride 2-methyl-4-ethylbenzophenone, b. p. 318—320°, was obtained, which on hydrogenation was converted into 2-methyl-4-ethyldiphenylmethane, b. p. 298—300°,  $d_4^{25}$  1.0141.

R. B.

**Alkylation of Primary Amines with Aluminium Alkoxides to give Secondary Amines Free from Tertiary Amines.** W. A. LAZIER and H. ADKINS (*J. Amer. Chem. Soc.*, 1924, 46, 741—746).—Both aromatic and aliphatic primary amines may be alkylated by heating with aluminium alkoxide in sealed tubes at 250—350°. Aniline with aluminium ethoxide yielded a colourless reaction product containing 94% of ethylaniline and 6% of aniline. Other secondary amines were prepared in good yield by alkylating aniline, *p*-toluidine, and *n*-amylamine, but the opti-

mum conditions have not yet been ascertained. The yields obtained, using acetanilide in place of aniline, were considerably lower. These results do not support Nef's dissociation hypothesis (A., 1901, i, 626), by which he explained the mechanism of alkylation.  
C. J. S.

**Highly Chlorinated Hydroaromatic Products containing Nitrogen.** DURAND und HUGUENIN A.-G. (Brit. Pat. 198676).—Amines containing negative substituents are chlorinated, in the absence of moisture, without previously protecting the amino group by salt formation, as is necessary in the case of the unsubstituted amines (cf. Brit. Pat. 193843). For example, chlorine is introduced into an ice-cooled solution of 20 g. of 2:5-dichloroaniline in 600 c.c. of chlorobenzene. The paste initially formed having become fluid, the mixture is heated at about 100°, filtered, and the chlorobenzene distilled under diminished pressure. A crystalline compound (containing eight chlorine atoms) separates, which crystallises from light petroleum in colourless laminæ, m. p. 125°.  
W. T. K. B.

**Nitration of *p*-Bromoacetanilide.** R. H. GRIFFITH (*J. Chem. Soc.*, 1924, 125, 940—941).—The nitration of *p*-bromoacetanilide at 10° with excess of nitric acid and sulphuric acid yields 2:4-dibromo-6-nitroacetanilide, m. p. 215°, 4-bromo-2:6-dinitroacetanilide, and 4-bromo-2-nitroacetanilide. 2:4-Dibromoacetanilide nitrated with excess of fuming nitric acid yields 2:4-dibromo-6-nitroacetanilide, which is hydrolysed to 2:4-dibromo-6-nitroaniline, m. p. 128°, with alcoholic hydrochloric acid. Nitration in the presence of sulphuric acid yields 2:4-dibromo-5-nitroacetanilide, m. p. 172°. 4-Bromo-2:6-dinitroaniline melts at 162°.  
R. B.

**Electrolytic Preparation of Metanilic Acid and its Commercial Possibilities.** A. K. DOOLITTLE (*Trans. Amer. Electrochem. Soc.*, 1924, 45, 43—62).—In only one particular is the electrolytic reduction of *m*-nitrobenzenesulphonic acid likely to be more advantageous than the usual iron reduction, and that is that the former process might be made continuous. The author has therefore investigated the electrolytic method, using lead electrodes and 10% sulphuric acid as electrolyte. To the cathode solution, contained in a porous vessel, pure calcium *m*-nitrobenzenesulphonate was added. Reduction did not take place at 24°. The best results were obtained at 70°, with a bright lead cathode, current density 0.585 amp. per sq. dm., and cathode solution 1%. The yield was 67% of theory and current efficiency 64%. [Cf. B., 1924, 288.]  
W. A. S.

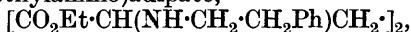
**Crystallographic Investigation of *p*-ββ-Dimethylpropylbenzenesulphanilide and Benzyltrimethylsilane-*p*-sulphanilide.** N. ZENZÉN (*Arkiv Kem., Min., Geol.*, 1923, 8, No. 34, 1—10).—*p*-ββ-Dimethylpropylbenzenesulphanilide,  
 $\text{CMe}_3\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHPh}$   
(cf. Bygdén, A., 1920, i, 478), crystallises in holohedral monoclinic

crystals,  $a : b : c = 0.6869 : 1 : 0.7536$ ,  $\beta = 113^\circ 17'$ , and benzyltrimethylsilicane-*p*-sulphanilide,  $\text{SiMe}_3 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NHPh}$  (cf. Bygdén, A., 1918, i, 134), also in holohedral monoclinic crystals,  $a : b : c = 0.6973 : 1 : 0.7698$ ,  $\beta = 113^\circ 38'$ . True mixed crystals of these two compounds are formed. The axial angle usually has appreciably different values at the two sides of a mixed crystal, probably on account of its zonal structure.

T. H. P.

### Decomposition of Quaternary Ammonium Hydroxides.

J. v. BRAUN and R. S. CAHN (*Annalen*, 1924, **436**, 262—273; cf. A., 1911, i, 610).—The decomposition of  $\beta$ -phenylethyltrimethylammonium hydroxide giving a quantitative yield of styrene and a tertiary base has been applied to the synthesis of tertiary bases previously difficult to obtain. By the action of  $\beta$ -phenylethylamine on ethyl  $\alpha\alpha'$ -dibromoadipate in chloroform solution are obtained ethyl  $\beta$ -phenylethylpyrrolidine-2 : 5-dicarboxylate, oil, b. p. 212—214°/14 mm. (chloroplatinate, decomp. 160—161°), and ethyl  $\alpha\alpha'$ -di( $\beta$ -phenylethylamino)adipate,



a thick oil; the free acid,  $\text{C}_{22}\text{H}_{28}\text{O}_4\text{N}_2$ , forms long, colourless needles, m. p. 118°. 1- $\beta$ -Phenylethylpyrrolidine-2 : 5-dicarboxylic acid, colourless crystals, decomp. 215° (hydrochloride, m. p. 177—178°), on dry distillation gives 1- $\beta$ -phenylethylpyrrolidine, a mobile oil, b. p. 138—139°/21 mm. (picrate, m. p. 139—140°, methiodide, m. p. 143°). The methiodide on treatment with silver oxide and distillation of the quaternary ammonium hydroxide gives 60% of the theoretical yield of styrene and 1-methylpyrrolidine, b. p. 78°. Reduction of ethyl 1- $\beta$ -phenylethylpyrrolidine-2 : 5-dicarboxylate with sodium and alcohol yields 1- $\beta$ -phenylethyl-2 : 5-dihydroxy-methylpyrrolidine, a viscous, colourless oil, b. p. 225°/13 mm. (hydrochloride, m. p. 127—129°, picrate, m. p. 108—111°, methiodide, oily), but the yield is small and no attempt was made to convert it into the corresponding 1-methylpyrrolidine.

$\beta$ -Phenylethyldimethylamine reacts readily with *o*-xylylene bromide (for the preparation of which a new method from *o*-toluidine is described), in chloroform solution, yielding the *diquaternary bromide*,  $\text{C}_{28}\text{H}_{38}\text{N}_2\text{Br}_2$ , colourless crystals, m. p. 206°, which on treatment with silver oxide and distillation gives 65% of the theoretical yield of styrene and 60% of tetramethyl-*o*-xylylenediamine,  $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{NMe}_2)_2$ , colourless oil, b. p. 105—106°/14 mm. [picrate, m. p. 187—188°, methiodide, m. p. 219° (decomp.)].

$\beta$ -Phenylethyldimethylamine and  $\alpha\epsilon$ -dibromopentane react readily at water-bath temperature, giving the *diquaternary bromide*,  $\text{CH}_2(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2 \cdot \text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Ph})_2$ , m. p. 121°, which on conversion into the hydroxide and distillation gives 60% of the theoretical yield of styrene and 25% of tetramethylpentamethylenediamine.

R. B.

### Tenacity of Organic Residues. II. J. v. BRAUN and H.

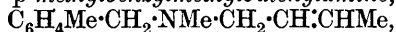
ENGEL (*Annalen*, 1924, **436**, 299—320; cf. A., 1923, i, 1193).—Further experiments have been undertaken to test the relative firmness of attachment of groups of the benzyl and allyl type to

nitrogen and to halogen. By decomposition of appropriate tertiary bases with cyanogen bromide, it is shown that the introduction of the groups Me, Et, Ph, respectively, into the para-position in the benzyl radical diminishes in the order named the firmness with which the substituted benzyl group is attached to nitrogen. A similar result was obtained from experiments in the allyl series with the radicals allyl, crotonyl, and cinnamyl. The affinity of the radicals for nitrogen (and also for carbon) accordingly stands in the order  $\text{Me} < \text{Et} < \text{Ph}$ , and the same order holds in regard to chlorine. These results are at variance with those of Meerwein (A., 1920, i, 2) and Skraup (A., 1919, i, 598; 1922, i, 574), but the order  $\text{Ph} < p\text{-C}_6\text{H}_4\text{Me} < p\text{-C}_6\text{H}_4\text{Et} < p\text{-C}_6\text{H}_4\text{Ph}$  is in accordance with Skraup's observations and those of Schlenk on the dissociation of hexa-arylethanes. A comparison of the allyl and benzyl series shows that in regard to nitrogen the radicals can be arranged in the following order of diminishing affinity:  $\text{CH}_2\text{Ph}\cdot$ ,  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot$ ,  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot$ ,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot$ ,  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot$ ,  $p\text{-C}_6\text{H}_4\text{Et}\cdot\text{CH}_2\cdot$ ,  $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{CH}_2\cdot$ , methylation of the benzyl residue in the para-position decreasing the firmness of its attachment to nitrogen more than phenylation of the allyl residue. Similar results were obtained by studying the reaction of benzyl, *p*-methylbenzyl, *p*-ethylbenzyl, and *p*-phenylbenzyl chlorides with sodium ethoxide.

*p*-Ethylbenzyl alcohol, b. p. 115–117°/9 mm., was obtained by the action of potassium hydroxide on the corresponding aldehyde, prepared by Gattermann's method (A., 1897, i, 519), and with hydrochloric acid was converted into *p*-ethylbenzyl chloride, b. p. 81–82°/11 mm. *p*-Phenylbenzyl chloride, m. p. 68°, is similarly prepared through *p*-phenylbenzyl alcohol, m. p. 101–102°, b. p. 183–184°/11 mm., from *p*-phenylbenzaldehyde (obtained from diphenyl by Gattermann's method), or alternatively from *p*-phenylbenzonitrile by catalytic reduction to *p*-phenylbenzylamine, colourless crystals, m. p. 127–128° (hydrochloride, sparingly soluble, m. p. 282°; picrate, m. p. 205°; acetyl derivative, m. p. 180°; benzoyl derivative, m. p. 162°; phenylthiocarbamide, m. p. 150°; methiodide, m. p. 221°), and conversion of the amide into the alcohol by the diazo reaction. The secondary base, di-*p*-phenylbenzylamine, m. p. 132° (hydrochloride, m. p. above 300°, nitroso compound, m. p. 170°), is also formed in the reduction.

Benzylmethylamine (obtained by catalytic reduction of benzylidenemethylamine with nickel at 100°) with *p*-methylbenzyl chloride yields benzyl-*p*-methylbenzylmethylamine, colourless liquid, b. p. 160°/11 mm. (methiodide, m. p. 190°), which is converted by cyanogen bromide into a quaternary salt, probably benzyl-di-*p*-methylbenzylmethylammonium bromide, m. p. 184°, *p*-methylbenzyltrimethylammonium bromide, m. p. 170–175°, and benzylmethylcyanamide, b. p. 139–140°/12 mm. In a similar manner benzyl-*p*-phenylbenzylmethylamine, m. p. 44°, b. p. 190–192° (hydrochloride, m. p. 187°; picrate, m. p. 146°; methiodide, m. p. 162°), is obtained and transformed by cyanogen bromide into an oily quaternary salt, *p*-phenylbenzyltrimethylammonium bromide, m. p. 200°, and benzylmethylcyanamide.

*p*-Methylbenzylmethylamine, b. p. 83°/11 mm. (hydrochloride, m. p. 174°; picrate, m. p. 145°), was obtained by reduction of the Schiff's base from *p*-tolualdehyde and methylamine with sodium and alcohol. With *p*-ethylbenzyl chloride this yields the tertiary base, *p*-methylbenzyl-*p*-ethylbenzylmethylamine, b. p. 181°/9 mm., which on treatment with cyanogen bromide yields the quaternary salt,  $C_6H_4Me \cdot CH_2 \cdot NMe(CH_2 \cdot C_6H_4Et)_2Br$ , m. p. 168°; *p*-ethylbenzyltrimethylammonium bromide (chloroplatinate, m. p. 216°), and *p*-methylbenzylmethylcyanamide. *p*-Methylbenzyl-*p*-phenylbenzylmethylamine, b. p. 253—255°/13 mm., was similarly obtained from *p*-phenylbenzyl chloride, and this base by treatment with cyanogen bromide yields an oily quaternary salt, *p*-phenylbenzyltrimethylammonium bromide, m. p. 200°, and a substance, m. p. 70°, containing bromine, probably formed by the action of cyanogen bromide on the primarily formed *p*-methylbenzylmethylcyanamide. In a similar way *p*-methylbenzylmethylbutenylamine,



b. p. 116—118°/11 mm., is obtained by the action of crotonyl bromide on *p*-methylbenzylmethylamine, and this base is transformed by cyanogen bromide into an oily quaternary compound, *p*-methylbenzyltrimethylammonium bromide (m. p. 184°), and methylcrotonylcyanamide,  $CHMe : CH \cdot CH_2 \cdot NMe \cdot CN$ , b. p. 92—93°/55 mm.

*p*-Methylbenzylcinnamylmethylamine, b. p. 218—220°/12 mm., is decomposed by cyanogen bromide with production of an oily quaternary salt, *p*-methylbenzyltrimethylammonium bromide (m. p. 194°), and cinnamylmethylcyanamide.

*p*-Ethylbenzylmethylamine, b. p. 105°/10 mm., obtained by the action of *p*-ethylbenzyl chloride on methylamine, reacts with *p*-phenylbenzyl chloride, yielding *p*-phenylbenzyl-*p*-ethylbenzylmethylamine, b. p. 255—257°/11 mm. (hydrochloride, m. p. 205°), which on decomposition with cyanogen bromide gives an oily quaternary salt, *p*-phenylbenzyltrimethylammonium bromide, and *p*-ethylbenzylmethylcyanamide.

*p*-Phenylbenzylmethylamine, b. p. 173—174°/11 mm., was obtained by condensing *p*-phenylbenzaldehyde with methylamine and reducing the Schiff's base (m. p. 51°) with sodium. With cinnamyl bromide, it yields an oily quaternary compound which on distillation in a vacuum yields a tertiary base,  $C_{23}H_{23}N$  (hydrochloride, m. p. 224°), which is converted by cyanogen bromide into an oily quaternary salt, *p*-phenylbenzyltrimethylammonium bromide (m. p. 198°), and cinnamylmethylcyanamide.

Cinnamylmethylamine is a mobile liquid, b. p. 110—112°/12 mm. With allyl bromide it yields cinnamylmethylallylamine,  $CHPh : CH \cdot CH_2 \cdot NMe \cdot CH_2 \cdot CH : CH_2$ , b. p. 166—168°/11 mm., which on decomposition with cyanogen bromide yields an oily quaternary compound (chloroplatinate,  $C_{44}H_{52}N_2 \cdot Cl_6Pt$ , m. p. 85°), cinnamyltrimethylammonium bromide (m. p. 165°), and methylallylcyanamide,  $CH_2 : CH \cdot CH_2 \cdot NMe \cdot CN$ . Similarly from cinnamylmethylamine and crotonyl chloride is obtained cinnamylmethylcrotonylamine, b. p. 180—182°/10 mm., from which the quaternary salt,  $(CHPh : CH \cdot CH_2)_2NMe(CH_2 \cdot CH : CHMe)Br$ , m. p. 79°, cinn-



amyl bromide, and methylcrotonylcyanamide are formed on treatment with cyanogen bromide.

R. B.

**Catalytic Reduction of Phenol and  $\alpha$ -Naphthol under High Pressure.** H. INOUE (*J. Chem. Ind. Japan*, 1923, 26, 1330—1334; cf. this vol., p. 628).—By the same method as that used in the catalytic preparation of tetralin, phenol was reduced at about  $200^{\circ}$  to cyclohexanol (b. p.  $135^{\circ}$ ,  $d_{20}^{20}$  0.9547,  $n_D^{20}$  1.4650), and  $\alpha$ -naphthol to a mixture of tetralin (46.6%), *ar*-tetrahydro- $\alpha$ -naphthol (40.9%), and  $\alpha$ -ketotetrahydronaphthalene (12.5%).

K. K.

**Esterification of cycloHexanol and some of its Homologues.** (MLLE.) G. CAUQUIL (*Compt. rend.*, 1924, 178, 1538—1540; cf. this vol., i, 280).—On heating 2-, 3-, and 4-methylcyclohexanol with acetic acid, 49.8%, 53.1%, and 54.1%, respectively, of the three alcohols has undergone esterification at equilibrium, showing a decrease of 5.8, 2.5, and 1.5%, compared with cyclohexanol. For 3:4-dimethylcyclohexanol the corresponding decrease is 8.1 and for 2-ethylcyclohexanol, 6.4%.

J. W. B.

**Preparation of Stereoisomerides in the Disubstituted cycloHexanol Series.** M. GODCHOT and P. BEDOS (*Compt. rend.*, 1924, 178, 1184—1186).—The action of hypochlorous acid on  $\Delta^3$ -methylcyclohexene results in the formation of a mixture of two isomerides of 4-chloro-1-methylcyclohexan-3-ol. These were separated by repeated fractionations, and the two fractions were converted by the Grignard reaction into two 1:4-dimethylcyclohexan-2-ols, yielding allophanates of m. p.  $158^{\circ}$  and  $125^{\circ}$ , respectively. The alcohols on regeneration from these esters were colourless liquids, b. p.  $175^{\circ}/760$  mm.,  $d_{17}^{17}$  0.9066,  $n_D^{17}$  1.4521, and b. p.  $177^{\circ}/760$  mm.,  $d_{17}^{17}$  0.9079,  $n_D^{17}$  1.4544, respectively. On oxidation with chromic acid, both alcohols give 1:4-dimethylcyclohexan-2-one, b. p.  $171$ — $172^{\circ}$ ; semicarbazone, m. p.  $122^{\circ}$ .

H. J. E.

**Auto-oxidation and Anti-oxygens. Catalytic Properties of Iodophenols.** C. MOUREU, C. DUFRAISSE, and J. P. DES TOUCHES (*Compt. rend.*, 1924, 178, 1497—1501; cf. A., 1922, i, 250; 1923, ii, 308).—The inhibiting action on the auto-oxidation of acetaldehyde of substances containing both a phenolic group and iodine in the same molecule has been studied. Within the limits of experimental error, neither exaltation nor diminution in the activity of the phenol group occurs. Thus *o*-iodophenol exhibits a very slight diminution in activity compared with phenol itself. The very slight activity of iodobenzene shows that iodine in the nucleus has very little effect; but the introduction of a second phenolic group in the *o*-position (pyrocatechol) increases the activity coefficient 200 times. The activities of 2:6- and 3:4-di-iodophenol, and 2:4:6-tri-iodophenol are only slightly greater than that of phenol itself, and in equal molecular concentration 2:6-di-iodoquinol has the same activity as quinol. The dimethyl ether of monoiodoquinol has the same activity as quinol

dimethyl ether, each exhibiting an initial retarding effect followed by a distinct acceleration of the auto-oxidation. J. W. B.

**Nitration. II. Mononitration of Phenol.** F. ARNALL (*J. Chem. Soc.*, 1924, **125**, 811—816; cf. *ibid.*, 1923, **123**, 3111).—Nitration of phenol in an organic solvent gives much better results than in aqueous solution, but the velocity of nitration depends on the nature of the solvent. At 10°, reaction in acetic anhydride containing 10% of nitric acid is apparently instantaneous. In acetone, nitration with 10% nitric acid proceeds to the extent of 80% in 3 hours; in ether, 68% in 12 hours; in alcohol (2 parts) and acetic acid (1 part), 75% in 48 hours; in absolute alcohol, 55% in 48 hours. The relative proportions of the isomerides are independent of the solvent. The best results were obtained with glacial acetic acid, without formation of tar, the yield being almost quantitative at temperatures up to 50°. Raising the temperature of nitration or increasing the concentration of the nitric acid slightly increases the proportion of *o*-nitrophenol formed. The best yields of the mononitrophenols were obtained with 10% nitric acid at 25°. The mixture of mononitrophenols was analysed by a method involving steam distillation of the *o*-nitrophenol and thermal analysis of the benzyl ethers of *m*- and *p*-nitrophenol.

The following derivatives of *m*-nitrophenol have been obtained: *acetate*, m. p. 55—56°; *picrate*, m. p. 170—171°; *benzyl ether*, m. p. 55°; *acetonyl ether*, m. p. 83—84°; acetophenonyl ether, m. p. 127°. R. B.

**Action of Bromine on Methyl Esters of Phenolsulphonic Acids. Determination of Sulphur in Phenolsulphonic Esters and Salts.** L. J. SIMON and M. FRÈREJACQUE (*Compt. rend.*, 1924, **178**, 1282—1284).—The action at a low temperature of bromine (1 atom) on methyl *o*-cresolsulphonate in methyl-alcoholic solution, yields (1) the *methyl bromo-o-cresolsulphonate*, m. p. 143°, which retains the methylating properties of the original compound and gives, in particular, the characteristic derivative of hexamethylenetetramine (cf. this vol., i, 665), and (2) the corresponding bromo-*o*-cresolsulphonic acid. At 100° a second bromine atom enters the nucleus, from which it displaces the sulphonic group, so that, if excess of bromine is employed, the sole products of the reaction are dibromo-*o*-cresol and sulphuric acid. Similar products are obtained from methyl anisole-*p*-sulphonate, which also takes up a second bromine atom only by elimination of the sulphonic group.

Methyl sulphate, which sulphonates the phenols so readily, has no action on their bromo derivatives, even at higher temperatures (cf. A., 1923, i, 462, 1098). This inertness is in harmony with the total elimination of the sulphonic group by bromine, which allows of the use of the latter for the determination of the sulphur in sulphonic derivatives of phenols. Desvergnès' method (A., 1920, ii, 563) gives satisfactory results with the methyl esters of various phenolsulphonic acids, and with the water-soluble additive products of

the sulphonic esters with tertiary bases. No sulphuric acid is, however, liberated from the acyclic methanesulphonic and sulphoacetic acids. [Cf. *B.*, 1924, 444.]

T. H. P.

**Ultra-violet Absorption Spectra of Eugenol.** G. THOMPSON (*J. Chem. Soc.*, 1924, 125, 962; cf. *ibid.*, 1923, 123, 1594).—The absorption spectrum of eugenol in thin films agrees closely with its spectrum in alcoholic solution, and the absorption bands previously recorded are therefore characteristic of the substance itself. Extinction coefficients could not be calculated, as it was not possible to measure the thickness of the films.

R. B.

**Catalytic Action. V. Catalytic Reduction of  $\alpha$ - and  $\beta$ -Naphthyl Methyl Ethers.** S. KOMATSU and S. KUMAMOTO (*Mem. Coll. Sci. Kyōtō*, 1924, 7, 135—142).—The catalytic reduction of  $\alpha$ -naphthol has previously been found to yield products containing *ar*- and *ac*-compounds in the ratio 1:9 (A., 1923, i, 782), whereas the presence of the amino group in  $\alpha$ -naphthylamine favours the formation of *ar*-derivatives, the ratio of *ar*- to *ac*-compounds being 9:1. When  $\alpha$ -naphthyl methyl ether is reduced by means of hydrogen and reduced nickel at 200°, the molecular ratio of *ar*- to *ac*-compounds is 19:81.  $\beta$ -Naphthyl methyl ether forms *ac*-derivatives less readily than does the  $\alpha$ -ether, the molecular ratio of *ar*- to *ac*-products being 37:63. When reduced with sodium and boiling amyl alcohol,  $\alpha$ - and  $\beta$ -naphthyl methyl ethers yield only *ar*-tetrahydronaphthyl ethers, but when  $\beta$ -naphthyl methyl ether is reduced with sodium and ethyl alcohol,  $\beta$ -*ar*-dihydronaphthyl methyl ether is obtained.

C. J. S.

**Preparation of 2- and 4-Nitro- $\alpha$ -naphthols.** H. H. HODGSON and E. KILNER (*J. Chem. Soc.*, 1924, 125, 807—811).—The 2- and 4-nitro compounds obtained by the nitration of aceto- $\alpha$ -naphthalide (cf. A., 1886, 754; T., 1905, 87, 928) can be easily separated by hydrolysing the mixture with boiling 5% sodium hydroxide, and distilling the acidified solution with steam, whereby 2-nitro- $\alpha$ -naphthol is removed. The mixture was thus found to contain the 2- and 4-nitroaceto- $\alpha$ -naphthalides in the proportion 1:3. The poor yields of 2-nitro- $\alpha$ -naphthol obtained in the oxidation of 2-nitroso-1-naphthol with dilute nitric acid (A., 1892, 861) are due to the action of nitrous acid, liberated during the reaction, on the nitronaphthol. 4-Nitro- $\alpha$ -naphthol is attacked more rapidly than the 2-nitro compound. The addition of carbamide to the oxidation mixture raises the yield of 2-nitro- $\alpha$ -naphthol to 50% of the theoretical. Better results were obtained by using 100 vol. hydrogen peroxide, the yield being 50—60%. The by-products are soluble derivatives of phthalic acid. Ammonium 2-nitro- $\alpha$ -naphthoxide, in contrast with the nitronaphthol itself, can be distilled in steam without resinification.

R. B.

**Manufacture of G-Acid [ $\beta$ -Naphthol-6:8-disulphonic Acid], using Fuming Sulphuric Acid.** T. KAWAGUCHI (*J. Chem. Ind. Japan*, 1923, 26, 1233—1256).—When 1 part of  $\beta$ -naphthol is sulphonated with 5 parts of fuming sulphuric acid containing

20% of sulphur trioxide at 20—25° during 8 hours, G acid is the principal product, with  $\beta$ -naphthol-3 : 6-disulphonic acid (R acid) and -6-sulphonic acid (Schäffer acid) as by-products. Separating the last by partial crystallisation as barium salt, and G and R acids through the difference in solubility of their sodium salts in aqueous alcoholic solution, 2 grams of barium salt of Schäffer acid, 61 grams of sodium salt of G acid, and 22 grams of sodium salt of R acid were isolated from 50 grams of  $\beta$ -naphthol. Neglecting Schäffer acid, if G and R acids are separated as acid potassium and sodium salts, the yields of the two salts are 75 grams and 17 grams, respectively, from the same amount of  $\beta$ -naphthol.

K. K.

**So-called Auxochromes and their Method of Action.** A. HANTZSCH (*Annalen*, 1924, **436**, 321—323).—A defence of the author's theory of isomeric change, in reply to Kaufmann (A., 1924, i, 37).

R. B.

**Reaction of Resorcinol and of Phloroglucinol with Formaldehyde.** A. ZAMPARO (*Boll. Chim. Farm.*, 1924, **63**, 161—164).—Resorcinol and phloroglucinol are the only ordinary phenolic compounds which react immediately in the cold to give coloured precipitates when 0.1 g. is dissolved in 3 c.c. of 95% alcohol and the solution is treated successively with 2 c.c. of 40% formaldehyde solution and 3 c.c. of concentrated hydrochloric acid; the two naphthols and thymol give precipitates soluble in alcohol. [Cf. B., 1924, 445.]

T. H. P.

**Dyes of the Aurin Type. II.** H. BAINES and J. E. DRIVER (*J. Chem. Soc.*, 1924, **125**, 907—910; cf. *ibid.*, 1923, **123**, 1214).—By the action of chloroform vapour on dry potassium phenoxide at 110° in the absence of oxygen, triphenyl orthoformate, m. p. 75°, and leucaurin,  $\text{CH}(\text{C}_6\text{H}_4\text{OH})_3$ , are produced. The reaction proceeds more slowly with boiling chloroform, but the yield is greatly diminished by the presence of water and is not appreciably increased by using alcohol as solvent.

R. B.

**Catalytic Preparation of Benzyl Ethers.** J. B. SENDERENS (*Compt. rend.*, 1924, **178**, 1412—1415).—The method previously described (this vol., i, 40) has now been applied to the preparation of benzyl ether, and of the mixed benzyl ethyl, benzyl propyl, benzyl isopropyl, benzyl butyl, benzyl isobutyl, and benzyl isomethyl ethers. For these mixed ethers, the boiling point rises, but the density diminishes as the molecular weight increases.

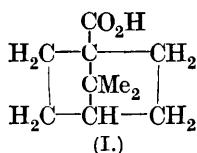
T. H. P.

**Chemical Nature of the Naphthenic Acids.** O. ASCHAN (*Ber.*, 1924, **57**, [B], 636—637).—A reply to a paper by Zelinsky and Pokrowskaja (this vol., i, 387) criticising work done by the author in 1892 (A., 1893, i, 209). The heptanaphthenecarboxylic acid was obtained pure by redistilling the methyl ester 30 times and boiled within 2°; it was probably purer than that obtained

by Zelinsky and Pokrowskaja. The author had suggested in 1892 that the naphthenic acids,  $C_7H_{12}O_2$  and  $C_8H_{14}O_2$ , were *cyclopentane* derivatives; the suggestions of Zelinski and Pokrowskaja are therefore not novel.

F. A. M.

**Ketopinic Acid. Conversion into Norcamphane-1-carboxylic Acid.** E. WEDEKIND [with C. WEINAND] (*Ber.*, 1924, 57, [B], 664—666).—Ketopinic acid (cf. Wedekind, Schenk, and Stüsser, A., 1923, i, 346) is converted



into its *semicarbazone*, m. p.  $226^\circ$ , which is transformed by sodium ethoxide and ethyl alcohol at  $170\text{--}180^\circ$  into *norcamphane-1-carboxylic acid* (I), m. p.  $221\text{--}222^\circ$ ; the *copper*, *lead*, *mercury*, *silver*, and *zinc* salts are described. The *calcium* salt is

particularly characteristic.

The *phenylhydrazide*, m. p.  $140^\circ$ , and the *amide*, m. p.  $192.5^\circ$ , of ketopinic acid are described. The acid is associated to a considerable degree in benzene even in dilute solution.

H. W.

**Catalytic Action. VI. Catalytic Action of Reduced Copper on Acid Amides.** S. KOMATSU and M. KURATA (*Mem. Coll. Sci. Kyōtō*, 1924, 7, 157—159).—The suggestion that at a high temperature reduced copper causes simultaneous dehydration and hydration has been confirmed by passing menthonisooxime over the catalyst at  $200^\circ$ , whereby menthonitrile and decenoic acid were obtained. Benzamide when passed over reduced copper at  $250^\circ$  gives benzonitrile and benzoic acid, whilst acetamide (at  $200^\circ$ ) yields acetonitrile and acetic acid.

C. J. S.

**Condensation of Nitriles with Thioamides. II. Acetonitrile with Thiobenzamide, and Benzonitrile with Thioacetamide.** S. ISHIKAWA (*Mem. Coll. Sci. Kyōtō*, 1924, 7, 93—98; cf. A., 1921, i, 728).—The combination of acetonitrile and thiobenzamide, induced by saturating their ethereal solution with dry hydrogen chloride, yields, not acetiminoisobenzamide, but benziminoisothiobenzamide. The fact that thioacetamide is found in the resulting solution indicates that the acetonitrile and thiobenzamide first condense similarly to benzonitrile and thiobenzamide, and that the condensation product is unstable and decomposes into benzonitrile and thioacetamide:  $\text{CH}_3\cdot\text{CN} + \text{NH}\cdot\text{CPh}\cdot\text{SH} \rightarrow \text{NH}\cdot\text{CMe}\cdot\text{N}\cdot\text{CPh}\cdot\text{SH} \rightarrow \text{NH}\cdot\text{CMe}\cdot\text{SH} + \text{C}_6\text{H}_5\cdot\text{CN}$ ; equilibrium is reached when about 20% of the reacting compounds is converted into the final products. From benzonitrile and thioacetamide, benziminoisothiobenzamide and thiobenzamide were obtained, the latter product representing about 71% of the benzonitrile.

T. H. P.

**Electrolytic Oxidation of *p*-Nitrotoluene and *p*-Chlorotoluene to their respective Acids.** R. DUNBROOK and A. LOWY (*Trans. Amer. Electrochem. Soc.*, 1924, 45, 97—117).—Using 20% nitric acid as the electrolyte and platinum electrodes, *p*-nitrotoluene and *p*-chlorotoluene were oxidised to *p*-nitrobenzoic and *p*-chloro-

benzoic acids, respectively. In the first case, the best conditions were with a current density of 4 amp. per sq. dm., at 100°, a current efficiency of 34.1% being obtained. In the second case, the current density was 0.5 amp. per sq. dm. and the current efficiency was 65%, but with acetic acid as solvent it rose to 96%. [Cf. *B.*, 1924, 444.] W. A. S.

**[*p*-Aminobenzoic] Esters of Substituted Aminopropyl Alcohol.** W. SCHULEMANN, L. SCHÜTZ, and K. MEISENBURG (U. S. Pat. 1474567).—dl- $\gamma$ -Dimethylamino- $\alpha\beta$ -dimethylpropyl *p*-aminobenzoate (crystalline hydrochloride) has m. p. 81–82°. dl- $\gamma$ -Diethylamino- $\alpha\beta$ -diethylpropyl *p*-aminobenzoate hydrochloride has m. p. 146°.  $\gamma$ -Diethylamino- $\beta$ -methyl- $\alpha$ -ethylpropyl *p*-aminobenzoate hydrochloride has m. p. 178°. CHEMICAL ABSTRACTS.

**Synthetic Anæsthetics [Alkylaminoalkyl *p*-Aminobenzoates.** E. H. VOLWILER and R. ADAMS (U.S. Pat. 1476934).— $\gamma$ -Butylallylaminopropyl *p*-aminobenzoate hydrochloride forms white needles, m. p. 147°. Butylallylamine, from butyl bromide and allylamine, has b. p. 132–133°/760 mm.  $\beta$ -Butylallylaminoethyl *p*-aminobenzoate hydrochloride has m. p. 184°. The hydrochlorides of propylallylaminopropyl and isopropylallylaminopropyl *p*-aminobenzoates are viscous oils. isoAmylallylaminomethyl alcohol, b. p. 132–133°/55 mm. (obtained by heating ethylene oxide with isoamylallylamine at 60°) yields a *p*-aminobenzoate hydrochloride, m. p. 194–195°. CHEMICAL ABSTRACTS.

**Identity of Abietic Acids Extracted from Different Colophonies.** G. DUPONT and R. UZAC (*Bull. Soc. chim.*, 1924, [iv], 35, 394–404; cf. Schulz, *Mon. Sci.*, 1920, 10, 109).—Crude abietic acid, obtained by extracting colophony with 95% alcohol and hydrochloric acid, was purified by crystallisation to a constant rotatory power. In this way, pure abietic acid of m. p. 173°, and  $[\alpha]$  –105° for the yellow light of the mercury arc, was obtained from colophony from the following sources: (1) *Pinus maritima*; (2) Aleppo pine; (3) *P. Laricio austriaca*; (4) *P. longifolia*; (5) *P. pinea*. Pimaric acid (A., 1921, i, 510),  $\alpha$ - and  $\beta$ -alepic acids, and the sapinic acids are easily isomerised to abietic acid ( $\beta$ -pimarabietic acid) by the influence of hydrochloric acid. For these reasons, the authors do not regard abietic acid as a constituent of the natural gums, but as the final stable isomeric form of the constituents of these gums. The suggestion of Knecht and Hibbert (cf. A., 1919, i, 338) that abietic anhydride forms a constituent of colophony is rejected because abietic acid has been obtained from colophony in dry tubes at 130°, when no water was present to convert the anhydride into acid and because abietic

**Phthalaldehydic Acid.** L. SEEKLES (*Rec. trav. chim.*, 1924, 43, 329–340).—Further details of the preparation of phthalaldehydic acid by the ozonisation of naphthalene are given (cf. A., 1923, i, 931). The normal phenylhydrazone of phthalaldehydic acid has not previously been described, as it readily loses water to

**$\alpha\alpha\beta$ -Triphenylpropionic Acid and some of its Derivatives.** (MLLE.) P. RAMART (*Bull. Soc. chim.*, 1924, [iv], 35, 196—200).—A more detailed account of work already published (this vol., i, 171). S. K. T.

**Calcium *o*-Benzyloxybenzoate.** E. A. WILDMAN (U.S. Pat. 1481779).—Saponification of the product obtained by the interaction of methyl salicylate, benzyl chloride, and sodium ethoxide yields *o*-benzyloxybenzoic acid, m. p. 75°. The calcium salt,  $\text{Ca}(\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\text{Ph})_2$ , is obtained by boiling the acid with water and calcium carbonate.

**A New Iodosalicylic Acid.** P. BRENANS and C. PROST (*Compt. rend.*, 1924, 178, 1010—1012; cf. A., 1923, i, 797).—4-Iodosalicylic acid, colourless needles, turning brown at 200°, m. p. 228° (decomp.), was prepared from 4-nitro-*o*-toluidine by acetylation, oxidation to 4-nitroacetylthranilic acid, deacetylation, and diazotisation to 4-nitrosalicylic acid, the ethyl ester of which was reduced; from the diazonium sulphate of the resulting amino compound hydriodic acid yielded ethyl 4-iodosalicylate (needles, m. p. 21°), which was hydrolysed. The acetyl derivative of the acid forms colourless crystals, m. p. 156°. H. J. E.

**Iodinated *m*-Hydroxybenzoic Acids.** P. BRENANS and C. PROST (*Compt. rend.*, 1924, 178, 1285—1287).—Certain of the results obtained by the authors have been already published by Beyer (A., 1922, i, 37). The iodo-*m*-hydroxybenzoic acid, m. p. 226° (decomp.), prepared by Weselsky's method (A., 1875, 139) is identical with that obtained from 4-amino-*m*-hydroxybenzoic acid by way of the diazo compound, and is, therefore, 4-iodo-*m*-hydroxybenzoic acid. 4-Iodo-*m*-acetoxybenzoic acid forms white crystals, m. p. 203°.

The iodohydroxybenzoic acid prepared from the amino-*m*-hydroxybenzoic acid obtained when 6-benzeneazo-*m*-hydroxybenzoic acid is reduced by means of stannous chloride and hydrochloric acid, is identical with that prepared from Griess' nitro-*m*-hydroxybenzoic acid (A., 1887, 485), which is hence the 6-nitro-acid. [Cf. Beyer, *loc. cit.*] T. H. P.

**A New Iodo-*p*-hydroxybenzoic Acid.** P. BRENANS and C. PROST (*Compt. rend.*, 1924, 178, 1555—1557; cf. A., 1923, i, 1203).—The preparation of the second isomeride of iodo-*p*-hydroxybenzoic acid (2 : 4 : 1) is described. Treatment of the diazonium sulphate derived from 4-nitroanthranilic acid with potassium iodide yields 2-iodo-4-nitrobenzoic acid (cf. Willgerodt and Gartner, A., 1908, i, 877), which on reduction yields 2-iodo-4-aminobenzoic acid, colourless needles, m. p. 188° (decomp.); hydrochloride, decomp. 210°; sulphate, white needles. The diazonium sulphate derived from this acid decomposes in aqueous solution, forming 2-iodo-4-hydroxybenzoic acid, white, refractive needles, m. p. 215° (decomp.); acetyl derivative, m. p. 146°. J. W. B.

**Phthalaldehydic Acid.** L. SEEKLES (*Rec. trav. chim.*, 1924, **43**, 329—340).—Further details of the preparation of phthalaldehydic acid by the ozonisation of naphthalene are given (cf. A., 1923, i, 931). The normal phenylhydrazone of phthalaldehydic acid has not previously been described, as it readily loses water to form phenylphthalazone. It has now been obtained by the action of phenylhydrazine on the sodium salt of the acid. *Benzaldehyde-phenylhydrazone-o-carboxylic acid* forms a yellow precipitate, m. p. 100° (decomp.); the dark yellow *sodium* salt contains 4H<sub>2</sub>O, and the yellow *silver* salt turns brown in the light. Similar compounds were obtained using *p*-bromo- and *p*-nitro-phenylhydrazine. *p*-Bromophenylphthalazone forms fine, colourless needles, m. p. 169.5°; *p*-nitrophenylphthalazone, orange crystals, m. p. 259° (sintering from 228°). Hydrogen cyanide combines with the aldehydic group of phthalaldehydic acid in the normal manner, forming *o*-carboxymandelonitrile, from which *o*-carboxymandelic acid is obtained, by hydrolysis with hydrochloric acid, in the form of its lactone, phthalide- $\alpha$ -carboxylic acid. With acetic anhydride, phthalaldehydic acid forms a monoacetyl derivative, which must also have the phthalide structure, C<sub>6</sub>H<sub>4</sub> $\left\langle \begin{smallmatrix} \text{CH}(\text{OAc}) \\ \text{CO} \end{smallmatrix} \right\rangle$ O. Its m. p. is 71°, not 60—63° as recorded elsewhere.

Comparison of the molecular refraction of phthalaldehydic acid in alcoholic solution with that of phthalide and phthalidecarboxylic acid shows that in this solvent phthalaldehydic acid has the phthalide structure, whilst in aqueous solution the aldehydic tautomeride is the more stable form.

E. H. R.

**Benzylidenepyruvic Acid [Styrylglyoxylic Acid] and its Esters. I. The Action of Sunlight on Crystalline Methyl Styrylglyoxylate.** M. REIMER (*J. Amer. Chem. Soc.*, 1924, **46**, 783—790).—Erlenmeyer's procedure for preparing styrylglyoxylic acid by condensing pyruvic acid and benzaldehyde in presence of sodium hydroxide (A., 1903, i, 698) has been improved and the yield increased to 80% of the theoretical. The *ethyl* ester is a yellow oil, b. p. 169—171°/7 mm.; the *methyl* ester forms long, yellow needles, m. p. 73—74°. After 1 month's exposure to sunlight, the methyl ester changes into a dimeric form, (C<sub>11</sub>H<sub>10</sub>O<sub>3</sub>)<sub>2</sub>, shown to be *methyl 2 : 4-diphenylcyclobutane-1 : 3-diglyoxylate*,

Ph·CH—CH·CO·CO<sub>2</sub>Me  
CO<sub>2</sub>Me·CO·CH—CHPh, colourless crystals, m. p. 154°, which by hydrolysis yields the corresponding *acid*, m. p. about 187° (in some cases after melting at 110—116°, with evolution of gas, and again solidifying). When re-methylated with methyl alcohol, the acid gives an *ester*, (C<sub>11</sub>H<sub>10</sub>O<sub>3</sub>)<sub>2</sub>, m. p. 155°, not identical with the ester having m. p. 154°, but readily obtained from it by the action of hydrogen chloride in methyl alcohol. Oxidation of the above acid gives  $\alpha$ -truxillic acid, which proves its constitution.

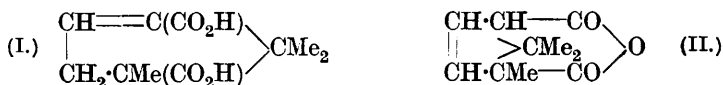
When methyl styrylglyoxylate dissolved in benzene is exposed to sunlight, a third isomeric *methyl* ester is obtained as colourless crystals, m. p. 117°. Hydrolysis of this ester gives an acid, m. p.



180°, which when esterified with methyl alcohol again forms the ester from which it had been produced. The free acid, when oxidised, is converted into  $\delta$ -truxinic acid and is therefore concluded to be 3 : 4-diphenylcyclobutane-1 : 2-diglyoxylic acid. C. J. S.

**Saponins and Related Compounds. X. Urson.** A. W. VAN DER HAAR (*Rec. trav. chim.*, 1924, **43**, 367—379).—The m. p. of chemically pure urson is 279—280° (cf. Dodge, A., 1919, i, 91). The generally accepted composition of urson,  $C_{30}H_{48}O_3$ , is incorrect, the correct formula being  $C_{31}H_{50}O_3$ . This formula explains the decomposition of urson, when distilled with zinc dust in a current of hydrogen, into sesquiterpenes, carbon dioxide, and water:  $C_{31}H_{50}O_3 \rightarrow 2C_{15}H_{24} + CO_2 + H_2O$ . The sesquiterpenes when heated with sulphur (Ruzicka's method) give an oil of which a *picrate*, m. p. 115—116°, was obtained; this is probably a picrate of a hydrocarbon of the naphthalene series, but is not identical with cadalene picrate. Urson contains one hydroxyl and one carboxyl group. *Acetylurson*, m. p. 200—201°, obtained by the action of acetic anhydride on urson, is deacetylated by boiling alcohol, consequently the "acetylurson" obtained by Gintl (A., 1893, i, 601) was urson itself. Dodge (*loc. cit.*) described a diacetylurson, and supposed urson to be a hydroxy-lactone, but his product probably contained occluded acetic anhydride. Methylation of urson takes place in the carboxyl group, giving methyl urson, which forms a *hydrate* containing  $1H_2O$ , m. p. 120°; anhydrous methyl urson has m. p. 165°, not 148° (cf. Nooyen, *Diss.*, Leyden, 1920). *Methyl acetylurson*, long, glistening needles, m. p. 245°, is more stable than acetylurson. The influence of the free carboxyl group on a neighbouring hydroxyl group has been also observed in the case of saponins (*e.g.*, hederagenin, A., 1922, i, 160). E. H. R.

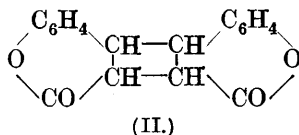
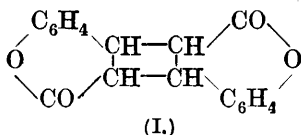
**Steric Hindrance in Bridged Rings (Bredt's Rule) and the meso-trans-Position in Condensed cycloHexane Ring Systems.** J. BREDT, H. THOUET, and J. SCHMITZ (*Annalen*, 1924, **437**, 1—13).—The author adduces facts in agreement with his rule (cf. A., 1902, i, 374; 1913, i, 281; 1917, i, 655) that double bonds cannot exist in conjunction with the "bridge-heads" in bridged cyclohexane structures. He now shows that a bridged (7-membered) ring of this kind cannot be formed. Thus, such a dicarboxylic acid as dehydrocamphoric acid (I) does not yield a simple anhydride, but gives ultimately the anhydride of isodehydrocamphoric acid (II):



Silver dehydrocamphorate and dehydrocamphoryl chloride heated together produce an amorphous *dianhydride*, sintering at 120°, but having no definite m. p. Dehydrocamphoric acid heated with acetyl chloride yields the acid chloride and a *mixed anhydride*, and the latter compound is also formed when the acid is heated with acetic anhydride. It forms a syrupy mass; when heated further,

it decomposes, giving a *poly-anhydride* of dehydrocamphoric acid, a vitreous substance, which when distilled in a vacuum yields *isodehydrocamphoric anhydride*, stout crystals, m. p. 184°. The conclusion that dehydrocamphoric acid can yield no simple anhydride is supported by steric considerations, and for these reasons the author concludes that the anhydrides obtained by Perkin (T., 1894, 65, 572, 890) are likewise polymeric compounds. W. A. S.

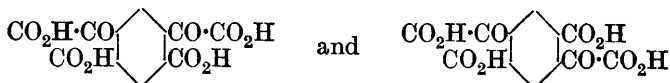
**Biscoumaric Acids.** A. W. K. DE JONG (*Rec. trav. chim.*, 1924, 43, 316—322).—The author suggests that the biscoumarins have structures similar to those of the truxillic and truxinic acids (A., 1923, i, 574). There are thus four possible isomerides, two corresponding with the plane formula (I) and two with (II):



The biscoumaric acid of Ström (A., 1904, i, 505) is formed by a method analogous to the formation of  $\alpha$ -truxillic acid from  $\alpha$ -cinnamic acid. It should therefore be called  $\alpha$ -biscoumaric acid, and the biscoumarin derived from it is  $\alpha$ -biscoumarin, m. p. 318° (decomp.). This should have formula I. It forms a *dimethyl ether*, colourless needles, m. p. 133°, which when hydrolysed gives  $\alpha$ -biscoumaric acid dimethyl ether, m. p. 261—262°, which appears to be identical with the product obtained by Bertram and Kürsten by the action of light on coumaric acid methyl ether. When the dimethyl ether is heated with acetic anhydride, it forms  $\gamma$ -biscoumaric acid dimethyl ether anhydride, m. p. 186—187°, which when hydrolysed gives  $\gamma$ -biscoumaric acid dimethyl ether, brilliant needles, m. p. 234°. Another acid,  $\epsilon$ -biscoumaric acid, m. p. 262°, was obtained by the action of fused potassium hydroxide on  $\alpha$ -biscoumaric acid. The biscoumarin obtained by Ciamician and Silber (A., 1914, ii, 234) and called by them dihydrocoumarin, by the action of light on coumarin, is now called  $\zeta$ -biscoumarin; m. p. 262°. This corresponds with formula II, and it is proposed to call the corresponding acids *biscoumarinic acids*, to correspond with the truxinic acids.  $\zeta$ -Biscoumarinic acid is a dibasic acid, m. p. 245°, forming fine needles which soon grow into larger crystals. *Dimethyl  $\zeta$ -biscoumarinate dimethyl ether* forms yellow crystals, m. p. 112—113°;  $\zeta$ -biscoumarinic acid dimethyl ether, m. p. 134°. By heating with fused potassium hydroxide  $\zeta$ -biscoumarinic acid is converted into  $\delta$ -biscoumarinic acid, m. p. 157°. The hydrodicoumarin obtained by Dyson (*Chem. Soc. Trans.*, 1887, 51, 66), by reducing dicoumarin with sodium amalgam, is not identical with  $\zeta$ -biscoumarin, as supposed by Ciamician and Silber. By hydrolysis, it gives a monobasic acid. E. H. R.

**Preparation of Pyromellitic Acid.** J. VON BRAUN and G. LEMKE (*Ber.*, 1924, 57, [B], 681—682).—The oxidation of octahydroanthracene with alkaline permanganate yields an acidic

product of approximately the formula  $C_{12}H_6O_{10}$ , which is probably a mixture of the two isomeric diphthalonic acids :



These could not, however, be separated. Further oxidation with acid permanganate gave a nearly quantitative yield of pyromellitic acid. From 30 g. of octahydroanthracene 41 g. of practically pure pyromellitic acid were obtained.

F. A. M.

#### Action of Aluminium Alkoxides on Mixtures of Aldehydes.

N. A. ORLOFF (*Bull. Soc. chim.*, 1924, [iv], 35, 360—363; cf. A., 1907, i, 282).—The action of aluminium ethoxide on three mixtures of aldehydes has been studied. Benzaldehyde and isobutyraldehyde gave a product from which three fractions were obtained, the first consisting of isobutyl isobutyrate, the second of isobutyl benzoate (19.3%) and benzyl isobutyrate (80.7%), and the third of pure benzyl benzoate. From a mixture of isobutyraldehyde and acetaldehyde, in addition to isobutyl isobutyrate, ethyl acetate, and aldolic products, a mixture, b. p. 110—117.5°, was obtained consisting of isobutyl acetate (75%) and ethyl isobutyrate (25%). Benzaldehyde and acetaldehyde gave, besides ethyl acetate, benzyl benzoate, and unchanged benzaldehyde, a mixture of benzyl acetate (96.2%) and ethyl benzoate (3.8%). The author concludes that of the two possible mixed esters, that one will be formed in larger amount in which the aldehyde of higher molecular weight yields the alcoholic component.

R. B.

**Catalytic Hydration of Schiff's Bases.** A. MAIHLE (*Bull. Soc. chim.*, 1924, [iv], 35, 379—382; cf. A., 1919, i, 395; 1920, i, 380).—Schiff's bases are easily hydrolysed when vaporised in a current of steam and passed over catalysts such as thoria and alumina heated at 400°. In this way, benzylideneaniline, for example, yields benzaldehyde and aniline. In the presence of vapours of methyl or ethyl alcohol the amine is immediately alkylated, the product of the reaction being the corresponding dialkylamine, but in the presence of higher alcohols such as propyl alcohol, alkylation does not take place.

R. B.

#### Thermochemical Researches on Stereoisomeric Aldoximes.

W. SWIENTOSLAWSKI and M. POPOFF (*Bull. Soc. chim.*, 1924, [iv], 35, 137—144).—Measurement of the heat evolved when sodium hydroxide or hydrochloric acid reacts with a stereoisomeric aldoxime (benzaldoxime, *m*-nitrobenzaldoxime) shows that the :N·OH group is more strongly acidic in the  $\alpha$ -(*anti*)-aldoximes than in the  $\beta$ -(*syn*)-aldoximes. The heat of solution in water is always negative, the  $\beta$ -isomeride having the higher absolute value.

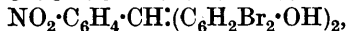
Dry hydrogen chloride converts concentrated ethereal solutions of  $\alpha$ -aldoxime into the  $\beta$ -stereoisomeride, but not always quantitatively. When a mixture of the two forms results, the  $\alpha$ -aldoxime

is in greater proportion the greater the speed of the conversion. A thermochemical method for the quantitative analysis of these mixtures is developed. Mixtures containing up to 40% of the hydrochloride of  $\alpha$ -benzaldoxime and of  $\alpha$ -*m*-nitrobenzaldoxime were prepared.

The heat of conversion in ether solution of  $\alpha$ - into  $\beta$ -benzaldoxime is  $-0.98$  Cal.; that for  $\alpha$ - into  $\beta$ -*m*-nitrobenzaldoxime is  $-1.18$  Cal. The heats of transformation in the free state are  $+2.64$  Cal. ( $\alpha_{\text{liq.}}$  to  $\beta_{\text{solid}}$ ) and  $-1.25$  Cal. ( $\alpha_{\text{solid}}$  to  $\beta_{\text{solid}}$ ), respectively. E. E. T.

**Derivatives of *p*-Nitrobenzaldehyde. II.** C. G. KING and A. LOWY (*J. Amer. Chem. Soc.*, 1924, **46**, 757—762; cf. A., 1921, i, 337).—The following new *p*-nitrobenzylidene compounds have been prepared: *p*-nitrobenzylidene-*o*-bromoaniline, m. p.  $106^\circ$ ; *m*-bromoaniline, m. p.  $102^\circ$ ; -2:6-dibromoaniline, m. p.  $137^\circ$ ; -2:4:6-tribromoaniline, m. p.  $142.5^\circ$ ; -3-bromo-4-toluidine, m. p.  $112^\circ$ ; -*p*-xylydine, m. p.  $100^\circ$ ; -*o*-nitroaniline, m. p.  $169^\circ$ . All form yellow needles except the last, which forms small plates.

*p*-Nitrobenzaldehyde condenses with 2 mols. of phenol by Danckworth's method, giving *p*-nitro-*p*'*p*''-dihydroxytriphenylmethane, which forms a 3':5':3'':5''-tetrabromo derivative,



small, yellow plates, m. p.  $215^\circ$ ; diacetyl derivative, m. p.  $168^\circ$ .

The condensation product from resorcinol and *p*-nitrobenzaldehyde gave, on bromination, a dibromo-*p*-nitrotetrahydroxytriphenylmethane,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : [\text{C}_6\text{H}_2(\text{OH})_2\text{Br}]_2$ , a yellow, amorphous powder which turns red at  $170^\circ$  and chars above  $200^\circ$ . From *o*-nitrophenol and the nitro-aldehyde was obtained 4:3':3'':4'-trinitro-4':4''-dihydroxytriphenylmethane,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : [\text{C}_6\text{H}_3(\text{OH})\text{NO}_2]_2$ , an orange, amorphous powder, m. p.  $177^\circ$ . The condensation product obtained from thymol and *p*-nitrobenzaldehyde was brominated and gave a dibromo derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : [\text{C}_6\text{HMePrBrOH}]_2$ , light orange crystals, m. p.  $115^\circ$ ; dibenzoyl derivative, a pale yellow, amorphous powder, m. p.  $82^\circ$ . C. J. S.

**Electrolytic Preparation of Salicylaldehyde from Salicylic Acid.** K. S. TESH and A. LOWY (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 325—333).—Sodium salicylate is reduced electrolytically in the usual type of diaphragm cell with a mercury cathode, sodium sulphate being used as anolyte and a mixture of boric acid and sodium sulphate as catholyte. A current density of 6 amp. per sq. dm. is employed, and the temperature maintained at  $15$ — $18^\circ$ ; less aldehyde and more resinous matter is obtained at higher temperatures. The salicylaldehyde produced is fixed as soon as formed by progressive addition of sodium hydrogen sulphite, and is recovered by acid hydrolysis and distillation with steam. The best yield obtained is 55% of the theoretical. W. T. K. B.

**Thermochemical Researches on Ketoximes. Non-stereoisomeric Ketoximes.** A. DORABIALSKA (*Bull. Soc. chim.*, 1924, [iv], **35**, 145—152).—A thermochemical investigation of dimethyl, diphenyl, and phenyl methyl ketoximes (cf. Swientoslawski and Popoff, p. 645). According to theory two stereoisomeric phenyl

methyl ketoximes should exist, but only one could be obtained, treatment of ether or toluene solutions of the oxime with hydrogen chloride failing to cause any conversion. The heats of formation of the hydrochlorides of the oximes in ether solution differ but little from those of the aldoximes; they diminish with increasing acidity. Phenyl methyl ketoxime is more acidic than its constitution indicates. This is probably due to the ketoxime having the  $\alpha$ -structure, since  $\alpha$ -aldoximes are more acidic than the  $\beta$ -forms. The heat of solution of the hydrochlorides in 10% sodium hydroxide decreases as the acidity of the ketoxime increases. The heat is made up of four portions, viz., heat of solution of the hydrochloride in water (which is negative and less than that of the aldoximes), heat of decomposition (negative) of the hydrochloride into hydrochloric acid and oxime, heat of reaction of the oxime with sodium hydroxide, and heat of neutralisation of hydrochloric acid and sodium hydroxide. The parallel increase of the first two of these quantities is the cause of the decrease of the total heat with increasing acidity.

E. E. T.

**Ethyl Mercaptol of Phenyl Ethyl Ketone; a New Disulphone.** A. SCHMIDT (*Bul. Soc. Chim. România*, 1924, **6**, 34—36).—On passing a stream of hydrogen chloride into a mixture of phenyl ethyl ketone (1 part) and ethyl mercaptan (2 parts) together with a small amount of anhydrous zinc chloride, the *ethyl mercaptol of phenyl ethyl ketone*,  $\text{CEtPh}(\text{SEt})_2$ , a colourless oil of disagreeable odour, is formed. On oxidation with potassium permanganate in presence of dilute sulphuric acid, the corresponding *disulphone* is obtained in small yield as colourless, monoclinic plates, m. p. 113.5°.

A. E. C.

**Two Oximes of  $\alpha$ -Ketotetrahydronaphthalene.** H. INOUE (*J. Chem. Ind. Japan*, 1923, **26**, 1335—1338; cf. *Chem. Soc. Trans.*, 1899, **75**, 150).—The oxime of  $\alpha$ -ketotetrahydronaphthalene, obtained by catalytic reduction of  $\alpha$ -naphthol, is separated by steam distillation into a more volatile isomeride, A, colourless needles, m. p. 88—89°, and a less volatile, B, large, colourless prisms, m. p. 102—103°. By the Beckmann rearrangement, A gives B and B gives a nitrile-like liquid and another isomeric compound, C, colourless needles or prisms, m. p. 134—136°. A and B are probably stereoisomeric forms of the ketoxime.

K. K.

**Influence of Constitution on the Rotatory Power of Optically Active Substances. XVI. Acetylene Derivatives, Ketones, Carbylamines.** H. RUPE (*Annalen*, 1924, **436**, 184—204; cf. A., 1909, i, 927).—A comparison has been made between the rotatory powers of compounds containing acetylenic linkings and the corresponding ethylenic and saturated compounds. Phenyl-acetylenylborneol, its dihydro- and tetrahydro-derivatives all exhibit normal rotation dispersion, and the ethylenic compound shows the greatest specific rotatory power. 1:2:2:3-Tetramethylcyclopentyl phenylacetylenyl ketone exhibits a large anomalous rotation-dispersion, whilst its dihydro and tetrahydro derivatives and also

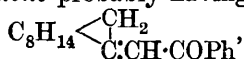
an isomeric ethylenic compound obtained by the condensation of 1:2:2:3-tetramethylcyclopentyl methyl ketone with benzaldehyde (Rupe and Kloppenburg, A., 1919, i, 539) are nearly normal. Amylcarbylamine, hexonitrile, hexylamine, and benzylidenehexylamine all exhibit anomalous rotation-dispersion, which is total in the case of the first substance. 3-Methylcyclohexylcarbylamine and 3-methylcyclohexylamine show very similar dispersions and it is doubtful whether these are normal or not.  $\alpha$ -Camphorcarbimide exhibits an enormous specific rotation in comparison with the other members of the series.

Phenylacetylenylborneol,  $C_8H_{14} \begin{smallmatrix} <CH_2 \\ | \\ C(OH) \cdot C: CPh \end{smallmatrix}$ , from magnesium phenylacetylenyl bromide and camphor, has b. p.  $190^\circ/13$  mm. or  $125-126^\circ/0.1$  mm., m. p.  $44-45^\circ$ ,  $[\alpha]_D^{25} -27.37^\circ$  in 10% benzene solution.

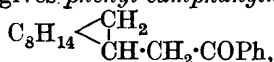
Styrylborneol,  $C_8H_{14} \begin{smallmatrix} <CH_2 \\ | \\ C(OH) \cdot CH: CHPh \end{smallmatrix}$ , was obtained from the preceding compound by regulated reduction with hydrogen and a nickel catalyst in a mixture of aqueous alcohol and ethyl acetate. It forms a colourless, viscous oil, b. p.  $183-186^\circ/11$  mm.,  $106-107^\circ/0.1$  mm.;  $[\alpha]_D -107.7^\circ$  in 10% benzene solution.

$\beta$ -Phenylethylborneol,  $C_8H_{14} \begin{smallmatrix} <CH_2 \\ | \\ C(OH) \cdot CH_2 \cdot CH_2Ph \end{smallmatrix}$ , was obtained from the preceding compound by further reduction under identical conditions. It is a colourless, limpid oil, b. p.  $176-179^\circ/14$  mm.,  $138-140^\circ/0.5$  mm.;  $[\alpha]_D -25.45^\circ$  in 10% benzene solution. By boiling for 12 hours with formic acid, it is dehydrated, and  $\beta$ -phenylethylbornylene, a limpid oil, b. p.  $165-168^\circ/12$  mm., is formed.

Phenylacetylenylborneol, on boiling with formic acid, undergoes rearrangement to a ketone probably having the formula



a yellowish-brown oil, b. p.  $193-196^\circ/12$  mm.,  $[\alpha]_D -39.97^\circ$  in 10% benzene solution; semicarbazone, white prisms, m. p.  $155-156^\circ$ ; phenylhydrazone, yellow needles, m. p.  $120-121^\circ$ . By catalytic reduction, the ketone gives phenyl camphanylmethyl ketone,



white plates, m. p.  $75-76^\circ$ ;  $[\alpha]_D -16.66^\circ$  in 10% benzene solution; phenylhydrazone, yellow needles, m. p.  $110-111^\circ$ ; semicarbazone, m. p.  $179-181^\circ$ . 1:2:2:3-Tetramethylcyclopentyl phenylacetylenyl ketone,  $C_8H_{14}Me \cdot CO \cdot C: CPh$ , was synthesised from magnesium phenylacetylenyl bromide and campholic chloride, and formed needles, m. p.  $53-54^\circ$ ;  $[\alpha]_D +45.38^\circ$  in 10% benzene. It was also obtained from sodium phenylacetylene and campholic chloride. The phenylhydrazone forms white needles, m. p.  $137-138^\circ$ , the hydrazone, needles, m. p.  $123-124^\circ$ . On warming with methyl-alcoholic potash, the ketone gave a viscous, yellow oil, b. p.  $215-217^\circ/13$  mm., apparently an additive compound with 1 mol. of methyl alcohol. This methoxy compound gave a phenyl-

*hydrazone*, m. p. 144—145°. 1 : 2 : 2 : 3-Tetramethylcyclopentyl styryl ketone, from the acetylenic compound by reduction as before, is a pale yellow, somewhat viscous oil, b. p. 192—194°/12 mm.,  $[\alpha]_D +45.31^\circ$  in benzene.

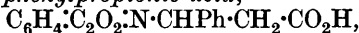
Its isomeride (cf. *supra*) has  $[\alpha]_D +54.24^\circ$  in 10% benzene solution. 1 : 2 : 2 : 3-Tetramethylcyclopentyl  $\beta$ -phenylethyl ketone may be obtained by the reduction of the acetylenic ketone (b. p. 178—181°/12 mm.;  $[\alpha]_D +40.51^\circ$  in 10% benzene solution) or of Rupe and Klottenburg's ketone (b. p. 188—189°/13 mm.;  $[\alpha]_D +48.24^\circ$  in 10% benzene solution), as well as by the method of Rupe and Jäggi (A., 1922, i, 840); (b. p. 178—181°/10 mm. and  $[\alpha]_D +38.84^\circ$  in 10% benzene solution).

Active amylcarbylamine has b. p. 137—138°/745 mm.;  $[\alpha]_D +0.35^\circ$  in benzene solution. Hexonitrile, hexylamine, and benzylidenehexylamine have  $[\alpha]_D +0.76^\circ$ ,  $0.86^\circ$ ,  $1.41^\circ$ , respectively. *Methylcyclohexylamine*, from the oxime of 3-methylcyclohexanone, has  $[\alpha]_D -2.09^\circ$ . By the action of chloroform and potassium hydroxide, 3-methylcyclohexylcarbylamine was obtained as an oil, b. p. 67—69°/10 mm.;  $[\alpha]_D -0.77^\circ$ . *Benzylidenehexylamine* is a colourless liquid, b. p. 130—132°/13 mm. A. E. C.

**Equilibrium between Benzaldehyde and Benzoin.** A. LACHMAN (*J. Amer. Chem. Soc.*, 1924, **46**, 708—723).—The condensation of 2 mols. of benzaldehyde to give 1 mol. of benzoin requires the combined action of hydroxyl and cyano ions. These catalysts also reverse the condensation, but at the same time they convert benzoin into benzyl benzoate and benzoic acid, this step not being reversible. When benzoin is heated at 300°, it is partly converted into benzaldehyde; under the same conditions, benzaldehyde yields no benzoin, but forms benzyl benzoate, benzoic acid, toluene, and dibenzyl ether. The benzoin and Cannizzaro condensations can be accounted for by two assumptions. Benzaldehyde combines with  $M\cdot OH$  (or  $\cdot OR$ ) to form the compound  $CHPh(OM)(OH)$  (A), in which  $\cdot OH$  is the more labile group; and with hydrogen cyanide to form  $CHPh(CN)(OH)$  (B), in which H is more labile. A reacts with benzaldehyde by transfer of hydroxyl to yield benzyl benzoate; it reacts with B according to the equation  $CHPh(CN)(OH) + CHPh(OH)(OK) = CPh(CN)(OK)\cdot CH(OH)Ph + H_2O$ ; if both benzaldehyde and B are present, it reacts with both; if A is absent, as in acidified solutions, benzoin fails to form. The unique function of the cyano ion as the only catalyst which will convert benzaldehyde into benzoin also becomes clearer. Benzaldehyde forms additive products of the general type  $CHPh(OH)(X)$  with sodium hydrogen sulphite, hydrogen chloride, and hydrogen cyanide, but of these the last is the only one capable of existing under conditions necessary for the presence of A, i.e., alkaline solution. A method is described for preparing benzoin without the use of alcohol. C. J. S.

**Optically Active  $\beta$ -Phthalimino- $\beta$ -phenylpropiophenones.** A. MCKENZIE and T. M. A. TUDHOPE (*J. Chem. Soc.*, 1924, **125**, 923—930; cf. *ibid.*, 1921, **119**, 69).—In the preparation of *r*- $\beta$ -amino-

$\beta$ -phenylpropionic acid from hydroxylamine and cinnamic acid (cf. A., 1905, i, 577), besides acetophenoneoxime, 3-phenylisoxazolone, m. p. 149—151°, is produced (cf. A., 1906, i, 955; 1912, i, 453). *r*- $\beta$ -Phthalimino- $\beta$ -phenylpropionic acid was resolved into its optically active components with cinchonine in rectified spirit. From the more sparingly soluble cinchonine salt was separated *d*- $\beta$ -phthalimino- $\beta$ -phenylpropionic acid,



glassy rosettes, m. p. 150—151°, having  $[\alpha]_{\text{D}} -5.5^\circ$  in ethyl acetate, and  $-2.2^\circ$  in ethyl alcohol. The same active acid was obtained by the resolution of *r*- $\beta$ -amino- $\beta$ -phenylpropionic acid (cf. A., 1910, i, 622) and heating the *d*-amino-acid with phthalic anhydride. In spite of its laevorotation in ethyl acetate, this acid is accordingly designated as *d*- $\beta$ -phthalimino- $\beta$ -phenylpropionic acid, taking *d*- $\beta$ -amino- $\beta$ -phenylpropionic acid as the reference compound. In methyl alcohol, the phthalimino acid is slightly dextrorotatory. Thionyl chloride converts the *d*-phthalimino acid into its acid chloride from which, by the Friedel-Crafts reaction, is obtained *d*- $\beta$ -phthalimino- $\beta$ -phenylpropiophenone,



m. p. 116—117°,  $[\alpha]_{\text{D}}^{15} -127.1^\circ$  in benzene and  $[\alpha]_{\text{D}}^{13} -96.2^\circ$  in acetone. *l*- $\beta$ -Phthalimino- $\beta$ -phenylpropiophenone was similarly obtained from the *l*-phthalimino acid. Hydrolysis of the laevorotatory *d*-ketone with alcoholic sodium hydroxide yields *d*- $\beta$ -benzoyl- $\alpha$ -phenylethylphthalamic acid,  $\text{COPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , feathery crystals, m. p. 147—147.5°,  $[\alpha]_{\text{D}}^{16.5} +38.8^\circ$  in ethyl alcohol, which on hydrolysis with a mixture of concentrated hydrochloric acid and glacial acetic acid yields phthalic acid and the laevorotatory *d*- $\beta$ -phthalimino- $\beta$ -phenylpropiophenone, dehydration as well as hydration of the phthalamic acid taking place. R. B.

**Migration of Groups in Derivatives of Benzoin and Desylamine.** A. MCKENZIE and R. ROGER (*J. Chem. Soc.*, 1924, 125, 844—854; cf. A., 1923, i, 213, 333, 788).—The dehydration of methylhydrobenzoin with concentrated sulphuric acid yields a methyldeoxybenzoin, m. p. 50—52° (cf. Tiffeneau and Orékhov, A., 1920, i, 672; 1921, i, 565; Lévy, A., 1921, i, 860), from which two semicarbazones were obtained, m. p. 213—215° (cf. A., 1920, i, 672) and 159—160°. The methyldeoxybenzoin thus appears to exist in two forms, one melting at 50—52° (cf. A., 1888, 703) and the other at 58—59°. Both forms are converted into  $\alpha\beta$ -triphenyl- $\alpha$ -propanol, m. p. 88—89°, with magnesium phenyl bromide. A small amount of *as*-diphenylacetone is also formed in the dehydration of the glycol as a result of slight semipinacolin transformation. The dehydration of  $\alpha\alpha$ -diphenylpropane- $\alpha\beta$ -diol with either dilute or concentrated sulphuric acid (cf. A., 1906, i, 724) yields *as*-diphenylacetone:  $\text{OH}\cdot\text{CPh}_2\cdot\text{CHMe}\cdot\text{OH} \rightarrow \text{CHPh}_2\cdot\text{COMe}$ , vinyl dehydration being the only change which occurs. The ketone has m. p. 58.5—59.5° and its semicarbazone m. p. 169—170° (cf. A., 1906, i, 581).  $\beta$ -Hydroxy- $\alpha\beta$ -diphenylpropylamine on treatment with sodium nitrite in acetic acid solution undergoes semi-



pinacolinic deamination and yields *as*-diphenylacetone, m. p. 45—47° when freshly prepared, rising to 58—59° after 4 weeks. The transformation:  $\text{OH}\cdot\text{CPhMe}\cdot\text{CHPh}\cdot\text{NH}_2 \rightarrow \text{COMe}\cdot\text{CHPh}_2$ , is in marked contrast to the vinyl dehydration of methylhydrobenzoin:  $\text{OH}\cdot\text{CPhMe}\cdot\text{CHPh}(\text{OH}) \rightarrow \text{CHPhMe}\cdot\text{COPh}$ . Other examples of the action of nitrous acid on amino-alcohols cited by McKenzie and Richardson (T., 1923, 123, 79) are interpreted on similar lines. In the light of this work, the product,  $\text{C}_{21}\text{H}_{18}\text{O}$ , m. p. 121.5—122°, obtained by McKenzie and Richardson by the action of nitrous acid on  $\gamma$ -hydroxy- $\alpha\gamma\gamma$ -triphenylisopropylamine,



is benzyldeoxybenzoin (cf. Meyer and Oelkers, A., 1888, 703), semipinacolinic deamination taking place. A further example of this change is the conversion by nitrous acid of  $\beta$ -hydroxy- $\alpha\beta\beta$ -triphenylethylamine into phenyldeoxybenzoin.

The dehydration of  $\alpha\beta$ -diphenyl- $\beta$ -( $\alpha$ -naphthyl)-ethane- $\alpha\beta$ -diol, m. p. 204—205° (cf. A., 1904, i, 742), with dilute sulphuric acid yields a compound,  $\text{C}_{24}\text{H}_{18}\text{O}$ , m. p. 180—181°, probably the ethylenic oxide,  $\text{O} \begin{smallmatrix} \diagup \text{CHPh} \\ \diagdown \text{CPh}\cdot\text{C}_{10}\text{H}_7 \end{smallmatrix}$ . Concentrated sulphuric acid yields an isomeride, m. p. 108—109°, identical with the product obtained by the action of nitrous acid on  $\beta$ -hydroxy- $\alpha\beta$ -diphenyl- $\beta$ -naphthylethylamine (T., 1923, 123, 79). R. B.

**Stereochemical Investigations in the Phenyl Styryl Ketone Series. Certain Derivatives of Dibenzoylmethane and of Phenyl Styryl Ketone.** C. DUFRAISSE and A. GILLET (*Compt. rend.*, 1924, 178, 948—950).—The phenyl  $\beta$ -alkoxystyryl ketones,  $\text{COPh}\cdot\text{CH}:\text{CPh}\cdot\text{OR}$  (A., 1923, i, 113) combine with bromine without forming any appreciable proportion of hydrogen bromide, but the dibromo compounds obtained,  $\text{COPh}\cdot\text{CHBr}\cdot\text{CBr}(\text{Ph})\cdot\text{OR}$ , are extremely sensitive to the action of moisture and undergo immediate transformation into bromodibenzoylmethane,  $\text{COPh}\cdot\text{CHBr}\cdot\text{COPh}$ . When special precautions are taken, it is, however, possible to replace by a second alkoxy group the bromine atom of the  $\cdot\text{CBr}(\text{Ph})\cdot\text{OR}$  group. In this way, good yields of the following monoacetals of bromodibenzoylmethane were obtained: *phenyl  $\alpha$ -bromo- $\beta\beta$ -dimethoxy- $\beta$ -phenylethyl ketone*,  $\text{CHBrBz}\cdot\text{CPh}(\text{OMe})_2$ , m. p. 91°; corresponding *diethoxy* compound,  $\text{CHBrBz}\cdot\text{CPh}(\text{OEt})_2$ , m. p. 72°; *dipropoxy* compound,  $\text{CHBrBz}\cdot\text{CPh}(\text{OPr})_2$ , m. p. 84°. Of the two possible racemic compounds represented by the formula,  $\text{CHBrBz}\cdot\text{CPh}(\text{OMe})\cdot\text{OEt}$ , only one, m. p. 90°, has yet been obtained.

These acetals are white compounds and are particularly sensitive towards acids, which convert them immediately into bromodibenzoylmethane. When heated, they lose 1 mol. of an alcohol giving pale yellow phenyl  $\alpha$ -bromo- $\beta$ -alkoxystyryl ketones, of which the following have been prepared: *phenyl  $\alpha$ -bromo- $\beta$ -methoxystyryl ketone*,  $\text{CBrBz}\cdot\text{CPh}\cdot\text{OMe}$ , m. p. 72° (stable form); corresponding  *$\beta$ -ethoxy* compound,  $\text{CBrBz}\cdot\text{CPh}\cdot\text{OEt}$ , m. p. 76° (stable form); and  *$\beta$ -propoxy* compound,  $\text{CBrBz}\cdot\text{CPh}\cdot\text{OPr}$ , m. p. 49°.

These undergo hydrolysis when heated with a dilute acid, bromodibenzoylmethane being formed. The action on them of an alkali alkoxide results in the fixation at the double linking of an alcohol molecule, the resulting monoacetals being either symmetrical or unsymmetrical.

The phenyl  $\alpha$ -bromo- $\beta$ -alkyloxystyryl ketones are prone to exist in several forms, each having characteristic crystallographic constants, melting point, and solubility. Thus, the methoxy compound exhibits two forms, m. p.  $64^\circ$  and  $72^\circ$ , and the ethoxy compound, three forms, m. p.  $65^\circ$ ,  $73^\circ$ , and  $76^\circ$ . The form with the highest melting point is the most stable, and when it has once made its appearance in a laboratory, the preparation there of the other form or forms is impossible unless the precautions employed in obtaining pure cultures of bacteria are taken.

The unstable form of phenyl  $\alpha$ -bromo- $\beta$ -methoxystyryl ketone, m. p.  $64^\circ$ , is isomorphous with the stable form of phenyl  $\alpha\beta$ -dibromostyryl ketone, m. p.  $80^\circ$ , and with the unstable form, m. p.  $71^\circ$ , of one of the di-iodo derivatives of phenyl styryl ketone. T. H. P.

**Stereoisomeric Semicarbazones.** F. J. WILSON and R. M. MACAULAY (*J. Chem. Soc.*, 1924, 125, 841—844; cf. *ibid.*, 1912, 101, 1482; 1913, 103, 377, 1504).—By exposure to ultra-violet light dypnone semicarbazone,  $\text{CPhMe}:\text{CH}\cdot\text{CPh}:\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , m. p.  $151^\circ$ , has been converted into a second of the four stereoisomerides required by theory. The new semicarbazone, m. p.  $175$ — $176^\circ$ , is obtained in a yield of 33% of theory, and partial reconversion is effected on further exposure. Similarly, the  $\delta$ -phenylsemicarbazone of mesityl oxide, m. p.  $134^\circ$ , yields about 33% of a more soluble *stereoisomeride*, m. p.  $99$ — $101^\circ$ , reconversion being accomplished by heating in alcoholic solution. The semicarbazone of phenyl  $\beta$ -phenylstyryl ketone, m. p.  $171$ — $172^\circ$  (cf. A., 1916, i, 821) yields, in the same way, the second stereoisomeric carbazone required by theory, a pale yellow, microcrystalline powder, m. p.  $204$ — $205^\circ$ , partial transformation of either stereoisomeride taking place on exposure in alcoholic solution. Attempts to obtain a stereoisomeride of styryl isobutenyl ketone semicarbazone,  $\text{CMe}_2\cdot\text{CH}\cdot\text{C}(\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CH}:\text{CHPh}$ , m. p.  $168^\circ$ , were unsuccessful. In the preparation of the semicarbazone, a small quantity of a substance, m. p.  $221$ — $222^\circ$ , possibly the semicarbazide-semicarbazone,

$\text{CMe}_2(\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CH}_2\cdot\text{C}(\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CH}:\text{CHPh}$ , was obtained. Attempts to obtain stereoisomerides of the semicarbazones of benzylacetone, benzylacetophenone, and styryl methyl ketone were also unsuccessful. R. B.

**Indones. V. Conversion of 3-Phenyl-2-methylindone into Diphenyldimethyltruxones by the Action of Ultra-violet Rays.** R. DE FAZI (*Gazzetta*, 1924, 54, 85—88; cf. A., 1920, i, 316; 1921, ii, 357).—It has been shown previously that, when treated with cold, concentrated sulphuric acid, ethyl  $\beta$ -hydroxy- $\beta\beta$ -diphenyl- $\alpha$ -methylpropionate yields 3-phenyl-2-methylindone, whereas ethyl

$\beta$ -hydroxy- $\beta\beta$ -diphenylpropionate gives 3-phenylindone and the two diphenyltruxones (A., 1915, i, 1063; 1916, i, 151; 1920, i, 316; 1921, ii, 357). Under the same conditions, 3-phenyl-2-methylindone yields no truxone, but may be recovered unchanged from the emerald-green solution formed.

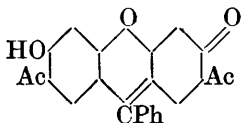
The two *diphenyldimethyltruxones* (cf. A., 1920, i, 317) are, however, formed when a benzene solution of 3-phenyl-2-methylindone is subjected in a quartz tube to the influence of the ultra-violet light from a quartz mercury vapour lamp. The first *isomeride* forms pale, canary-yellow crystals, m. p. 259–260°; the second *isomeride* forms white crystals, m. p. 307–308°, appears to be phototropic, and, after repeated crystallisation from alcohol, yields 3-phenyl-2-methylindone when treated with concentrated sulphuric acid.

T. H. P.

**The Benzil Rearrangement. VI. A. LACHMAN** (*J. Amer. Chem. Soc.*, 1924, 46, 779–782; cf. A., 1923, i, 784, 785).—In the benzil rearrangement there are two opposing reactions: one, consisting of intramolecular oxidation and reduction, giving benzilic acid; and the other, a process of rupture, producing benzaldehyde and ethyl benzoate. The first reaction will not occur in the absence of water, but a much smaller quantity of water will suffice if ether is used as a part of the solvent, and if potassium hydroxide is employed in place of sodium hydroxide. As the proportion of water increases, less benzoic acid, but more benzilic acid, results. Schönberg and Keller (A., 1923, i, 928) ascribe the formation of benzoic acid during the benzil rearrangement to oxidation by atmospheric oxygen, but it is shown that such an action does not occur.

C. J. S.

**Condensation of Benzoic Acid and Substituted Benzoic Acids with Resacetophenone.** G. C. CHAKRAVARTI (*J. Amer. Chem. Soc.*, 1924, 46, 682–685).—A number of dyes belonging to the benzein series have been prepared by heating, in presence of anhydrous zinc chloride, 2 mols. of resacetophenone with rather more than 1 mol. of benzoic or a substituted benzoic acid. The



dyes show strong fluorescence in alkaline solution and yield colourless acetyl derivatives. Benzoic acid condensed with resacetophenone gives *resacetophenonebenzein* (annexed formula), forming rose-red crystals, m. p. 141°; *acetyl* derivative, m. p. 125°. *Resacetophenone-p-hydroxybenzein*,  $C_{23}H_{16}O_6 \cdot 4H_2O$ , from *p*-hydroxybenzoic acid, has m. p. 107–108°, and when kept for several weeks is transformed into a “homochromo-isomeride,” m. p. 192°; *acetyl* derivative, m. p. 102°. Salicylic acid yields a *benzein*, m. p. 133–135° (*acetyl* derivative, m. p. 128°). The *benzeins* obtained from anisic acid, *m*-bromobenzoic acid, and gallic acid have m. p. 161°, 147°, and 126°, respectively. Similarly constituted products of high m. p. are obtained from *m*- and *p*-nitro- and *p*-chlorobenzoic acids.

C. J. S.

**Constitution of Biochemically Formed Hydroxyketopropylbenzene.** C. NEUBERG (*Biochem. Z.*, 1924, **144**, 44—46).—A reply to Auwers and Jordan (this vol., i, 384). It is pointed out that the structure ascribed by these authors to the  $\beta$ -ketol is in agreement with the views of Neuberg and Ohle, and that the exact constitution of the product formed by the action of carboligase in the presence of benzaldehyde is of little importance to the biological aspect of the activity of the enzyme. J. P.

**Functions of Chromophores. IX. The Quinone Chromophore.** I. J. LIFSCHITZ, H. LOURIE, J. ZIMMERMANN, and G. A. TEN BOKKEL HUININK (*Rec. trav. chim.*, 1924, **43**, 269—282; cf. A., 1921, ii, 286, 287).—The absorption spectrum of *p*-benzoquinone in alcoholic solution consists of three bands with maxima at 2150 (A), 3400 (B), and 4400 (C). These bands may be assumed to correspond with the three groups of absorption bands of the vapour spectrum, and may therefore be attributed to different species of electrons or different groups of atoms. Substitution of the hydrogen atoms of *p*-benzoquinone by alkyl groups, as in toluquinone and *p*-xyloquinone, moves A without weakening it towards shorter wave-lengths, B and C in the opposite direction. Unsaturated hydrocarbon groups, as in anthraquinone, weaken A and strengthen B. Chlorine has a similar effect, but influences C irregularly. Chloranil owes its intense yellow colour to the broadening of B. Auxochromic groups having no residual valency, such as the ethoxy group, have a similar effect to chlorine, but intensified, whilst auxochromic groups having residual valency ( $\cdot\text{OH}$  and  $\cdot\text{NR}_2$ ) have such an extreme effect as to give the substance the character of a dyestuff. From the effect of chlorine on band A it is argued that this band is associated with the carbon atoms, since chlorine has the effect of weakening the conjugated system of the carbonyl groups and ethylenic linkings. This deduction is supported by the fact that A is strengthened and deepened in polynuclear quinones. Band B is attributed to the oxygen electrons, since the broadening of this band by alkyl groups and its shifting towards the red by halogens is similar to the effect of these radicals on the oxygen band of acetone. E. H. R.

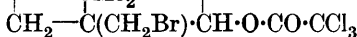
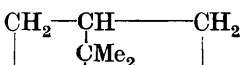
**Quinhydrone Salts.** S. GOLDSCHMIDT and F. CHRISTMANN (*Ber.*, 1924, **57**, [B], 711—715).—The sodium salt of *p*-benzoquinhydrone,  $\text{C}_6\text{H}_4\text{O}_2 + \text{C}_6\text{H}_4\text{O}_2\text{Na}_2$ , was obtained practically pure by treating a mixture of quinone and quinol with sodium ethoxide in dry ethereal solution; it formed a deep blue precipitate sufficiently stable, when dry, to be weighed in air. The blue sodium salt of *o*-benzoquinhydrone was obtained in a similar manner, in complete absence of air or moisture. Both salts are at once decomposed by water to give greenish-yellow or brown solutions respectively. The sodium salt of phenanthraquinhydrone was obtained as a deep green precipitate by dissolving phenanthraquinol in alcohol or pyridine, adding 10% sodium hydroxide and 10% sodium chloride solution, and then blowing in oxygen. It is practically insoluble in water in absence of air, but dissolves in

pyridine to a deep green solution. The corresponding *barium* salt was also prepared. On treating a benzene solution of phenanthraquinol with lead dioxide, an emerald-green solution is obtained which is believed to contain a complex salt of the type  $(x\text{C}_8\text{H}_{14}\text{O}_2 + y\text{C}_8\text{H}_{14}\text{O}_2\text{Pb})$ .  
F. A. M.

**Direct Amination of Anthraquinone.** J. KNIATOWNA (*Bull. Soc. chim.*, 1924, [iv], 35, 207—211).—According to a German patent (D.R.-P. 287756), the product obtained by heating anthraquinone with hydroxylamine sulphate in concentrated sulphuric acid, in presence of ferrous sulphate for 2 hours at 180—190°, is practically pure 1-aminoanthraquinone. This claim cannot be substantiated. Only a very small portion of the product dissolves in hydrochloric acid, and the residue, after repeated crystallisation, gives anthraquinone. From the mother-liquors of these crystallisations molecular compounds of anthraquinone and aminoanthraquinone are obtained which melt between 253° and 271°. The formation of such compounds may be the cause of the contradictory values given in the literature for the melting point of 1-aminoanthraquinone.  
E. E. T.

**Anthraquinonylsemicarbazides.** M. BATTEGAY and P. DASSIGNY (*Bull. Soc. chim.*, 1924, [iv], 35, 211—213).—Dianthraquinonylsemicarbazides are prepared by boiling together nitrobenzene solutions of  $\beta$ -anthraquinonylcarbonyl chloride and  $\alpha$ - or  $\beta$ -anthraquinonylhydrazine.  $\beta\beta'$ -Dianthraquinonyl-1:4-semicarbazide,  $\beta\text{-C}_{14}\text{H}_7\text{O}_2\text{-NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\beta\text{-C}_{14}\text{H}_7\text{O}_2$ , is an orange substance which turns orange-yellow at 300°, sublimes, and leaves a residue melting above 330°.  $\alpha\beta'$ -Dianthraquinonyl-1:4-semicarbazide is a reddish brown substance which turns orange at 270—275° and melts at about 310°. Both these compounds dye cotton from a hyposulphite vat, but the dyeings are irregular owing to partial decomposition taking place in the bath.  
E. E. T.

**Constitution of so-called  $\beta$ -Bromocamphor.** P. LIPP and F. LAUSBERG (*Annalen*, 1924, 436, 274—286).—Although Wedekind, Schenk, and Stüsser have shown (A., 1923, i, 346) that Reychler's camphorsulphonic acid is an  $\omega$ -derivative, the formation of " $\beta$ "-bromocamphor from camphorsulphonyl bromide (*Chem. Soc. Proc.*, 1901, 17, 244, 245) affords no proof of the  $\omega$ -constitution of the bromocamphor owing to the possibility of isomeric change. The authors have accordingly attempted the preparation of " $\beta$ "-bromocamphor from compounds containing the bromine atom in the  $\omega$ -position. *d*-Camphene was converted into  $\omega$ -bromocamphene,



which by digestion with trichloroacetic acid at 40° yields the well-crystallised *trichloroacetate* (annexed formula), which was obtained in two stereoisomeric forms, m. p. 80°

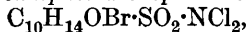
and 101—102°. On hydrolysis, the expected  $\omega$ -bromo-borneol or -isoborneol was not obtained but by reduction with sodium amalgam in alcoholic solution the ester yields the  $\alpha$ -campholen-

aldehyde of Ciamician and Silber (A., 1910, i, 496), b. p. 93·5—96°/19 mm. (*semicarbazone*, m. p. 160—162°). The aldehyde is easily resinified by alkalis and a resinous *substance*,  $(C_{10}H_{16}O)_n$ , b. p. 165—175°/4 mm., was isolated as a by-product in the reduction.

On oxidation with nitric acid, *d*- $\omega$ -2-dibromocamphane gives an acid,  $C_{10}H_{15}O_4Br$ , m. p. 208—210°, an oily product containing nitrogen and halogen, which yields a yellow potassium salt, and a neutral substance, probably  $C_8H_{13}Br \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{NO}_2 \end{smallmatrix}$ . The acid is

identical with the “ $\beta$ ”-bromocamphoric acid obtained by the oxidation of “ $\beta$ ”-bromocamphor, the identity being confirmed by a comparison of the anhydrides. The m. p. of  $\omega$ -bromocamphoric anhydride is given as 149—150° (cf. P., 1901, 17, 244). *dl*- $\omega$ -2-Dibromocamphane similarly gives *dl*- $\omega$ -bromocamphoric acid (decomp. 208—210°), and the corresponding anhydride, m. p. 149—149·5°. For comparison *dl*- $\omega$ -camphorsulphonic acid was prepared from synthetic camphor by Reyehler's method (A., 1899, i, 445) and from this, by Armstrong and Lowry's procedure, the *dl*- $\omega$ -bromocamphor, m. p. 76—77°, was obtained. On oxidation with nitric acid, this yields *dl*- $\omega$ -bromocamphoric acid, m. p. 210—211°, and anhydride, m. p. 149—150°, identical with the products obtained from *dl*- $\omega$ -2-dibromocamphane, and the authors accordingly assign the  $\omega$ -structure to “ $\beta$ ”-bromocamphor. R. B.

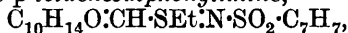
**Optically Active Sulphilimines.** F. G. MANN and W. J. POPE (*J. Chem. Soc.*, 1924, 125, 911—918).—Attempts have been made to prepare sodium *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonchloroamide and by condensation with methyl ethyl sulphide to obtain the corresponding sulphilimine,  $C_{10}H_{14}OBr \cdot SO_2N : SMeEt$ , which, owing to the trihedral disposition of the three valencies of the doubly-linked nitrogen atom, should exist in two enantiomorphous forms. *d*-Bromocamphor- $\pi$ -sulphonamide, on treatment with sodium hypochlorite, gives *d*-bromocamphor- $\pi$ -sulphondichloroamide,



white crystals, m. p. 123—125°, which slowly lose chlorine on standing. No sodium or potassium salt could be obtained, and by treatment with alcoholic potassium hydroxide (either with or without ethyl sulphide) the dichloroamide yielded unchanged  $\alpha$ -bromocamphor- $\pi$ -sulphonamide and *d*- $\alpha'$ -chloro- $\alpha$ -bromocamphor- $\pi$ -sulphonamide,  $C_{10}H_{13}OCIBr \cdot SO_2 \cdot NH_2$ , colourless needles, darkening at 225°, m. p. 232° (decomp.) (cf. Lapworth, T., 1899, 75, 558). For comparison, the *d*- $\alpha$ -chloro- $\alpha'$ -bromocamphor- $\pi$ -sulphonamide, colourless needles, darkening at 224°, m. p. 232° (decomp.), was prepared by brominating ammonium *d*- $\alpha$ -chlorocamphor- $\pi$ -sulphonate, treating the product with phosphorus pentachloride, yielding *d*- $\alpha$ -chloro- $\alpha'$ -bromocamphor- $\pi$ -sulphonyl chloride, colourless crystals, m. p. 194—197° (effervescence), which with ammonia gives the sulphonamide. The two sulphonamides differ only in rotatory constants. *d*- $\alpha$ -Bromocamphor- $\pi$ -sulphonethylechloroamide,  $C_{10}H_{14}OBr \cdot SO_2 \cdot NEtCl$ , white crystals, m. p. 122—124° (efferv.), from *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonyl chloride and ethylamine is

more stable than the dichloroamide, and can be crystallised from alcohol.

Sodium ethyl sulphide condenses with *d*-chloromethylenecamphor, giving *ethylthiolmethylen*-*d*-camphor,  $C_{10}H_{14}O:CH:SEt$ , pale green liquid, b. p. 169—171°/17 mm.,  $d_{40}^{14.8}$  1.0362. *Ethylthiolmethylen*-*l*-camphor, obtained similarly, is a pale green liquid, b. p. 168—169°/16 mm.,  $d_{40}^{15.0}$  1.0357. Both sulphides condense with hydrated "chloramine-T" in boiling alcohol to give *d*- and *l*-camphorylidene-methylethylsulphine-*p*-toluenesulphonylimine,



white crystals, m. p. 172° (efferv.). The rotatory powers of these sulphilimines are less than those of the parent substances, and no indication was obtained of the expected stereoisomerism. Rotatory powers are given for all the above compounds. R. B.

**The Beckmann Rearrangement. X.** S. KOMATSU (*Mem. Coll. Sci. Kyōtō*, 1924, 7, 147—150).—The author cites various examples of the Beckmann change and of nitrile formation, and points out that the latter reaction may be due to direct elimination of water from the oxime or to dehydration after the Beckmann change. C. J. S.

**The Beckmann Rearrangement. XI. Catalytic Action of Reduced Copper on *l*-Menthonoxime.** S. KOMATSU and M. KURATA (*Mem. Coll. Sci. Kyōtō*, 1924, 7, 151—156).—When *l*-menthonoxime and pure hydrogen were passed over reduced copper at 200°, the product contained menthone, dimethylamine, *l*-menthylamine, *d*-menthylamine, menthonitrile, decenoic acid and its amide, and a basic substance, probably 4-methyl-7-isopropyl-cyclohexenimine,  $Pr^s \cdot CH < \begin{smallmatrix} NH \cdot CH \cdot CH \\ CH_2 \text{---} CH_2 \end{smallmatrix} > CHMe$  (cf. Wallach, A., 1903, i, 104). The production of the last is regarded as evidence of the momentary formation of menthoneisooxime, which undergoes the Beckmann rearrangement by catalytic action of the reduced copper. The menthonitrile and decenoic acid are supposed to be formed respectively by catalytic dehydration and hydration of decenamides. C. J. S.

**Camphor Oils. I. Reaction between Camphor-red Oil and Sulphuric Acid.** K. ONO (*Mem. Coll. Sci. Kyōtō*, 1924, 7, 99—105).—According to Sugiyama (Japanese Pat. 37119, 1920), terpin hydrate is obtained when camphor-red oil is treated with sulphuric acid. The author shows that this result is due to the action of the acid on the terpineol present in the oil (cf. Aschan, A., 1919, i, 336) and gives the conditions to be employed in order to obtain the optimum yield of terpin hydrate. [Cf. B., 1924, 447.] T. H. P.

**Origin of Terpenes and Crystalline Acids in Pine Resins.** G. DUPONT (*Compt. rend.*, 1924, 178, 1560—1562).—The hypothesis that the terpenes and resin acids in conifers have a common origin in a material secreted by the resin cells is developed. The secreted material, which has the formula  $C_{10}H_{16}O$  (Köhler, A., 1912, i, 638),

is converted by the action of a diastase into the terpene,  $C_{10}H_{16}$ , and the oxygen acting on two other molecules produces the resin acids,  $3C_{10}H_{16}O = C_{10}H_{16} + C_{20}H_{30}O_2 + H_2O$ . This requires that the refined turpentine should contain 31% of the essential oil and 69% of resin acids, numbers which are in close agreement with the proportions actually found. The proportions of *d*- and *l*-pimaric acids and resin acids in the extract of the maritime pine, the fact that *d*-pimaric acid is found only in turpentines rich in nopinene, whilst the Aleppo pine, which yields only pinene, gives an extract containing alepic acid only, all support the hypothesis. J. W. B.

**Eutectics of Camphene with other Terpenes.** G. AUSTERWEIL (*Compt. rend.*, 1924, 178, 1174—1175).—The separation of camphene from other terpenes (when the former is not present in excess of 30% of the mixture) by crystallisation at a low temperature is rendered impracticable by the formation of eutectic mixtures of low freezing point, which are comparatively rich in camphene. The melting points of a series of mixtures of camphene with  $\alpha$ -pinene,  $\beta$ -pinene, mixtures of  $\alpha$ - and  $\beta$ -pinene, and dipentene are given.

H. J. E.

**Melting Points of Mixtures of Camphene and Pinene.** E. DARMOIS (*Compt. rend.*, 1924, 178, 1546).—Austerweil's conclusion (preceding abstract) that French turpentine contains practically no camphene and that the low melting points of natural camphenes are explained by the presence of small quantities of impurities, was anticipated by the author (A., 1911, ii, 352).

J. W. B.

**Phellandrenes. II.** H. G. SMITH, P. G. CARTER, and J. READ (*J. Chem. Soc.*, 1924, 125, 930—940; cf. *ibid.*, 1923, 123, 1657).—By solution in carbon disulphide, in which the  $\alpha$ -nitrite is relatively insoluble, and fractional precipitation, the  $\beta$ -nitrite of *l*- $\alpha$ -phellandrene has been prepared from the essential oils of *Melaleuca acuminata*, *Eucalyptus dives*, and *E. phellandra* in a much higher state of purity than has hitherto been attained. The process of separation can only be controlled effectively by considering the melting points of the various fractions in association with the corresponding rotatory powers. The  $\beta$ -nitrite, m. p. 105—106°, is crystallographically indistinguishable from *l*- $\alpha$ -phellandrene  $\alpha$ -nitrite, and has  $[\alpha]_D^{20} -160^\circ$  when freshly dissolved in chloroform, the values previously recorded being  $-36^\circ$  (Schreiner, A., 1901, i, 600) and  $-40.82^\circ$  (Wallach, A., 1904, i, 1035). The striking mutarotative changes of the  $\beta$ -nitrite in acetone, benzene, or chloroform solution, particularly in the presence of piperidine, are similar to those previously observed with the  $\alpha$ -nitrite, but optical inversion only takes place in acetone solution. The  $\alpha$ - and  $\beta$ -nitrites yield chemically and optically identical specimens of nitro- $\alpha$ -phellandrene and carvotanacetone ( $\Delta^5$ -menthen-3-one), and are thus both derived from *l*- $\alpha$ -phellandrene. It is probable that the low rotatory powers of the terpene fractions obtained from eucalyptus oils of the "peppermint group" are due to the presence of partly racemised *l*- $\alpha$ -phellandrene, and a similar remark applies to the essential oil of *Melaleuca acuminata*.

R. B.



**Oil of Turpentine extracted from the Firs of Bucovina.** O. CZERNY (*Bul. Soc. Chim. România*, 1924, 6, 39—41).—By submitting the greenish-yellow oil obtainable from the bark of the tree to distillation in a current of steam, an oil was obtained which after treatment with sodium hydroxide and subsequent distillation under diminished pressure, had b. p. 155—216°,  $d_{20}^{16}$  0.875,  $[\alpha]_D -39.2^\circ$ , acid value 124, saponification value 107, esterification value 13. It was separated by fractional distillation into pinene, a mixture of sylvestrene and dipentene, an ester which on hydrolysis with alcoholic potassium hydroxide yielded borneol, and, probably, a sesquiterpene. The non-volatile residue from the steam distillation, amounting to some 75% of the total weight, was a hard, brittle solid, m. p. 55°, which on distillation yielded traces of acetic and succinic acids and a large amount of coloured oils of very low oxygen content.

A. E. C.

**Refractive Index of Gums.** A. MALLOCK (*Nature*, 1924, 113, 643).—A corrected table of refractive indices of certain organic solvent liquids and gums is given.

A. A. E.

**Method for obtaining Pure Glucosides Soluble in Water from Plants.** S. GHOSH (*J. Amer. Pharm. Assoc.*, 1923, 12, 1080—1081).—Steam is passed into an aqueous extract of the bark to which lead chloride and oxide have been added; lead remaining in solution after addition of sodium carbonate and filtration is removed with hydrogen sulphide. Sodium chloride can, if necessary, be removed from the product obtained on evaporation by recrystallisation from ethyl alcohol.

CHEMICAL ABSTRACTS.

**Nature of the Methyl Salicylate Glucoside present in the Bark of *Betula lenta*.** M. BRIDEL (*Compt. rend.*, 1924, 178, 1310—1312).—The glucoside isolated by Schneegans and Gerock (A., 1895, i, 109) from the bark of *Betula lenta* and named gaultherin yields, not merely methyl salicylate and dextrose, but also xylose, on hydrolysis. It is, indeed, identical with the author's monotropitin (A., 1923, i, 1275), and it is suggested that the latter name be retained and gaultherin discarded.

T. H. P.

**Biochemical Resolution of Rutin. Formation of a New Glucide, Rutinose.** C. CHARAUX (*Compt. rend.*, 1924, 178, 1312—1314).—The formation of rhamninose by the action of rhamninase on rutin (cf. Ter Meulen, A., 1911, i, 391) is questioned. From the defatted, dehusked seeds of *Rhamnus utilis* the author has obtained, by maceration with water followed by precipitation with alcohol, an enzyme which hydrolyses rutin with formation of quercetin and of a new sugar, termed *rutinose*. The latter is hygroscopic and has no sharp melting point, softening at about 140° and becoming liquid and darkening at 189—192°. It reduces Fehling's solution and exhibits mutarotation in aqueous, but not in alcoholic, solution. When hydrolysed by means of dilute hydrochloric acid, it yields rhamnose (1 mol.) and dextrose (1 mol.).

The same enzyme hydrolyses: robinin, giving a glucide composed of rhamnose (2 mols.) and galactose (1 mol.); a yellow glucoside

obtained from the flowers of *Spiræa ulmaria*, yielding a glucide (apparently different from rutinose), xanthorhamnin, primeverin, baptisin, helicin, and amygdalin. It is without action on isohesperidin.  
T. H. P.

**Plant Pigments. I. Yellow Colouring Matter of the Acacias.** J. M. PETRIE (*Proc. Linnean Soc. N.S. Wales*, 1923, 48, 356—367).—The soluble colouring matter of the yellow inflorescence of *Acacia discolor*, *A. linifolia*, *A. decurrens* (var. *mollis*), and *A. longifolia* is a rhamnose glucoside of kaempferol, fine, hair-like crystals. No free flavinol was found; the yellow flavinol (0.06%) on reduction with nascent hydrogen gave a red solution resembling that of the natural anthocyanilidine. Carotene and xanthophyll (0.14—0.3%) were present as plastid pigments. The tannins were composed of phloroglucinol, protocathechuic and gallic acids, and on hydrolysis gave red phlobaphen anhydrides.

CHEMICAL ABSTRACTS.

**Insecticides. I. Isolation and Constitution of the Active Constituent of Dalmatian Insect Powder.** H. STAUDINGER and L. RUZICKA.—(See i, 700.)

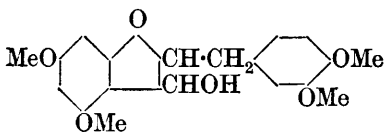
**Electrolytic Reduction of Carbonyl Derivatives.** H. HIBBERT and R. R. READ.—(See i, 613.)

**Humic Acids.** H. TROPSCH and A. SCHELLENBERG.—(See i, 619—621.)

**Degradation Product of Brazilin obtained by Schall and Dralle.** P. PFEIFFER (*Ber.*, 1924, 57, [B], 738; cf. this vol., i, 413, 537).—Tschitschibabin and Nikitin had already prepared 3-methoxychromanone from the corresponding methoxyphenoxypropionic acid.  
F. A. M.

**Tannins and Similar Substances. XV. A New Degradation of Catechin.** K. FREUDENBERG, L. ORTHNER, and H. FIKENTSCHER (*Annalen*, 1924, 436, 286—298).—The series of reactions which led to the elucidation of the structure of diacetone-dextrose and -lævulose (A., 1923, i, 652) has now been applied to the case of catechin. By the action of toluene-*p*-sulphonyl chloride on tetramethyl-*d*-catechin in pyridine solution, the *p*-toluenesulphonic ester,  $C_{26}H_{28}O_8S$ , m. p. 87—88°, is obtained, which with hydrazine yields: (1) the primary *hydrazide*,  $C_{19}H_{24}O_5N_2$  (+ $H_2O$ , lost in *vacuo* at 65°), m. p. 101—104°, this substance being oxidised by potassium permanganate to give a little tetramethyl-*d*-catechin, m. p. 145°. (2) The highly unstable 3-*mp*-dimethoxyphenylpyrazoline, m. p. 144—145° (*picrolonate*, m. p. 207—208°), which on oxidation with potassium permanganate yields veratric acid, demethylation with hydriodic acid giving a substance having m. p. about 240°. (3) Phloroglucinol dimethyl ether, identified as the dibromotrimethyl ether and as

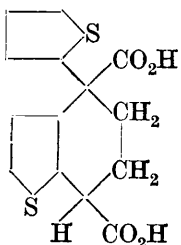
*phenacylphloroglucinol dimethyl ether*, m. p. 89°. The condensation of veratraldehyde with acetaldehyde in alcoholic potassium hydroxide gives 3:4-dimethoxycinnamaldehyde, bright yellow, rhombic



crystals, m. p. 82—83°, which with hydrazine affords the above 3-*mp*-dimethoxyphenylpyrazoline. The constitution favoured for tetramethylcatechin is that represented by the annexed formula,

although two other possibilities are discussed. Dichloropentacetyl-d-catechin (*Ber.*, 1880, **13**, 694), when treated with methyl sulphate and methyl-alcoholic potassium hydroxide, affords *dichlorotetramethyl-d-catechin*, long, white needles, m. p. 156—157°. R. B.

**Thiophen Series. XVIII. Synthesis of the "Thiophen-isologue" of Atropine.** W. STEINKOPF and A. WOLFRAM (*Annalen*, 1924, **437**, 22—36).—Ethyl thienyl-2-glyoxylate (b. p. 138—140°/13 mm.) was prepared by treating thiophen with ethyl oxalic chloride (cf. Scholl and Egerer, A., 1913, i, 588) in presence of aluminium chloride. With magnesium methyl bromide, it gives *ethyl α-hydroxy-α-2-thienylpropionate*, an oil, b. p. 134—135°/13 mm., readily hydrolysed by barium hydroxide to the corresponding *acid*, needles, m. p. 107°. When alkali hydroxide is used as hydrolysing agent, side reactions take place and an amorphous product resembling that described below is obtained. It was found impossible to



isolate  $\alpha$ -2-thienylacrylic acid; the above hydroxy-acid, treated with acid in various ways, gives solely a mixture of two *isomerides*, one amorphous (decomp. 95°), the other crystalline, m. p. 216°. The latter, termed di- $\alpha$ -thienylacrylic acid, has properties which suggest that it has the annexed formula. The amorphous substance was also obtained as a by-product in the preparation of  $\beta$ -chloro- $\alpha$ -2-thienylpropionic acid, which was eventually isolated by treating  $\alpha$ -hydroxy- $\alpha$ -2-

thienylpropionic acid with hydrogen chloride in ether solution at -40° to -30°. It forms rhombs, m. p. 77°. Hydrolysed with calcium carbonate, it gives  $\beta$ -hydroxy- $\alpha$ -2-thienylpropionic acid, prisms, m. p. 95.5—96°, the *acetyl* derivative of which is oily, and when treated with thionyl chloride yields  $\beta$ -acetoxy- $\alpha$ -2-thienylpropionyl chloride, also an oil. Tropine with the latter compound in benzene solution affords  $\beta$ -hydroxy- $\alpha$ -2-thienylpropionyltropine, "*thiophen-cocaine*" (*chloroplatinate*, decomp. 240—241°, and *picrate*, m. p. about 142°, described). The quantity obtained was insufficient for pharmacological tests. W. A. S.

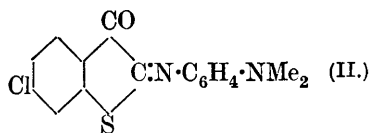
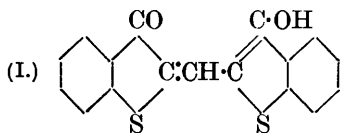
**Thiophen Series. XVII. Preparation of the "Thiophen-isologue" of Cocaine.** W. STEINKOPF and W. OHSE (*Annalen*, 1924, **437**, 14—22).—"Thiophen-cocaine" was obtained by methylating the product of interaction of ecgonine and thiophen-2-carboxylic anhydride. Thiophen-2-carboxylic acid is best pre-

pared (yield: 96%) from 2-bromothiophen (Steinkopf, A., 1923, i, 124) by the Grignard reaction (cf. Schlenk and Ochs, A., 1915, i, 579). The best yield (62%) of 2-cyanothiophen, the intermediate in an alternative preparation of the acid, was obtained when cyanogen chloride was used; the bromide, iodide, and cyanogen itself gave poor yields (cf. Karrer and others, A., 1919, i, 591). Thiophen-2-carboxylic acid heated with acetic anhydride yields

the *anhydride*, needles, m. p. 62°, b. p. 218–220°/15 mm., rapidly reacting in warm aqueous suspension with ecgonine to give *thiophen-2-carboxyecgonine* (annexed formula), which sinters at 94°, solidifies and melts at 186°, and has  $[\alpha]_D^{25} -19.07^\circ$  to  $-17.49^\circ$  in chloroform. Its *hydrochloride* has m. p. 225° (decomp.). The *methyl ester*, viz. "*thiophen-cocaine*," has m. p. 107°; its *hydrochloride*, m. p. 184.5°, the *picrate*, yellow needles, m. p. 175°, and *chloroplatinate* are described. Pharmacologically the substance closely resembles cocaine but appears to be less toxic.

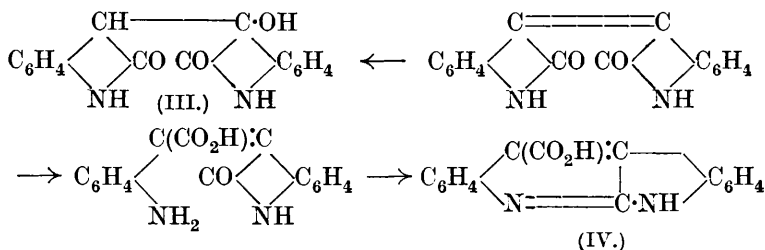
W. A. S.

**Fission of Indigoid Dyes by Alkalis.** P. FRIEDLÄNDER and L. SANDER (*Ber.*, 1924, 57, [B], 648–652; cf. A., 1922, i, 764).—Thioindigotin when heated with 45% potassium hydroxide and a little alcohol is converted into oxythionaphthen, thionaphthen-quinone, and a little of the known substance (I). 6:6'-Dichloro-



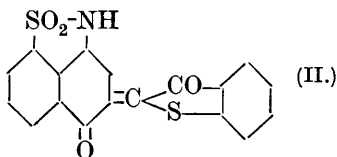
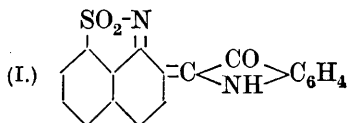
thioindigotin is much more resistant to the above treatment and affords 6-chloro-3-oxy(1)thionaphthen (colourless needles, m. p. 143°) (cf. Ruppel, *Dissert.* Darmstadt, 1921), and 6-chlorothionaphthen-quinone. The latter (orange needles, m. p. 134°) was also prepared by condensing the chloro-oxythionaphthen with *p*-nitrosodimethylaniline, the resulting 6-chlorothionaphthenquinone-*p*-dimethylamino-2-anil (II) (dark green, metallic prisms, m. p. 190°) being hydrolysed by hydrochloric acid. 6:6'-Dichloro-4:4'-dimethylthioindigotin, on treatment with alkali, gives only a trace of 6-chloro-4-methylthionaphthenquinone, orange needles, m. p. 132°, which was also prepared from the *anil*, m. p. 123.5°. *iso*Indigotin has been prepared by an improved method (due to B. Homolka) from isatin and an aqueous solution of sodium sulphide and ammonia. It is converted by hot aqueous-alcoholic sodium hydroxide into *hydroxy-dihydroisoindigotin*, (III), colourless leaflets or needles, m. p. 250–280° (decomp.) (converted by hot acetic anhydride into diacetyl-*isoindigotin*), and *quinindolinecarboxylic acid* (IV), yellow needles (sodium salt,  $C_{16}H_9O_2N_2Na \cdot 3H_2O$ , yellow needles), a little isatin and other substances also being formed. The acid, when heated at 300°, affords quinindoline (cf. Gabriel and Eschenbach, A.,

1898, i, 199). The decomposition by alkali probably occurs as shown below :



F. A. M.

**Indigoid Dyes.** P. FRIEDLÄNDER and L. SANDER (*Ber.*, 1924, 57, [B], 637—648).—The following new indigoid dyes are described : the *dye* (I) from naphthasultam and isatinanilide by condensation in presence of acetic anhydride, forms deep bluish-violet needles with red iridescence which give a yellow solution in alkali.



The condensation of 3-oxy(1)thionaphthen with naphthasultam-quinone in acetic acid yields a *dye* (II) which forms purple-black needles. No dye could be obtained on attempting to condense isatinanilide with the *p*-tolylsulphamide of  $\alpha$ -naphthylamine, although the latter couples with diazo compounds in alkaline solutions. A re-examination of the “2-dihydronaphthalene-2'-indoleindigo” described by Herzog and Kreidl (*A.*, 1923, i, 61) showed that their product was probably an impure “2-naphthalene-2-indoleindigo.” The substance described by Herzog and Kreidl as 1-keto-2 : 3'-oxy-2'-thionaphthentetrahydronaphthalene may, however, have the structure ascribed to it, although analysis alone is insufficient to determine the presence or absence of the two hydrogen atoms; on warming with concentrated aqueous-alcoholic sodium hydroxide, it forms a yellow solution from which acetic acid precipitates a yellow, amorphous *additive* compound with water possibly  $\text{C}_{10}\text{H}_8\text{O} \cdot \text{C}(\text{OH}) \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{SH}$ . Above  $100^\circ$ , the dye is re-formed; the hydrated compound behaves like an enol and like a mercaptan. 6-Ethoxythionaphthenquinone-2-anil was prepared from 6-ethoxythionaphthen and nitrosobenzene as yellow needles, m. p.  $118\text{--}119^\circ$ . It condensed with  $\alpha$ -ketotetrahydronaphthalene in acetic anhydride to give the brownish-red dye, “3 : 4-dihydro-2-naphthalene-6'-ethoxy-2'-thionaphthenindigo.” 2-Chloro-1 : 4-naphthaquinone monoanil was obtained by condensing 2-chloro- $\alpha$ -naphthol with nitrosobenzene in presence of ammonia as fiery red needles, m. p.  $112^\circ$ ; it was not possible to obtain an indigoid dye

from it by condensation with oxythionaphthen; by using sodium hydroxide in the above condensation in place of ammonia, the product was almost entirely Euler's anilinnaphthaquinone-mono-anil, the chlorine atom being removed. The following *acyl* derivatives of indigoid dyes were also prepared: "N-Acetyl-2-indole-2'-thionaphthenindigo," from the corresponding indigoid dye, acetic anhydride, and acetyl chloride, forms light red needles; *di*(N-acetyl)isoindigotin, obtained similarly from isoindigotin, forms brick-red crystals. N:N'-bis(chloroacetyl)indigotin was obtained from indigotin and chloroacetyl chloride as ruby-red, quadratic, double pyramids; it is sensitive to water-vapour and gradually becomes coated with indigotin; "4-acetyl-amino-2-naphthalene-2'-indoleindigo" is a violet-blue product, and "4-acetyl-amino-2-naphthalene-2'-thionaphthenindigo" reddish-violet. Treatment of indigotin with oxalyl chloride in boiling nitrobenzene afforded oxalylindigotin as yellow needles, m. p. above 200°. It is extremely easily hydrolysed by dilute alkali with regeneration of indigotin and is sulphonated by warm fuming acid (20% SO<sub>3</sub>). These observations confirm Friedländer's view (A., 1922, i, 765) that saturation of the nitrogen atoms in indigoid dyes leads to lightening of the colour. F. A. M.

**Derivatives of 3-Oxy(1)thionaphthen.** L. R. HART and S. SMILES (*J. Chem. Soc.*, 1924, 125, 876—881).—*o*-Thiolbenzoic acid condenses with compounds containing a labile methylene group to give 3-oxythionaphthen derivatives (cf. T., 1923, 123, 2907), but in no case are 2:2-disubstituted derivatives formed; one of the groups originally attached to the methylene group is always displaced, and if this cannot happen the reaction does not take place. *o*-Thiolbenzoic acid and oxalacetic, acetylpyruvic, or pyruvic acid react in sulphuric acid solution to give 3-oxy(1)thionaphthen-2-glyoxylic acid,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \text{S} \diagdown \end{smallmatrix} CH \cdot CO \cdot CO_2H, H_2O$ , m. p. 174° when anhydrous. The calcium salt is described. The phenylhydrazone forms orange needles, m. p. 187°, and the anil yellow plates, m. p. 190°. The *o*-amino-anil forms yellow prisms (converted into the following compound before melting). When *o*-phenylenediamine and the acid were mixed in boiling acetic acid, "2-thionaphthen-2-quinoxalineindigo,"  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \text{S} \diagdown \end{smallmatrix} C : C \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \diagup \text{NH} \cdot \text{C}_6\text{H}_4 \end{smallmatrix}$ , was readily formed as a red, crystalline powder not melting below 315°. 2-Benzoyl-3-oxy(1)thionaphthen was produced by condensation of *o*-thiolbenzoic acid and benzoylacetone; it forms orange or pale yellow needles, m. p. 116—117°. Its phenylhydrazone crystallises in orange plates, m. p. 160°. Its acetyl derivative, 2-benzoyl-3-acetoxy(1)thionaphthen, forms needles, m. p. 106°. 2-Acetyl-3-benzoyloxy(1)thionaphthen, formed by benzoylating 2-acetyl-3-oxythionaphthen, has m. p. 145°. The disinclination to form 2:2-disubstituted derivatives is again shown here. 2-Benzoyl-3-benzoyloxy(1)thionaphthen crystallises in plates, m. p. 113°.

W. A. S.

**Constitution of Evodiamine and Rutæcarpine.** Y. ASAHINA (*J. Pharm. Soc. Japan*, 1924, No. 503, 1—7; cf. Asahina and Mayeda, A., 1921, i, 48).—Indole- $\beta$ -ethylamine (3-aminoethyl-indole) is obtained by the decomposition of evodiamine. The constitutions of evodiamine and rutæcarpine are, therefore, as stated by Kermack, Perkin, and Robinson (T., 1921, **119**, 1615).

K. K.

**Methylation of Tertiary Amines and Alkaloids by means of Methyl Sulphonic Esters derived from Phenols.** L. J. SIMON and M. FRÉREJACQUE (*Compt. rend.*, 1924, **178**, 945—947).—When treated with methyl iodide or sulphate or with one of various sulphonic esters derived from aromatic hydrocarbons, hexamethylenetetramine yields the salt of a quaternary methylated base, one methyl group being fixed by a tertiary nitrogen atom:  $C_6H_{12}N_4 + R \cdot OMe = C_6H_{12}N_3(NMe) \cdot OR \rightarrow C_6H_{12}N_3 \cdot NMe \cdot OH$ . This reaction is effected very readily and completely by the methyl sulphonates derived from phenols (A., 1923, i, 462, 1098), giving the phenolsulphonates of the same base. The reaction is best carried out in chloroform solution and, even in the cold, is extremely sensitive, 0.02 g. of hexamethylenetetramine rapidly yielding the characteristic crystalline compounds. The compounds obtained, with their approximate decomposition temperatures, are as follows:  $OH \cdot C_6H_4 \cdot SO_3Me$  [1 : 4], 225°;  $OH \cdot C_6H_3Me \cdot SO_3Me$  [2 : 1 : 5], 134°;  $OH \cdot C_6H_3Me \cdot SO_3Me$  [OH : Me = 1 : 4], 175°;  $OMe \cdot C_6H_4 \cdot SO_3Me$  [1 : 4], 195°;  $OMe \cdot C_6H_3Me \cdot SO_3Me$  [2 : 1 : 5], 190°;  $OMe \cdot C_6H_3Me \cdot SO_3Me$  [OMe : Me = 1 : 4], 215°;  $OH \cdot C_6H_3(CO_2Me) \cdot SO_3Me$  [OH :  $CO_2Me$  = 2 : 1], 230°. These salts yield the corresponding *picrates* when treated with picric acid in aqueous solution.

*Compounds* of similar type are obtainable from antipyrine, pyramidone, dimethylaniline, and pyridine, a solvent other than chloroform being sometimes necessary. The products obtained from antipyrine by means of the methyl sulphonates of methyl salicylate and anisole have m. p. 135° and 96°, respectively. The salt formed from pyramidone and methyl anisolesulphonate has m. p. 162°, and that from pyramidone and dimethyl sulphosalicylate, m. p. 97°. The reaction is applicable also to the alkaloids.

T. H. P.

**Kinetics of Catalytic Dehydrogenation.** II. N. ZELINSKY and G. PAWLOW (*Ber.*, 1924, **57**, [B], 669—671; cf. A., 1923, i, 767).—Palladium is a much more active catalyst than platinum in effecting the dehydrogenation of piperidine, which, with the first metal, only follows a normal course at temperatures below 250°; at higher temperatures the catalyst becomes partly inactivated owing to subsidiary reactions. The phenomenon is due to the chemical nature of piperidine, since the dehydrogenation of *cyclohexane* (*loc. cit.*) occurs normally within much wider limits of temperature. With piperidine, as with *cyclohexane*, dehydrogenation commences at about 150°; between 150° and 200°, piperidine is much more energetically dehydrogenated by palladium than is *cyclohexane*.

H. W.





$C_{12}H_{20}N_2.HCl.ZnCl_2$ , colourless prisms, m. p. 271—272°. Certain analytical figures relating to the compound obtained from cotarnine and 6-nitropiperonal are corrected (cf. T., 1914, 105, 1468).

W. A. S.

**Intramolecular Condensation Reactions of Aminoaldehydes and Aminoacetals. II. Course of the Reaction in the Formation of Dihydroquinoline and a New Preparation of Indole Derivatives.** C. RÄTH (*Ber.*, 1924, 57, [B], 715—718; cf. this vol., i, 555).—When *o*-aminopropylbenzene is heated with chloroacetal at 250° the expected 4-ethyl-1:2-dihydroquinoline, a pale yellow oil (b. p. 125—135°) with slightly tarry odour (*hydrochloride*, pinkish, hygroscopic, and amorphous), is formed together with 3-ethoxy-4-ethyl-1:2:3:4-tetrahydroquinoline, a yellow, viscous oil (b. p. 180—185°/21 mm., or 175—185°/17 mm.).  $\beta$ -Chloropropionacetal and aniline when heated together at 250° give a little dihydroquinoline and (mainly) 4-ethoxytetrahydroquinoline, a yellowish-brown, viscous oil (b. p. 264—270°), which darkens in air (*picrate*, fine, yellow needles). 3-Ethoxy-1-ethyl-2:3-dihydroindole (*hydrochloride*, amorphous), a thick, yellow liquid, b. p. 153—163°/11 mm., is obtained from ethylaniline and bromoacetal, although the chief product in this case is 1-ethylindole.

F. A. M.

**Synthesis of 2:4:7- and 2:4:8-Trimethylquinolines.** S. YAMAGUCHI (*J. Pharm. Soc. Japan*, 1924, No. 503, 8—33).—The author has synthesised 2:4:7- and 2:4:8-trimethylquinolines and their salts, from acetone, paraldehyde, and *m*- and *o*-toluidines, respectively. Generally speaking, 2:4:6- and 2:4:7- but not 2:4:8-derivatives have a large affinity for water and for methyl iodide.

2:4:8-Trimethylquinoline is a white solid, m. p. 42°, b. p. 269—270°, and gives the following salts: *hydrochloride*, m. p. 238°; *hydrobromide*, m. p. 251° (decomp.); *hydriodide*, m. p. 224°; *chloroaurate*, m. p. 191°; *chloroplatinate*, m. p. 275° (decomp.); *mercurichloride*, m. p. 234°; *zincichloride*, m. p. 295—296° (decomp.); *hydrogen sulphate*, m. p. 263°; *dichromate*, decomp. at about 180°; *picrate*, m. p. 193°; *methiodide*, m. p. 229° (decomp.).

2:4:7-Trimethylquinoline is a colourless, oily liquid, b. p. 280—281°,  $d_{20}^{20}$  1.0337,  $n_D^{20}$  1.59732. On exposure to air, or when crystallised from water, it forms a crystalline *hydrate*, m. p. 48°. The following salts are described: *hydrochloride*, sublimes at about 310°; *hydrobromide*, m. p. 351° (decomp.); *hydriodide*, m. p. 320° (decomp.); *chloroaurate*, m. p. 152°; *chloroplatinate*, m. p. 272° (decomp.); *mercurichloride*, m. p. 244°; *zincichloride*, m. p. 258°; *hydrogen sulphate*, m. p. 223°; *dichromate*, decomp. at about 179—180°; *picrate*, decomp. 232°; *methiodide*, subliming at about 322°.

K. K.

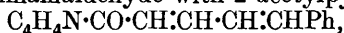
**Relations between Chemical Constitution and Taste.** (MISS) C. RICCOMANNI (*Atti R. Accad. Lincei*, 1924, [v], 33, i, 145—148).—1:4-Di- $\delta$ -phenyl- $\Delta^8$ -pentenoylpiperazine, prepared by heating piperazine at 100—105° with  $\delta$ -phenyl- $\Delta^8$ -pentoic acid (cf.

aa\*

Staudinger and Schneider, A., 1923, i, 361; Staudinger and Müller, A., 1923, i, 363), is obtained as a dense, brownish-yellow oil with a pungent, aromatic taste, yields a yellow *picrate*, m. p. 245°, and when mixed in the proportion of 2% with flour produces a taste similar to, although less intense than, that of pepper. Evidently piperidine is not necessary for obtaining the flavour of pepper.

When added in the proportion of 1% to flour, styryl methyl ketone exhibits a markedly sharp taste (cf. Nomura, T., 1917, i, 769; A., 1918, i, 446; Nomura and Nozawa, A., 1918, i, 438); cinnamylidenemethyl methyl ketone has an intense, biting taste which appears after a time; benzyl methyl ketone has also an acute taste and acetophenone a pungent taste which disappears almost immediately. With compounds which lack the phenyl group or which contain a partly hydrogenated aromatic ring, such as ionone, the acute taste disappears almost completely.

2-Acetylpyrrole, 2-pyrrol styryl ketone, and the product of the condensation of cinnamaldehyde with 2-acetylpyrrole,



have sweet, and in no way pungent, tastes.

T. H. P.

**Preparation of New Salts of CC-Disubstituted Barbituric Acids.** E. LAYRAUD (Brit. Pat. 202660).—New salts are obtained by mixing hot aqueous solutions of *as*-CC-disubstituted barbituric acids and piperazine. *Piperazine ethylbutylbarbiturate* melts at about 150—155°. The piperazine salts (acid : base = 1 : 1 mol.) afford stable aqueous solutions. *Salts* are also obtained by treating ethylisobutyl-, ethylisoamyl-, propylbutyl-, propylisobutyl-, and propylisoamyl-barbituric acids with either an organic base, other than piperazine, or an inorganic base, other than sodium.

W. T. K. B.

**Synthetic Hypnotics of the Barbituric Acid Series.** A. W. DOX (*J. Amer. Pharm. Assoc.*, 1923, 12, 602—609).—A consideration of the nature of the group producing hypnotic effect. In the veronal class, the group  $\cdot\text{CR}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot$  is a "hypnophore." Macht's "specific benzyl effect" is simply a higher alcohol effect. To manifest hypnotic action without undesirable after-effects, the two 5-alkyl groups of the pyrimidine ring should together contain between 4 and 8 carbon atoms; at least one such group must be of open-chain form. The benzyl group is undesirable, the carbamide group may not be replaced by the amidine group, and the molecular weight should not exceed about 250. CHEMICAL ABSTRACTS.

**Hypnotic and Analgesic Compounds from Dimethylamino-phenyldimethylpyrazolone and Dialkylbarbituric Acids.** E. H. VOLWILER (U.S. Pat. 1478463).—Yellow or orange-yellow, crystalline compounds, m. p. 94.5—96.5°, 88—90°, 84—86°, and 90—94°, are produced from dibutyl-, ethylbutyl-, ethylsec.butyl-, and ethylisoamyl-barbituric acids, respectively. *Ethylsec.butylbarbituric acid* is obtained by condensing ethyl ethylsec.butylmalonate (b. p. 133°/48 mm.) with carbamide in the presence of sodium ethoxide. CHEMICAL ABSTRACTS.

**Mother Substance of Indian-yellow.** F. MAYER (*Arch. Exp. Path. Pharm.*, 1924, **101**, 383—385).—The formulæ proposed by Wiechowski (A., 1923, i, 591) for mangin and euxanthone are at variance with the accepted conclusions of Fischer and Piloty (A., 1891, i, 677) and other workers; they are therefore to be regarded as erroneous.

W. O. K.

**Constitution of Pyrazoles, Indazoles, and Anthranils.** K. VON AUWERS (*Annalen*, 1924, **437**, 63—86).—A discussion of the bearing of data previously obtained (see i, 666) on the constitution of these compounds. To assist in calculating atomic refractivities for singly-linked or doubly-linked nitrogen, refractivity measurements were made on eleven substituted hydrazines, whilst the constants for five more indazole derivatives, anthranil itself, and three substituted anthranils are also recorded. The author's conclusion is that none of the indazole compounds contains a 3-membered ring structure and that the 1- and 2-derivatives differ only in the arrangement of the double bonds. Anthranil and related compounds should be formulated as analogous to indazole, not as internal amides.

W. A. S.

**Sulphonation of Glyoxalines. II.** R. FORSYTH, J. A. MOORE, and F. L. PYMAN (*J. Chem. Soc.*, 1924, **125**, 919—923).—Attempts to remove the methyl group from 2-methylglyoxaline-4-sulphonic acid so as to determine the constitution of glyoxalinesulphonic acid (T., 1920, **117**, 1429) failed. Oxidising agents either did not act or completely disrupted the molecule. A benzylidene compound was not formed. When glyoxaline is treated with 70% oleum at 160° for 36 hours the product contains 15% of a *disulphonic acid*. 2-Methylglyoxaline, similarly treated for 3—6 hours, gives 2-methylglyoxaline-4-sulphonic acid,  $C_4H_5N_2 \cdot SO_3H \cdot H_2O$ , prisms, m. p. (decomp.) about 279° when anhydrous. The *ammonium*, *barium*, and *sodium* salts are described. In some experiments, a small proportion (up to 17%) of the 4 : 5-*disulphonic acid* was produced. This forms needles containing  $1.5H_2O$  and has m. p. 280°; its *barium* salt is described. Neither glyoxalinesulphonic acid nor methylglyoxalinesulphonic acid afforded esters or chlorides. Partial hydrolysis took place when they were heated at 170° with concentrated hydrochloric acid. Treated with bromine (1 mol.) in aqueous solution, glyoxalinesulphonic acid gives ammonium bromide, oxalic acid, and 2 : 4 : 5-tribromoglyoxaline, 65% of the acid being recovered unchanged; methylglyoxalinesulphonic acid behaves similarly, yielding a little 4 : 5-dibromo-2-methylglyoxaline and 4-bromo-2-methylglyoxaline-5-sulphonic acid (cf. Light and Pyman, T., 1922, **121**, 2626).

W. A. S.

**Indoleninocyanines [Indocyanines].** W. KÖNIG [with E. WAGNER] (*Ber.*, 1924, **57**, [B], 685—692; cf. A., 1923, i, 1188).—1 : 2 : 3 : 3-Tetramethylindolenium iodide is converted by ethyl orthoformate in boiling acetic anhydride solution into 1 : 3 : 3 : 1' : 3' : 3'-hexamethylstreptomonoxyethylene-2 : 2'-indocyanine iodide (annexed formula), golden needles, m. p. about 229° (decomp.).

$\alpha \alpha^* 2$

The corresponding *bromide*, m. p. 250° (decomp.), *chloride*, decomp. 250°, *perchlorate*, m. p. 245° (decomp.), and *picrate*, m. p. 205°, are described. The new dye is remarkable

among quinocyanines on account of its relatively great stability towards mineral acids and light. It is converted by a very large excess of sodium hydroxide into the corresponding pale yellow  $\psi$ -base, m. p. about 96° (decomp.), which when suspended in water passes into equilibrium with the red onium base. 5-*Chloro-1:2:3:3-tetramethylindolenium iodide*, pale yellow needles, m. p. 198°, prepared by fusing acetone-*p*-chlorophenylhydrazone with zinc chloride, is converted in a similar manner into 5:5'-*dichloro-1:3:3:1':3':3'-hexamethylstreptomono-vinylene-2:2'-indocyanine iodide*, needles, m. p. 265°; the corresponding *carbinol base*, a pale yellow, amorphous substance, has m. p. about 130° (decomp.).

H. W.

**Preparation of Diaminodiarlyldialkylmethanes.** FARBW. VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 204722).—Aniline, or a nuclear alkyl-substituted derivative with a free *p*-position, is caused to react, in the form of a salt in aqueous solution, with an aliphatic ketone (e.g., by heating under pressure at 120–150°). *pp'*-Diaminodiphenyldimethylmethane,  $\text{CMe}_2(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$ , forms colourless needles, m. p. 132°. *pp'*-Diaminodi-*m*-tolyl-dimethylmethane (from *o*-toluidine and acetone) has m. p. 71°, and *pp'*-diaminodiphenylmethylethylmethane (from aniline and methyl ethyl ketone), m. p. 78°. These compounds are valuable as intermediates for dyes.

W. T. K. B.

**Dyes derived from Carbazole and Thiodiphenylamine.** S. DUTT (*J. Chem. Soc.*, 1924, 125, 802–807).—Carbazole condenses with aldehydes and ketones in presence of concentrated sulphuric acid or zinc chloride to form triarylmethane compounds which may be oxidised to dyes. As 3-nitro-, but not 3:6-dinitro-, carbazole will so condense it is inferred that substitution takes place in position 3. With formaldehyde the compound,  $\text{CH}_2(\text{C}_{12}\text{H}_8\text{N})_2$ , colourless needles, m. p. 287°, is obtained; benzaldehyde affords the *leuco-base*,  $\text{CHPh}(\text{C}_{12}\text{H}_8\text{N})_2$ , needles, m. p. above 300°, which, oxidised with nitrosyl chloride in sulphuric acid solution, gives the dark green *chloride* of the dye, the colourless *carbinol base* of which is obtained by boiling with pyridine and forms needles, m. p. above 290°. Similar compounds were prepared using *p*-dimethylamino-benzaldehyde [dark violet needles; *carbinol base*, m. p. 282° (decomp.)], *m*-nitro- and *m*-chloro-benzaldehydes. When sulphonated, all these products dye unmordanted cotton in green to violet shades. Benzophenone, *pp'*-tetramethyldiaminobenzophenone, and 2:3:4-trihydroxybenzophenone yield (with phosphoryl chloride as condensing agent) compounds of the type,  $\text{C}_{12}\text{H}_8\text{N}\cdot\text{CPh}_2\text{Cl}$ . The *carbinol base* of the first named forms colourless needles, m. p. 172°, and its *chloride* violet needles, m. p. 280–285°; the remainder have m. p.

above  $290^{\circ}$ . All dye wool in violet shades and the last-named dyes chrome-mordanted textiles dark violet or black shades. Thiodiphenylamine yields analogous derivatives. With oxalic acid, a green compound,  $C(C_{12}H_8NS)_3 \cdot CO_2H$ , giving a colourless base,  $C(C_{12}H_8NS)_3 \cdot OH$ , m. p.  $225-227^{\circ}$ , was formed. Benzaldehyde (carbinol base, decomp.  $200^{\circ}$ ) and *p*-dimethylaminobenzaldehyde gave compounds dyeing cotton green and grey, respectively, from a sulphide bath. *p*-Hydroxy- and *m*-nitro-benzaldehydes also condense. With benzophenone, and its 2:3:4-trihydroxy and *pp'*-tetramethyldiamino derivatives, compounds were produced which dye wool or unmordanted cotton blue or violet shades. These substances are decomposed by concentrated sulphuric acid. Thiodiphenylamine will also condense with nitrosophenols (*p*-nitrosophenol, *p*-nitroso-*m*-dimethylaminophenol, dinitrosoresorcinol,  $\alpha$ -nitroso- $\beta$ -naphthol,  $\beta$ -nitroso- $\alpha$ -naphthol), giving products which, unlike the carbazole-indophenols, will dye cotton from a hyposulphite or sulphide "vat." By fusion with sodium polysulphide at  $250-300^{\circ}$ , they yield sulphur dyes giving green, brown, or black shades. Compounds with similar properties are formed with diketones (benzil, phenanthraquinone, isatin).

W. A. S.

**Preparation of Acylacetyl Compounds.** CHEM. FABR. GRIESHEIM-ELEKTRON (Brit. Pat. 211772).—Diacylacetyl compounds are prepared by heating, preferably in a solvent (*e.g.*, a benzene hydrocarbon, chlorobenzene, nitrobenzene, naphthalene, or a large excess of the acylacetic ester used), at least 2 mols. of an acylacetic ester with 1 mol. of a diamine of the general formula  $NH_2 \cdot Y \cdot NH_2$ , where Y represents an aryl or substituted aryl residue, a diaryl or substituted diaryl residue, or a residue of a diaryl compound of the type  $-Ar \cdot Z \cdot Ar'$ , where Ar and Ar' stand for the same or different aryl or substituted aryl residues united by a connecting link, Z, which may be  $\cdot O \cdot$ ,  $\cdot S \cdot$ ,  $\cdot CH_2 \cdot$ ,  $\cdot CO \cdot$ ,  $\cdot NH \cdot$ ,  $\cdot NHCO \cdot$ ,  $\cdot N \cdot N \cdot$ ,  $O < \begin{smallmatrix} N \\ | \\ N \end{smallmatrix}$ ,  $\cdot NH \cdot CO \cdot NH \cdot$ ,  $\cdot O \cdot CH_2 \cdot CH_2 \cdot O \cdot$ , or the like.

The diacylacetyl compounds have a substantive character, so that they can be fixed on the cotton fibre in alkaline solution and developed with diazo compounds, giving shades which are fast to washing. Details of the preparation of several representatives are given, and the following new compounds described. *Diacetoacetyl-p-phenylenediamine*: slender, colourless needles, m. p.  $167^{\circ}$  (decomp.); *diacetoacetyl-o-tolidine*: slender, lustrous needles, m. p.  $204-205^{\circ}$  (decomp.); *diacetoacetyl-o-dianisidine*: feebly yellow needles, m. p.  $164-165^{\circ}$  (decomp.); *dibenzoylacetyl-o-tolidine*: slender, colourless, lustrous needles, m. p.  $233^{\circ}$  (decomp.); *diacetoacetyl-4:4'-diaminobenzophenone*: colourless, lustrous needles, m. p.  $175-176^{\circ}$  (decomp.); *diacetoacetyl-4:4'-diaminoazobenzene*: orange-yellow, crystalline powder, decomp.  $233-234^{\circ}$ ; *diacetoacetyl-1:4-naphthylenediamine*: colourless needles, m. p.  $197^{\circ}$  (decomp.); *diacetoacetyl-1:5-naphthylenediamine*: silvery scales, m. p.  $249-250^{\circ}$  (decomp.); *diacetoacetyl-2:6-naphthylenediamine*: lustrous needles, m. p.  $203-204^{\circ}$  (decomp.); *diacetoacetyl-o:o'-dichloro-*

*benzidine*: colourless, crystalline flocks, decomp. 145—147°; *diacetoacetyl-m:m'-dichlorobenzidine*: colourless needles, decomp. 212°; *dibenzoylacetylbenzidine*: yellow, crystalline powder, m. p. 248° (decomp.); *diacetoacetyl-4:4'-diamino-3:3'-dichlorodiphenylmethane*: colourless, small crystals, m. p. 138—139° (decomp.); *diacetoacetyl-4:4'-diamino-3:3'-ditolylmethane*: colourless, felted needles, m. p. 143—144° (decomp.); *diacetoacetyl-4:4'-diamino-azoxybenzene*: brownish-yellow, crystalline powder, m. p. 219—220° (decomp.); *diacetoacetyl-4:4'-diamino-3:3'-azotoluene*: bright yellow powder, m. p. 215° (decomp.); *diacetoacetyl-4:4'-diamino-diphenylcarbamide*: colourless, lustrous leaflets, melting above 320°.

W. T. K. B.

**Preparation of [Azo] Dyestuffs derived from Pyrazolone and of Intermediate Products therefor.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 210669).—1-Aryl-5-pyrazolones are prepared by condensing the hydrazine derivative of an aromatic primary amine containing a sulphonamido group (e.g., 3-aminobenzene-1-sulphonamide) with a suitable derivative of a  $\beta$ -ketonic acid (e.g., ethyl acetoacetate or ethyl oxaloacetate). By coupling these pyrazolones with a diazo compound, azo dyes are obtained which are remarkable for their uniformity and purity of tint (yellow to red). More particularly is this the case with the mordant dyes obtained by coupling the new pyrazolones with diazo derivatives of *o*-aminophenol and *o*-aminonaphthol, and especially with the acid dyes containing chromium produced by treating these mordant dyes with a chroming agent (e.g., chromium formate). [Cf. *B.*, 1924, 412.]

W. T. K. B.

**Scission of Disulphides. Synthesis of Triazoles.** E. FROMM, L. BRÜCK, R. RUNKEL, and E. MAYER (*Annalen*, 1924, 437, 106—124).—A continuation of earlier work (cf. *A.*, 1922, i, 377; Arndt and others, *A.*, 1921, i, 813; 1922, i, 277, 375). 5-Amino-3-phenylamino-1:2:4-triazole has m. p. 163°, not 77° or 157°, as previously given. It forms a *benzylidene* compound, yellow needles, m. p. 225°, and a *tribenzoyl* derivative, yellow crystals, m. p. 126°. 3-Phenylamino-5-thiol-1:2:4-triazole may be oxidised to the corresponding disulphide which, treated with hot 25% sodium hydroxide, gives an equimolecular mixture (cf. *pp'*-dinitrodiphenyl-disulphide, Fromm and Wittmann, *A.*, 1908, i, 631) of the parent thioltriazole and 3-phenylamino-1:2:4-triazole, m. p. 180°, yielding a *dibenzoyl* derivative, m. p. 111—112°. 3-*p*-Tolylamino-5-thiol-1:2:4-triazole, from *p*-tolylidithiobiuret and hydrazine hydrate, forms colourless crystals, m. p. 271°; its *dibenzoyl* derivative, yellow leaflets, has m. p. 129°, and the *benzyl(thio)ether*, needles, m. p. 182°; this also yields a *benzoyl* derivative, scales, m. p. 133°. 5-Amino-3-*p*-tolylamino-1:2:4-triazole, the subsidiary product of the above reaction, has m. p. 178—180°, its *benzylidene* derivative, m. p. 219°. The thioltriazole, oxidised with ferric chloride, yields the *disulphide*, a yellow powder, m. p. 229°, which, treated with sodium hydroxide, gives, as above, 3-*p*-tolylamino-1:2:4-triazole, m. p. 199°, the

*benzoyl* derivative of which forms yellow leaflets, m. p. 172°. Similar compounds containing the *o*-tolyl and *o*-anisyl radicals were prepared. *Cyano-o-tolylcarbamide* has m. p. 65—68°; *3-o-tolylamino-5-thiol-1:2:4-triazole* forms needles, m. p. 263°; its *dibenzoyl* derivative has m. p. 133°, the *benzyl(thio)ether*, m. p. 161°, and this also yields a *dibenzoyl* derivative, leaflets, m. p. 125°. *5-Amino-3-o-tolylamino-1:2:4-triazole* has m. p. 165°, and easily decomposes; its *hydrochloride* forms needles, m. p. 187°, the *benzoyl* derivative, scales, m. p. 220°. *o-Tolylthiocarbamide* has m. p. 158°; the corresponding *triazole disulphide* forms a yellow powder, m. p. 277°. *o-Anisylthiobiuret*, m. p. 148°, treated with iodine, gives *o-anisylthiuret hydriodide*, m. p. 200°, and with benzyl chloride a compound, m. p. 130°. *3-o-Anisylamino-5-thiol-1:2:4-triazole* has m. p. 280°; its *benzyl(thio)ether*, m. p. 108°; its *dibenzoyl* derivative forms yellow scales, m. p. 138°. *Aminoguanidino-o-anisylthiocarbamide* crystallises in needles, m. p. 134—135°, its *hydrochloride* has m. p. 178—180°, and its *benzylidene* compound forms pale yellow scales. *5-Amino-3-p-phenetyl-amino-1:2:4-triazole* has m. p. 191°, its *dibenzoyl* derivative, a yellow substance, melts at 176°, and its *diacetyl* derivative at 168°. *3-p-Phenetyl-amino-5-thiol-1:2:4-triazole* has m. p. 268°, its *dibenzoyl* compound, m. p. 145°, its *benzyl(thio)ether* forms needles, m. p. 172°, and yields a *benzoyl* derivative, yellow needles, m. p. 122°. The corresponding *disulphide* is an amorphous powder convertible, as above, into *3-p-phenetyl-amino-1:2:4-triazole*, m. p. 185°. *5-Amino-3-ethylphenylamino-1:2:4-triazole* forms scales, m. p. 198°; its *benzoyl* derivative, yellow crystals, has m. p. 188.5°, its *acetyl* derivative m. p. 157°. The corresponding *5-thioltriazole* forms needles, m. p. 127°, *dibenzoyl* derivative, m. p. 118°, *benzyl(thio)ether*, m. p. 94°, and the *benzoyl* derivative of the latter, m. p. 65°. The by-product of the hydrazine hydrate reaction here is *3-amino-5-thiol-1:2:4-triazole* (cf. Fromm and Arndt, *loc. cit.*), ethylaniline being split off. This triazole yields a *1:4-dibenzoyl* derivative, m. p. 178°. The *benzoyl* derivative of *5-benzoylamido-3-thiol-1:2:4-triazole* has m. p. above 260°.

W. A. S.

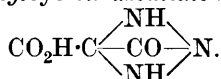
### Derivatives of *cyclo*Triazobutane [*cyclo*Triazomethene].

O. DIELS and H. BEHNCKE (*Ber.*, 1924, 57, [B], 653—656).—The formation of additive products from azodicarboxylic ester and compounds containing an "acidic" methylene group is described (cf. A., 1923, i, 391, and previous abstracts).

Ethyl azodicarboxylate reacts with ethyl cyanoacetate in the presence of potassium acetate at 60° to form the compound,  $\text{CO}_2\text{Et}\cdot\text{C}(\text{CN})\cdot[\text{N}(\text{CO}_2\text{Et})\cdot\text{NH}\cdot\text{CO}_2\text{Et}]_2$ , an unstable, yellow liquid, b. p. 150—155°/0.4 mm. Ethyl malonate reacts with ethyl azodicarboxylate to yield the substance,  $(\text{CO}_2\text{Et})_2\text{C}[\text{N}(\text{CO}_2\text{Et})\cdot\text{NHCO}_2\text{Et}]_2$ , colourless, prismatic plates, m. p. 107°, which is remarkably stable towards acids and oxidising agents, and with methyl azodicarboxylate gives the corresponding *methyl* ester, m. p. 140—141°. Either ester is transformed by methylalcoholic potassium hydroxide solution into *potassium cyclo*triazomethene-1:3:4:4-tetracarboxylate,

$(\text{CO}_2\text{K})_2\text{C} \begin{array}{c} \swarrow \text{N}(\text{CO}_2\text{K}) \\ \searrow \text{N}(\text{CO}_2\text{K}) \end{array} \begin{array}{c} \nearrow \\ \searrow \end{array} \text{NH}$ , which could not be freed completely

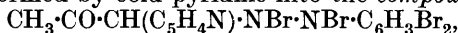
from potassium carbonate, but is converted by acetic acid into *potassium hydrogen cyclotriazomethene-4 : 4-dicarboxylate*, pyramids, m. p. 287° (decomp.). The latter salt with sulphuric acid affords *cyclotriazomethene-4 : 4-dicarboxylic acid* (long prisms, m. p. 237°, after softening and decomposing at 218°), which passes in a vacuum at 100° into 2 : 4-carbonylcyclotriazomethene-4-carboxylic acid,



The monocarboxylic acid loses carbon dioxide at 218°, to give 2 : 4-carbonylcyclotriazomethene, colourless prisms, m. p. 237°.

H. W.

**Action of Pyridine on Hydrazono-acid Chlorides.** C. BÜLOW and F. SEIDEL (*Ber.*, 1924, 57, [B], 629—633).—The compound [m. p. 186°, not 168°, as erroneously recorded by Bülow and Neber (*A.*, 1913, i, 999)] obtained from 2 : 4-dichlorophenylhydrazinopyruvyl chloride and pyridine is shown to have the constitution,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}(\text{C}_5\text{H}_4\text{N})\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Cl}_2$ , since the basic properties of the pyridine nitrogen atom are retained in it, as is proved by the formation of a *hydrochloride*, m. p. 168°, a *chloroaurate*, and a *chloroplatinate*. Similarly, the pentabromo derivative obtained from 4-phenylazo-3-methylisoxazolone (Hecking, *Diss.*, Tübingen, 1913) or from ethyl phenylazoacetoacetate (Memminger, *Diss.*, Tübingen, 1910) is transformed by cold pyridine into the compound,



red needles, m. p. 162° (*hydrochloride*, m. p. 159—160°), which is converted by zinc and alcoholic hydrochloric acid into pyridine and *p*-bromoaniline. The composition  $\text{C}_{15}\text{H}_{13}\text{ON}_3\text{Br}_4$  is assigned to the product of the action of pyridine on the pentabromo compound from 4-*o*-tolylazo-3-methylisoxazolone (Memminger, *loc. cit.*). The 2 : 4-dichlorophenylhydrazone of ethyl  $\alpha$ -chloroglyoxylate is transformed by pyridine into the substance  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_3\text{Cl}_3\cdot\text{H}_2\text{O}$ , yellow crystals, m. p. 142° after darkening at 130°.

H. W.

**Colour of Azo Compounds and their Salts.** F. KEHRMANN and S. HEMPEL (*Ber.*, 1924, 57, [B], 751; cf. *A.*, 1917, i, 593).—An acknowledgment of the priority of V. Piccard (*A.*, 1913, i, 895), regarding the colours of 4 : 4'-diaminoazobenzene, its tetramethyl derivative, and their salts in different solvents.

F. A. M.

**Indoleazobenzene.** W. MADELUNG (*Ber.*, 1924, 57, [B], 751; cf. this vol., i, 423).—An acknowledgment of the preparation by Pieroni [*Atti R. Accad. Lincei*, 1921, (v), 30, i, 267] of indoleazobenzene.

F. A. M.

**Preparation of Acylacetyl Compounds.** CHEM. FABR. GRIESHEIM-ELEKTRON (Brit. Pat. 211814).—Acylacetyl compounds are obtained, under exactly similar conditions to those required in the preparation of diacylacetyl compounds (cf. *Chem. Fabr.*



Griesheim-Elektron, this vol., i, 671), by the interaction of an acylacetic ester and a monoamine of the general formula  $\text{NH}_2 \cdot \text{R} \cdot \text{X} \cdot \text{R}'$ , where R represents an aryl residue, R' the same or a different aryl residue or a heterocyclic or acyclic residue containing a methylene group capable of coupling with diazo compounds, X an azo or azoxy group, or the residue of a 5-membered heterocyclic nucleus. The products resemble the diacylacetyl compounds in their substantive character. The following compounds are described. *Acetoacetyldehydrothiotoluidine*: colourless, crystalline powder, m. p. 170—172° (decomp.); *acetoacetylbenzene-azo-1-naphthylamine*: slender, orange needles, m. p. 154—155° (decomp.); *acetoacetyl-4-aminoazobenzene*: yellowish-orange, finely-crystallised powder, m. p. 130—131°; *acetoacetyl-4'-aminobenzene-azo-1-phenyl-3-methyl-5-pyrazolone*: slender, orange-yellow, lustrous needles, decomp. 208°; *acetoacetyl-o-aminoazotoluene*: slender, orange-yellow needles, m. p. 147°; *acetoacetyl-m-aminoazotoluene*: orange, opalescent scales, m. p. 133—134°; *acetoacetyl-4'-chloro-4-aminoazobenzene*: slender, orange-yellow, felted needles, m. p. 188°; *acetoacetyl-3'-nitro-4-aminoazobenzene*: slender, orange-yellow, felted needles, m. p. 138° (decomp.); *acetoacetyl-4'-nitro-4-aminoazobenzene*: orange-red, lustrous scales, m. p. 190—191° (decomp.); *acetoacetyl-4-aminoazoxybenzene*: small, pale yellow rods, m. p. 138° (decomp.); *acetoacetyl-4'-amino-2'-methylbenzeneazo-2-naphthalene*: orange-yellow, spherical aggregates, m. p. 153—154°; *acetoacetyl-4'-aminobenzeneazo-p-cresol*: clusters of orange-yellow needles, m. p. 165°.

W. T. K. B.

**Dimorphism of Diphenylarsenious Chloride (Diphenylchloroarsine).** C. S. GIBSON and D. C. VINING (*J. Chem. Soc.*, 1924, **125**, 909—911).—Diphenylarsenious chloride (b. p. 178.6°/10 mm.) crystallises in two forms. The unstable modification, obtained by spontaneous crystallisation of freshly redistilled material, or by heating the stable form at 130° and cooling under "aseptic" conditions, forms needles, m. p. 18.2—18.4°, whilst the stable modification forms rhombic, biaxial crystals, m. p. 38.7—38.9°. [Cf. T., 1920, **117**, 777, 1447.]

W. A. S.

**Organo Derivatives of Bismuth. VII. Iodo and Nitro Derivatives of Triphenylbismuthine.** J. F. WILKINSON and F. CHALLENGER (*J. Chem. Soc.*, 1924, **125**, 854—864).—The red substance obtained by Challenger and Allpress (T., 1915, **107**, 17) consists mainly of phenyldi-iodobismuthine. *Triphenylbismuthine di-iodide*,  $\text{Ph}_3\text{BiI}_2$ , seems to be formed by direct union of triphenylbismuthine and iodine in ether solution at  $-78^\circ$ , but decomposes at the ordinary temperature, giving the red solid. Triphenylbismuthine reacts with cyanogen bromide at 120°, giving diphenylbromobismuthine, bismuth oxybromide, and benzonitrile, whilst with cyanogen chloride scarcely any action takes place. This is in remarkable contrast to the action with cyanogen iodide (Challenger and Allpress, *loc. cit.*). Triphenylstibine and cyanogen iodide yield, presumably by interaction with moisture, in cold ether solution, *triphenylstibine hydroxyiodide*,  $\text{Ph}_3\text{Sb}(\text{OH})\text{I}$ , m. p. 196°; tri-

a a\*\*

phenylarsine and triphenylphosphine gave, with the same reagent, what appeared to be similar additive compounds which decomposed on contact with water (cf. Steinkopf and others, A., 1922, i, 72). A nitric-sulphuric acid mixture at  $-15^{\circ}$ , or fuming nitric acid at its melting point, completely disrupts triphenylbismuthine, giving *m*-dinitrobenzene as the organic product; with benzoyl nitrate, however, a *dinitrate*,  $\text{Ph}_3\text{Bi}(\text{O}\cdot\text{NO}_2)_2$ , was obtained; *tri-p-chlorophenylbismuthine dinitrate*, m. p.  $163-165^{\circ}$ , was obtained in a similar way. Triphenylbismuthine dinitrate is converted by cold nitric acid (*d* 1.52), into, according to conditions, a *mononitro* derivative, convertible into an unstable *dichloride*, m. p.  $105-110^{\circ}$ ; a *dinitro* derivative, yielding a *dichloride*, m. p.  $136^{\circ}$  (decomp.); a *tetranitro* derivative, convertible into the *dichloride*, m. p.  $146^{\circ}$ , which when heated until it decomposes gives *m*-chloronitrobenzene, the presumption being therefore that one nitro group in the bismuthine is in the meta-position (cf. Gillmeister, A., 1898, i, 138). *Tetranitrotriphenylbismuthine dihydroxide* was also obtained as an insoluble yellow powder, m. p.  $108^{\circ}$  (decomp.); boiled with alcohol it gives trinitrotriphenylbismuthine (?). Lastly, *hexanitrotriphenylbismuthine dinitrate* was obtained and converted into a *dichloride*, m. p.  $148-149^{\circ}$ .  
W. A. S.

**Action of Inorganic Halides on Organo-metallic Compounds.** F. CHALLENGER and F. PRITCHARD (*J. Chem. Soc.*, 1924, 125, 864—875).—A general discussion of earlier work (T., 1922, 121, 104; cf. also Goddard and others, *ibid.*, 1923, 123, 1163, etc.) and the following new observations. '*Tri- $\alpha$ -naphthylstibine*, m. p.  $218^{\circ}$ , from antimony trichloride and magnesium  $\alpha$ -naphthyl bromide, gives a *dichloride*, m. p.  $260^{\circ}$ , and a yellow *dibromide*, m. p.  $229^{\circ}$  (decomp.). *Tri-m-tolylbismuthine dibromide* has m. p.  $92^{\circ}$ . Although tri-*m*-tolylarsine may be obtained in a similar way from the appropriate Grignard reagent, *tri-m-tolylstibine hydroxychloride*, m. p.  $209^{\circ}$ , was the only product obtained by treating antimony trichloride with magnesium *m*-tolyl bromide. Triphenylstibine and phosphorus trichloride interact in the cold to give mainly triphenylstibine dichloride; triphenylarsine only reacts with the same reagent at  $160^{\circ}$ , and then incompletely, yielding diphenylchloroarsine; triphenylphosphine gives the dichloride and decomposition products. Arsenic trichloride and triphenylstibine at  $80^{\circ}$  yield triphenylstibine dichloride and a little arsenic. Antimony trichloride and triphenylarsine form an additive compound, m. p.  $78^{\circ}$ . The same reagent with triphenylphosphine produces a similar compound, m. p.  $96^{\circ}$ . Triphenylphosphine forms analogous compounds with arsenic trichloride [product has m. p. about  $100^{\circ}$  (decomp.) and a little arsenic separated] and with bismuth chloride (m. p.  $100-105^{\circ}$ ). The latter, heated at  $270^{\circ}$  and treated with water, gave metallic bismuth and triphenylphosphine oxide. Triphenylbismuthine and stannic chloride also form an additive compound. Triphenyl-bismuthine and -stibine react to some extent with silicon tetrachloride, giving diphenylchlorobismuthine and triphenylstibine dichloride, respectively; triphenylarsine does

not react. Titanium tetrachloride and triphenylbismuthine form a red compound and eventually yield diphenylchlorobismuthine; triphenylstibine gives only the dichloride, whilst triphenylarsine gives an unstable additive product. Attempts to prepare organic titanium compounds by interaction of titanium tetrachloride and magnesium phenyl bromide failed.

W. A. S.

**Fractionation of Gelatin by Extraction with Alcohol and Precipitation with Aluminium Hydroxide and Barium Chloride.** M. A. RAKUSIN (*Chem.-Ztg.*, 1924, 48, 249—250).—A sample of commercial "*Gelatina albissima*" was extracted with 95% alcohol, and the extract and the residue were investigated by precipitation with 10% aluminium hydroxide, the filtrate being precipitated with barium chloride. The various fractions were tested by the biuret, Ostromisslenski, and Molisch reactions, and the composition of the gelatin is given as follows: free amino compounds, 0.50%; free carbohydrates, 0.96%; biuret complex, 49.27%; combined carbohydrates, 23.77%; combined chondroitin-sulphuric acid, 25.50%. The distribution of the mineral matter (3.29%) is uncertain. All the sulphur present in gelatin is combined in the form of chondroitin-sulphuric acid, which contains 5.71% of sulphur. Gelatin is therefore not an individual chemical substance, and gelatins obtained from different raw materials may have different properties.

H. C. R.

**Gelatin-sulphuric Acid and Casein-sulphuric Acid.** J. HATANO (*Biochem. Z.*, 1924, 145, 182—185).—By the action on gelatin and casein, in the presence of pyridine, of chlorosulphonic acid dissolved in dry chloroform, stable sulphates of these proteins are obtained. The preparation of gelatin sulphate obtained contained 1.7% of sulphur against 0.35% in the original gelatin, whilst casein sulphate preparations contained 0.84% and 1.38% of sulphur as compared with 0.62% in the original protein.

J. P.

**Products of Prolonged Tryptic Digestion of Casein.** S. FRÄNKEL, H. GALLIA, A. LIEBSTER, and S. ROSEN (*Biochem. Z.*, 1924, 145, 225—241).—After prolonged hydrolysis (2 months) of casein, the following products have been isolated: *d*-tyrosine anhydride, *d*-tryptophan anhydride, *d*-leucine anhydride, and histidine anhydride. The first three dextrorotatory anhydrides are supposed to arise from the laevorotatory amino-acids by the successive actions of the enzymes waldenase—bringing about an optical inversion—and anhydrase. In addition *d*-alanine, *d*-glutamic acid, *l*-oxyproline, *l*-serine, and *d*-valine were obtained, in part as such, and in part as the racemic forms. *l*-Proline,  $[\alpha]_D^{25} -74.08^\circ$  in water, *d*-isoleucine,  $[\alpha]_D^{25} +12.77^\circ$  in water, and *l*-aspartic acid were isolated in the unchanged condition, whilst glycine was partly converted into methylamine by the action of a decarboxylase. In the course of such prolonged hydrolysis, leucine is converted into the anhydride whilst isoleucine remains unchanged (cf. also A., 1922, i, 184; 1923, i, 398).

J. P.

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**Protein Coagulation in Drops. IV. Influence of the Nature of the Proteins and Precipitants on the Precipitate.**

L. ČIKÁNEK, J. HAVLÍK, and F. KUBÁNEK (*Biochem. Z.*, 1924, **145**, 98—103).—The influence of a large number of substances on the coagulation of serum proteins has been studied, using the Bečka drop method. The presence in the precipitant of halogens, hydroxyl, sulphonyl, and nitro groups increases the precipitating action, whilst amino groups lower it. The precipitating powers of the aliphatic alcohols decrease with increase in the number of hydroxyl groups. With certain solutions of sodium sulphide, potassium hydroxide, and potassium cyanide, the albumin, but not the globulin, fraction is precipitated, whilst the reverse result is obtained with solutions of copper sulphate, cadmium nitrate, aluminium chloride, and disodium hydrogen phosphate. Certain pathological horse sera show a characteristic behaviour on precipitation with ferrous sulphate, pyrogallol, and tannin. J. P.

**Influence of Hydrolysis on the Capacity of Proteins to Bind Acids and Bases.**

T. B. ROBERTSON (*Austral. J. Exp. Biol.*, 1924, **1**, 31—37).—The ratio, equivalents of acid or base bound/equivalents of free amino-nitrogen, has been determined for casein and gelatin before and after hydrolysis by trypsin at  $p_H$  2.0, 8.2, and 10.5. Except for gelatin at  $p_H$  10.5, the ratio decreases as a result of hydrolysis. It is concluded, therefore, that the predominant method of union of proteins with acids and bases is through internal  $-CO\cdot NH-$  groups rather than through free amino or carbonyl groups. O. O.

**Halogenated Proteins. I. Bromo-ovalbumin.**

A. J. J. VANDEVELDE (*Rec. trav. chim.*, 1924, **43**, 158—162).—The action of bromine dissolved in carbon tetrachloride on some proteins in the form of a dry powder afforded bromo derivatives of higher halogen content than previously recorded. This is stated to be due to the fact that secondary reactions brought about by the presence of water were obviated. The following bromo derivatives (hygroscopic, orange-coloured powders of penetrating odour) are described: *Bromo-ovoprotein A*, soluble in water, yielding a strongly acid solution in which 87.1% of the total bromine is in the form of hydrobromic acid. At 100°, the substance loses hydrogen bromide to give *bromo-ovoprotein C*, which also yields an acid solution. Its colour, however, prevents it being examined with a coloured indicator. On dissolving the first-named substance in *N*-sodium hydroxide and then acidifying with acetic acid, a precipitate of *bromo-ovoprotein S* is formed. The percentages of bromine in these three substances are 37.5, 31.48, and 4.73, respectively. H. J. E.

**Protein Phytotoxins, with Special Reference to the New "Modeccin."**

H. H. GREEN and P. KAMERMAN (*J. S. Afr. Chem. Inst.*, 1924, **7**, 3—5).—The roots of *Modecca digitata* (more correctly, *Adenia digitata*) contain a highly poisonous phytotoxin to which the name *modeccin* has been given; the fatal dose is

0.0005 mg. per kg. of body-weight, when injected intravenously or subcutaneously. In its general properties the substance resembles the other known phytotoxins, namely, ricin (from *Ricinus communis*), abrin (from *Abrus precatorius*), crotin (from *Croton tiglium*), robin (from *Robinia pseudacacia*), and curcin (from *Jatropha curcus*); all are stable up to about 70°, but destroyed rapidly at 100°. They are insoluble in 60% alcohol and are precipitated by ammonium sulphate and other salts. Modeccin resists hydrolysis by pepsin or trypsin for 3 days at 37°, but is destroyed by trypsin in 14 days; it does not possess hæmagglutinative properties and in this respect differs from ricin.

W. P. S.

**Protein Studies. III. Decomposition of Silk Fibroin by Fermentation.** F. WESSELY.—(See i, 696.)

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## Biochemistry.

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¶ **Effect of Salts of Calcium, Sodium, and Potassium on Respiratory Exchanges. I. Effect of Parenteral Administration of these Salts.** W. ARNOLDI and J. FERBER (*Z. klin. Med.*, 1923, **97**, 208—216; from *Chem. Zentr.*, 1924, i, 494).—Injection of salts of calcium, sodium, and potassium produced increased utilisation of oxygen and diminution in respiratory quotient and the output of carbon dioxide in humans. Respiration within the tissues was increased. G. W. R.

**Catalytic Action of Blood.** L. WALLING and O. O. STOLAND (*Amer. J. Physiol.*, 1923, **66**, 503—518).—Blood catalase is accurately determined by reaction at  $p_H$  8.9, 22°, for 0.5 hour; it is destroyed above 47° and is only slightly affected at 0°. In acid hydrogen peroxide at 22° it is apparently destroyed and its action complete in 10 minutes; with optimum alkalinity it acts for 3 hours or more. Sodium chloride (0.9%) in acid hydrogen peroxide increases, and in alkaline retards, the catalytic effect of blood.

CHEMICAL ABSTRACTS.

**Influence of Rarefied Air on the Gaseous Metabolism of the Blood.** A. LOEWY and J. FÖRSTER (*Biochem. Z.*, 1924, **145**, 318—323).—The blood of rabbits which had been kept under diminished pressure (430—460 mm.) for 24 to 33 hours showed a greater oxygen consumption than that of normal rabbits. The average figures found per 100 c.c. of blood per hour were 5.272 c.c. in the former and 2.733 c.c. in the latter case. J. P.

**Cell Volume and Electrical Conductivity of Blood.** H. C. GRAM (*J. Biol. Chem.*, 1924, **59**, 33—40).—The conductivity of whole blood and of serum, and the cell volume, were measured. An empirical curve has been obtained from which the cell volume

may be read, if the ratio of the conductivity of the whole blood to that of the serum is known.

W. O. K.

**Rarefied Air and Blood Regeneration by "Hæmopoietins."**

J. FÖRSTER (*Biochem. Z.*, 1924, **145**, 309—317).—Serum from rabbits which had been kept in atmospheres at a pressure of 410 to 480 mm. for 1—2 days injected into rabbits rendered anæmic by bleeding, produced an increase in the rate at which the number of the red blood-corpuscles returned to the normal value. Normal sera and the proteins of milk did not produce this effect, which is ascribed to the production in the bone marrow, under the stimulus of the diminished pressure, of active substances—"hæmopoietins" (Carnot and Deflandre, *Compt. rend.*, 1906, **143**, 384)—which then find their way into the blood-stream.

J. P.

**Ultrafiltration of Blood Serum and Cerebrospinal Fluid.**

G. EGERER-SEHAM (*J. Lab. Clin. Med.*, 1923, **8**, 818—824).—A new apparatus is described. The ammonium sulphate globulin test is negative in the majority of ultrafiltrates of normal blood serum. The ultrafiltrates of non-syphilitic and syphilitic blood give a reduction of the colloidal gold solution in almost all cases. The ultrafiltrates of normal cerebrospinal fluid give no colloidal gold curve. The reduction of colloidal gold solution by ultrafiltrates from syphilitic spinal fluids seems to vary with the quantity of the substance reducing the colloidal gold solution present in the original spinal fluid. The substance giving the Wassermann reaction in syphilitic blood does not seem to be ultrafiltrable.

CHEMICAL ABSTRACTS.

**Calcium-ion Concentration of Blood Plasma.** E. J. BIGWOOD (*Bull. Soc. Chim. biol.*, 1924, **6**, 118—141).—In 20 normal subjects the calcium-ion concentration varied from 22 to 28 mg. per litre of venous blood plasma. The individual variations in any one subject are closely parallel to the variations in  $p_H$ , increasing with increasing acidity and *vice versa*. Such a parallelism does not exist between the calcium-ion and bicarbonate-ion concentrations.

J. P.

**Effect of Fasting (and Re-feeding) on the Calcium and Inorganic Phosphorus in Blood Serums of Normal and Rachitic Rats.** A. W. CAVINS (*J. Biol. Chem.*, 1924, **59**, 237—242).—After fasting, the subnormal quantities of inorganic phosphorus present in the serum of rachitic rats increased approximately to normal, and the rickets healed concurrently. In the case of normal rats, there was no similar rise in the inorganic phosphorus in the serum after fasting.

W. O. K.

**Dynamics of Phosphoric Acid in the Blood.** H. LAWACZECK (*Biochem. Z.*, 1924, **145**, 351—371).—The free phosphoric acid of whole blood was found to vary between 7.8 and 18.2 mg.%. When the blood was kept at or below body temperature part of the inorganic was converted into organic phosphate and this con-

version was increased by the passage of air or hydrogen through the blood, but it did not occur if the blood had been previously warmed at 44–45°. The reverse conversion of organic into inorganic phosphate resulted from passing carbon dioxide. The reversible interconversion: inorganic  $\rightleftharpoons$  organic phosphate was found to proceed towards the right in the presence of phosphates, bicarbonate, and calcium, and towards the left in the presence of chlorides, water (hæmolysis), potassium, and sodium, but the cations mentioned were active only in hæmolysed blood. Both inorganic and organic phosphorus compounds passed from the serum into the corpuscles, and *vice versa*.

The phosphates taking part in the above changes are acid-soluble, but hexosephosphate, which appears to be a product of the synthetic phase of the reaction, is not subject to the reverse hydrolytic change. J. P.

**Proteins of Immune Sera, especially the Ratio of Globulin to Albumin (Protein Index).** S. BÄCHER and M. M. KOSIAN (*Biochem. Z.*, 1924, 145, 324–343).—An investigation of the amounts of protein precipitable from various normal and immune sera by one-third and one-half saturation with ammonium sulphate. Wide differences exist in the values obtained from the same types of sera from different animals, whilst old sera have a higher protein index than fresh sera and are thus regarded as more labile. Diphtheria sera (horse) show a higher total protein content than the normal, and absolute and relative increases in globulin, notably in pseudoglobulin, and decreases in albumin. During immunisation the lability of horse sera progressively increases, but this is not directly related to the formation of antitoxin. Immunisation of the horse against toxins other than diphtheria does not produce analogous results, nor does diphtheria toxin produce the same effects when injected into oxen. The increased lability of the proteins of old sera is associated with a similar alteration in the ease with which the antitoxin may be salted out with ammonium sulphate. J. P.

**Action of Thrombin. IX. Blood Clotting.** E. WÖHLISCH (*Biochem. Z.*, 1924, 145, 279–285).—The observation of Stuber and Sano (A., 1923, i, 410) that thrombin prepared by Schmidt's method, when separated from a solution of fibrinogen by a semi-permeable membrane, causes the fibrinogen to clot, was not confirmed when proper controls were employed. The views of these authors (*loc. cit.*) regarding the difference between the thrombin of fresh serum and that precipitated by alcohol according to Schmidt's process are not supported. J. P.

**Nature of the Antihæmolytic Property of Heated Sera.** G. MILKOVITCH (*Compt. rend. Soc. Biol.*, 1923, 89, 877–879; from *Chem. Zentr.*, 1924, i, 356).—Hæmolysis is conditioned, not simply by the presence of a hæmolytic agent, but also by certain chemical factors, in particular the reaction, which must be to a certain degree alkaline. From experiments with human sera heated at



56° it is concluded that the presence of a specific "antihæmolyisin" is improbable and that heating simply results in the production of chemical conditions unfavourable to hæmolysis. G. W. R.

**Coagglutinating and Precipitating Action of Ricin.** G. DI MACCO (*Z. Immunitt.*, 1923, **38**, I, 467—488; from *Chem. Zentr.*, 1924, i, 493—494).—In addition to the direct agglutinative effect of ricin on certain blood-corpuscles, agglutination with corpuscles on which it cannot by itself exert any action, can be produced in the presence of serum from other animals. This coagglutination is not shown when ricin is first allowed to react with the serum in the absence of blood-corpuscles. Coagglutination is related to the precipitating action of ricin; it is considered to be physico-chemical in nature. G. W. R.

**Precipitin Reactions of a Crystalline Globulin from Human Urine.** H. S. EVERETT, S. BAYNE-JONES, and D. W. WILSON.—(See ii, 432.)

**Potassium Fluoride as Preservative for Blood.** R. H. MAJOR (*J. Amer. Med. Assoc.*, 1923, **81**, 1952).—In the absence of bacteria, clotting is prevented, and the sugar and carbon dioxide tension are unchanged during 7 days when potassium fluoride is added to blood. CHEMICAL ABSTRACTS.

**Use of Formaldehyde for the Preservation of Blood Specimens.** J. C. BOCK (*J. Biol. Chem.*, 1924, **59**, 73—76; cf. *ibid.*, 1920, **44**, 203).—The use of formaldehyde for preservation of blood for determinations of sugar by the method of Folin and Wu is inadvisable, as five of the six samples of formalin tested gave rise to markedly high results. W. O. K.

**Animal Calorimetry. XXIV. Oxidation of Mixtures of Carbohydrates and Fat. A Correction.** G. LUSK (*J. Biol. Chem.*, 1924, **59**, 41—42).—Corrections are given of errors in the standard table of Luntze and Schumberg ("Studien zu einer Physiologie des Marsches," Berlin, 1901, 361), showing the caloric value of 1 litre of oxygen used to oxidise mixtures of carbohydrates and fats. W. O. K.

**Clinical Calorimetry. XXXV. A Graphical Representation of the Respiratory Quotient and the Percentage of Calories from Protein, Fat, and Carbohydrate.** E. F. DU BOIS (*J. Biol. Chem.*, 1924, **59**, 43—49).—Graphs have been constructed from which it is possible to determine rapidly the number of calories produced by each litre of oxygen, knowing the total respiratory quotient and the percentage of calories furnished by protein. W. O. K.

**Clinical Calorimetry. XXXVI. A Graphic Method of Determining certain Numerical Factors in Metabolism.** A. M. MICHAELIS (*J. Biol. Chem.*, 1924, **59**, 51—58).—A graph is given from which it is possible to determine easily the total calories

produced when 1 litre of oxygen is used in the combustion of a mixture of fats, proteins, and carbohydrates, from a knowledge of the urinary nitrogen, the total oxygen consumed, and the total respiratory quotient. From another graph, the percentage of calories derived from protein, fat, and carbohydrate, and that of oxygen used in the oxidation of each, may be read. W. O. K.

**Thermochemistry of Protein Behaviour.** J. H. MATHEWS and B. W. ROWLAND (*Colloid Symposium Monograph, Univ. Wisconsin*, 1923, 227—243).—Fixed amounts of 0.5*N*-hydrochloric acid were added to gelatin solutions of varying concentrations at 40° and the thermal change was recorded in Browne's adiabatic calorimeter. When in concentration greater than about 2%, gelatin containing 1.3% of ash shows markedly different results from ash-free isoelectric gelatin. Collateral experiments are described with gelatin and glycine. CHEMICAL ABSTRACTS.

**Formation in the Injured Liver of a Compound Similar to Dextrose but Unsuitable for the Organism.** VARELA and RUBINO (*Arch. exp. Path. Pharm.*, 1924, 101, 316—334).—The occurrence of hypoglycæmia or of abnormally low hyperglycæmia after the oral administration of 10—20 g. of dextrose or lævulose is taken as an indication of the presence of a sugar unsuitable for utilisation. In certain diseases of the liver, this appears to obtain. It is suggested that the formation of glycogen does not involve merely the polymerisation of dextrose, but that there is a complex assimilation process. W. O. K.

**Stimulus of Food on Intermediary Metabolic Processes.** I. W. LAUFBERGER and J. A. ŠEFČÍK (*Biochem. Z.*, 1924, 145, 274—278).—The oral administration of peptone or egg-albumin to rabbits produced a hyperglycæmia within 5 minutes. Mechanical stimulation of the gastric mucous membrane or the administration of olive oil had no influence on the blood-sugar. J. P.

**Preparation of Insulin.** N. F. FISCHER (*Amer. J. Physiol.*, 1923, 67, 57—64).—The method of Doisy, Somogyi, and Shaffer (*J. Biol. Chem.*, 1923, 55, xxi) is modified by effecting the final precipitation in two stages, with 1 and 8 volumes of alcohol, respectively. The first fraction is toxic, and produces a rise in the blood-sugar; the second is active, and of a potency which is the greater the smaller the amount of toxic substance present. Pancreas from old cows yielded only 100 units of insulin per kg., whilst that from calves yielded 1000 units. A. A. E.

**Insulin-like Substance in the Kidney, Spleen, and Skeletal Muscle.** J. S. ASHBY (*Amer. J. Physiol.*, 1923, 67, 77—82).—A substance extracted from the kidney, spleen, and muscle of normal dogs and cattle, after the removal of the "toxic fraction," behaved similarly to insulin in producing hypoglycæmia in rabbits. Hypoglycæmia produced by the kidney extract was maintained for the unusually long period of at least 24 hours. A. A. E.

**Amount of Available Insulin in the Pancreas of Domestic Animals.** F. FENGER and R. S. WILSON (*J. Biol. Chem.*, 1924, **59**, 83—90).—The average yield of insulin from 1 kg. of fresh pancreas of cattle, sheep, or pig was from 1500 to 2200 rabbit units. The methods of purification and standardisation of the insulin are described in detail.  
W. O. K.

**Disposal of Fat in the Organism.** F. KÖSZEG (*Arch. exp. Path. Pharm.*, 1924, **101**, 305—315).—Iodipin (Merck), a fat containing iodine, was introduced in an emulsified form into the jugular vein of a dog. The quantities of iodine, up to about 2% of the weight of tissue, accumulated in the lung, were larger than was found in the liver or spleen. These results lend support to the view that the lung is active in the removal of fat from the blood-stream.  
W. O. K.

**Autolysis. X. The Autolysis of Muscle.** K. K. CHEN and H. C. BRADLEY (*J. Biol. Chem.*, 1924, **59**, 151—164).—The rate of autolysis of the muscles of warm-blooded animals, as measured by the production of amino-acids not precipitated by trichloroacetic acid, is at a maximum at  $p_H$  4.5—5.0. This agrees with the fact that *in vivo* atrophy of muscle-tissues follows conditions leading to an acidosis in the muscle-cells. In warm-blooded animals, there appears to be a relation between the activity and pigmentation of the muscle and the degree of autolysis, and similarly in the case of fish-muscle, the degree of autolysis appears to be determined by the activity of the muscles. In the molluscs examined, autolysis is slight and practically unaffected by reaction.  
W. O. K.

**Amino-acids in Nutrition. VI. Nature of the Supplementary Value of Protein-free Milk to the Total Proteins of the Milk. VII. Cause of Nutritive Inadequacy of the Proteins of the Georgia Velvet Bean (*Stilzlobium Deeringianum*).** B. SURE (*J. Metabolic Res.*, 1923, **3**, 373—382, 383—391).—VI. The effect is attributed to cystine or some other organic sulphur compound which may be transformed into cystine, and to traces of tyrosine in addition.

VII. The inadequacy is due to indigestibility and to deficiency of amino-acids, the latter being remedied by the addition to the diet of casein and cystine.  
CHEMICAL ABSTRACTS.

**Metabolism of Sulphur. VI. Oxidation of Cystine in the Animal Organism. II.** H. B. LEWIS, H. UPDEGRAFF, and D. A. MCGINTY (*J. Biol. Chem.*, 1924, **59**, 59—71).—The sulphur in dibenzoylcystine which has been subcutaneously injected into rabbits is not oxidised, but as in the case of phenyluraminocystine (Lewis and McGinty, *ibid.*, 1922, **50**, 303; **53**, 349) it is partly reduced to form the sulphydryl group before excretion in the urine. When dibenzoylcystine is administered orally, a part of the sulphur is oxidised, but this is probably because the compound is partly hydrolysed into benzoic acid and cystine in the alimentary canal.  
W. O. K.

**Substitution of Taurine for Cystine in the Diet of Mice.** M. L. MITCHELL (*Austral. J. Exp. Biol.*, 1924, 1, 5—9).—That taurine can replace cystine to a considerable extent is suggested by the fact that the addition of either to a cystine-deficient diet produces growth which does not take place otherwise, and ceases immediately the taurine or the cystine is removed. O. O.

**Metabolism of Benzoic Acid in the Human Organism.** J. NEUBERG (*Biochem. Z.*, 1924, 145, 249—273).—After the administration of 10 to 15 grams of sodium benzoate to human subjects with normal or impaired kidney functions, no free benzoic acid was found in the urine. The sodium benzoate appears in the urine, not only as hippuric acid (90%), but also as (possibly) benzoylglucuronic acid (10%). It is concluded that methods of determining hippuric acid based on the determination of the benzoic acid freed by hydrolysis give results which are too high. J. P.

**Nutrition and Growth on Diets Highly Deficient or Entirely Lacking in Preformed Carbohydrates.** T. B. OSBORNE and L. B. MENDEL [with H. C. CANNON] (*J. Biol. Chem.*, 1924, 59, 13—32).—Rats fed on a diet composed of protein, with varying proportions of fat, inorganic salts, and some source of vitamins, but containing no preformed carbohydrates, showed in many instances good growth, although, as a rule, the male rats did not attain weights greater than about 250 g. W. O. K.

**Vitamin Potency of Cod-liver Oil.** A. D. HOLMES (*J. Metabolic Res.*, 1923, 3, 393; cf. *ibid.*, 1922, 2, 113, 361).—The liver oil of emaciated cod caught in March has not so high a vitamin-A potency as that from well-nourished fish caught in later seasons. CHEMICAL ABSTRACTS.

**Experimental Rickets. XXIV. Effect of certain Extracts of Plant Tissues on Florid Rickets.** P. G. SHIPLEY, E. M. KINNEY, and E. V. McCOLLUM (*J. Biol. Chem.*, 1924, 59, 165—175).—Ether, alcohol, and water extract from lucerne leaves a substance which cures rickets in rats. Lucerne, extracted by ether, does not induce healing. Ether extracts an antirachitic vitamin from clover blossom, but, on the other hand, extracts of dry spinach, Brussels sprouts, cabbage, celery, tomato, and sweet potato were without antirachitic effect. W. O. K.

**Experimental Rickets. XXV. Antirachitic Effect of certain Oils.** P. G. SHIPLEY, E. M. KINNEY, and E. V. McCOLLUM (*J. Biol. Chem.*, 1924, 59, 177—182).—The following oils have no antirachitic effect: oil of sandalwood, oil of lemon, oil of orange-peel, oil of palm, fraction of butter fat insoluble in alcohol, Japan wax, oil of spice, oil of fennel seed, spermaceti, and sperm oil. Oil of cloves and the alcoholic extract of butter fat contain antirachitic vitamin. W. O. K.

**Value of Bezssonoff's Reaction for indicating the Presence of Vitamin-C in the Juice of Sauerkraut.** P. E. WEDGWOOD and F. L. FORD (*Bull. Soc. Chim. biol.*, 1924, 6, 217).—A sample

of the juice of sauerkraut which gave a blue coloration with Bezssonoff's reagent (*ibid.*, 1923, 4, 83) failed to protect guinea-pigs from scurvy. It is concluded that Bezssonoff's reagent is not an infallible indicator of vitamin-C. C. T. G.

**Additional Requirement for the Test with the Reagent for Vitamin-C.** N. BEZSSONOFF (*Bull. Soc. Chim. biol.*, 1924, 6, 220).—A reply to Wedgwood and Ford (see preceding abstract). A blue coloration indicates the presence of vitamin-C only if the colour is intensified on heating the liquid for a short time. If the colour is reduced or disappears on heating, vitamin-C is absent. The maximum dose used by Wedgwood and Ford in their experiments on guinea-pigs is considered to be too small to prove that vitamin-C is absent. C. T. G.

**Persistence of Vitamin-C in the Livers of Rats on a Scorbatic Ration.** S. LEPKOVSKY and M. T. NELSON (*J. Biol. Chem.*, 1924, 59, 91—96).—The livers of rats fed from soon after the time of weaning on a ration as far as possible free from vitamin-C contain marked quantities of this vitamin as shown by the effect on the growth of guinea-pigs fed on a diet free from vitamin-C. A second generation of rats also fed on a diet free from vitamin-C likewise showed no diminution of this vitamin in the liver.

W. O. K.

**Importance of Zinc on the Nutrition of Animals. Experiments on Mice.** BERTRAND and BENZON (*Bull. Soc. Chim. biol.*, 1924, 6, 203).—It was found impossible to remove all traces of zinc from natural food materials without also removing vitamin-B, with which the zinc appeared to be associated. A synthetic food, based on the composition of wheat, was therefore used. Mice receiving the synthetic food with the addition of an amount of zinc as sulphate equivalent to that present in a normal diet of wheat lived 25—50% longer than those receiving the synthetic food alone. In the absence of any supply of zinc in the food, the amount present at the beginning is retained throughout life, whilst, if zinc be given, the original amount present is about doubled.

C. T. G.

**Non-reciprocal Permeability. III. Non-reciprocal Permeability of Ions and of Colouring Matters.** E. WERTHEIMER (*Pflüger's Archiv*, 1923, 200, 354—365; from *Chem. Zentr.*, 1924, i, 346; cf. *Pflüger's Archiv*, 1923, 200, 82).—The non-reciprocal permeability shown by the cuticular membrane of frogs is confined to sodium ions. Other cations pass equally freely in both directions. Anions are without influence. Colouring matters behave differently according as they are acidic or basic, the former passing the membrane in an inward direction and the latter in an outward direction. Some acidic and basic colouring matters can pass in either direction. The phenomena are influenced by the reactions on the inner and outer side of the membrane. By making use of non-reciprocal permeability, mixtures of colouring matters may be separated.

G. W. R.

**Radioactivity of Living Cells.** A. NODON (*Compt. rend.*, 1924, **178**, 1101—1102).—The radioactivity of living cells has been demonstrated by photographic means. A sample of barium-radium sulphate, a living insect (*Pæcicoloris*), and a green leaf were confined separately in boxes so as to be able to affect a photographic plate, without coming into contact with the sensitive surface. After 20 hours' exposure, the radium salt gave a strong impression, the insect a more feeble impression, and the leaf a thin film. The activity indicated is of the same order as that indicated by electrometric measurements. [Cf. this vol., i, 347.]

A. B. H.

**Coagulation and Structure of the Egg.** J. AMAR (*Compt. rend.*, 1924, **178**, 803—805; cf. this vol., ii, 144).—Desiccation of birds' eggs over sulphuric acid showed that egg-white and egg-yolk contain 86% and 48% of water, respectively. Desiccation and re-hydration are completely reversible, unless structural changes (such as are caused by heating or by alcohol) intervene. The dried white contains spiraloid forms (insoluble albumin) in a homogeneous mass (soluble albumin). Sodium chloride does not cause the coagulation of the white or the yolk. The chlorides of potassium, magnesium, calcium, barium, and zinc effect coagulation to an increasing amount (in the order given). Sodium phosphate (present in the egg) hinders coagulation.

E. E. T.

**Sugar in the Cerebrospinal Fluid.** G. H. MOATES and J. J. KEEGAN (*J. Lab. Clin. Med.*, 1923, **8**, 825—828).—The normal range of cerebrospinal fluid sugar is 0.040—0.068%. The concentration is increased in most cases of epidemic encephalitis but decreased in infectious meningitis. There is no apparent relation between the sugar content of the cerebrospinal fluid and the Wassermann reaction, colloidal gold curve, cell count, globulin, or total protein.

CHEMICAL ABSTRACTS.

**Bile Secretions. IV. Colorimetric Determination of Bile Acids in Human Body Fluids.** F. ROSENTHAL and F. LAUTERBACH.—(See ii, 431.)

**Mechanism of Muscular Action.** O. W. TIEGS (*Austral. J. Exp. Biol.*, 1924, **1**, 11—29).—It is considered that lactic acid is liberated from only one of the excitable membranes, and at the same time the other membrane must liberate a basic substance, hitherto unrecognised. When this happens, the processes constituting a muscle twitch must occur and their nature can be explained on a physico-chemical basis.

O. O.

**Alteration of the Constituents of Preserved Flesh.** I. A. SMORODINZEV and A. N. ADOWA (*Z. physiol. Chem.*, 1924, **135**, 41—48).—Large quantities of salt solution were pumped into the aorta shortly after killing, and the extractive substances in the muscle-tissues examined after storage for 15 months. The creatinine content was the same as that of fresh flesh, whilst the creatine was

reduced to one-fifth or one-tenth. The fact that there was no increase in the amount of methylguanidine suggests that this compound does exist in the tissues and is not necessarily the product of an oxidation occurring during the extraction of creatinine (cf. Ewins, A., 1916, i, 528).  
E. M. C.

**Oxidising Power of the Nuclei of the Epithelium of the Renal Canaliculi of *Perca fluviatilis*.** M. MANQUAT (*Compt. rend.*, 1924, 178, 972—974).—The nuclei of the epithelial cells of the renal canaliculi of the perch appear to possess oxidising properties, since they become blue when indigo-carmin is injected into the alimentary canal, whereas the cytoplasm remains colourless. This phenomenon was not observed with any of the other species of fresh-water fish examined.  
T. H. P.

**Venom of *Lachesis ammodytoides*.** B. A. HOUSSAY and J. NEGRETE (*Compt. rend. Soc. Biol.*, 1923, 89, 751—753; from *Chem. Zentr.*, 1924, i, 491).—The venom of this Argentine snake is golden-yellow and contains 34—40% of water. It precipitates the anti-serum for *Lachesis alternatus*, but only slightly that for *Crotalus terrificus*. It has no amylolytic effect and does not attack neutral fats. A description of its physiological effects is given.  
G. W. R.

**Excretion of Creatinine by the Kidneys.** V. CANTINIEAUX (*Compt. rend. Soc. Biol.*, 1923, 89, 848—851; from *Chem. Zentr.*, 1924, i, 358).—The amount of creatinine eliminated in the urine of healthy men is a function of the total creatinine (preformed creatinine + creatine) in the blood. The relationship is expressed according to Ambard's formula by the constant 0.07 for normal individuals. In cases of depressed renal activity there is a parallelism with the constant for urea. The formulæ of Austin, of Stillman, and of Van Slyke give similar results. No constant results are given when the amount of preformed creatinine in the blood alone is used in the above formulæ.  
G. W. R.

**Electropy. VII. Excretion of Electropic Dyestuffs and Carbinols.** L. KARCZAG and L. PAUNZ (*Biochem. Z.*, 1924, 145, 345—350).—Electropic dyestuffs of the triphenylmethane group administered subcutaneously or intravenously to rabbits or guinea-pigs were found in the urine, bile, cerebrospinal fluid, aqueous humour of the eye, peritoneal exudate, and amniotic fluid as colourless carbinols. The less the dispersion of the dyestuff the more slowly is it excreted; the most highly dispersed dyestuffs are excreted by the kidney whilst less highly dispersed dyes are found in the bile. The electrostatic charge on the particles of the dyestuffs is of importance in their conversion and excretion.  
J. P.

**Porphyrin Formation. I.** O. SCHUMM (*Z. physiol. Chem.*, 1924, 133, 303—320).—The increase in the porphyrin content of the faeces, associated with diet (A., 1923, i, 732), is considered as originating from a constituent of the flesh. The porphyrin prepared from rotting flesh has been examined spectroscopically; it

differs from coproporphyrin, but appears to resemble closely the porphyrin prepared from blood by the author, and also that described by Kämmerer and Fischer (cf. Fischer and Schneller, A., 1923, i, 1244). Coproporphyrin could not be found in fresh beef or in frozen meat. O. O.

**Correction of "Natural Porphyrins." III.** O. SCHUMM (*Z. physiol. Chem.*, 1924, 133, 298—307; cf. Fischer and Schneller, A., 1923, i, 1244).—Mainly polemical. The author claims priority in this work, and sees no reason to change the views put forward in his previous paper (A., 1923, i, 631). O. O.

**Menstruation and the Choline Balance.** E. SIEBURG and W. PATZSCHKE (*Z. ges. exp. Med.*, 1923, 36, 324—343; from *Chem. Zentr.*, 1924, i, 572).—The choline content of the sweat was found to be 80—100 times normal and of the serum 2—15 times normal during menstruation. Intravenous injection of 0.5 g. of choline chloride in women resulted, in half the cases investigated, in a diminished rate of coagulation of the blood. G. W. R.

**Relation of the Chemical Constitution of certain Organic Arsenical Compounds to their Action on the Optic Tract.** A. G. YOUNG and A. S. LOEVENHART (*J. Pharm. Expt. Ther.*, 1924, 23, 107—126).—Arsenical drugs with quinquevalent arsenic, such as atoxyl, arsacetin, and tryparsamide, frequently affect the optic tract and may produce blindness, whilst certain trivalent arsenic compounds, such as arsphenamine, do not have this effect. Sixteen arsenical compounds of similar constitution were tested by intravenous administration to rabbits, and it was found that the valency of the arsenic was not the most important factor. Optic lesions were produced by compounds containing an amino group or a substituted amino group in the para-position to the arsenic, but were not produced when the amino group was in the ortho- or meta-position. E. M. C.

**Effect of Compounds Related to Hydrazine in Producing Anhydræmia and Experimental Anæmia.** M. BODANSKY (*J. Pharm. Expt. Ther.*, 1924, 23, 127—132).—The destruction of red corpuscles by subcutaneous injection into dogs of certain hydrazine derivatives has been studied with a view to the experimental production of anæmia. Hydrazine gave a temporary increase in blood concentration (anhydræmia) followed by a slight anæmia. Phenylhydrazine, acetylphenylhydrazine, and *p*-bromophenylhydrazine produce rapid destruction of red corpuscles; methylphenylhydrazine and diphenylhydrazine have similar although less marked effects, whilst *s*-diisopropylhydrazine, hydrazobenzene, and 2:2'-azobispropane cause a moderate amount of destruction. Mild anæmias were produced in rabbits by azobenzene, azoxybenzene, diazobenzene, and aminoazobenzene; diphenylcarbazine and *p*-hydrazinobenzoic acid have no effect on the blood. Compounds which are especially destructive of liver-tissue were found most effective in producing anhydræmia. E. M. C.



**Chemotherapeutic Experiments with Chaulmoogra and Allied Preparations.** O. SCHÖBL (*Philippine J. Sci.*, 1923, **23**, 533—542).—Chaulmoogra oil and its derivatives exert, *in vitro*, a pronounced growth-inhibiting action on *Bacillus tuberculosis*. This inhibition is specific and is noticeable at dilutions of the oil at which no inhibition of non-acid-fast bacilli can be discerned. Oils obtained from plants related to *Taraktogenos Kurzii* have a property similar to that of chaulmoogra oil with regard to *B. tuberculosis*. *Hydnocarpus Wightiana*, *H. alcala*, *H. subfalcata*, and *H. venenata*, all containing the optically active acids, show antiseptic power *in vitro*, decreasing in the order mentioned. Oil derived from *Gynocardia odorata*, a plant closely related to *T. Kurzii*, was inactive towards *B. tuberculosis*; it lacks the optically active fatty acids. The growth-inhibiting power of the sodium salts of chaulmoogra oil acids appears to vary, the soap made from the total fatty acids inhibiting the growth of *B. tuberculosis* to a higher degree than does that made from a fraction of the acids. A sodium salt prepared from the isolated hydnocarpic acid approaches closely in strength the soap from the total fatty acids, whilst the sodium salt of chaulmoogric acid is much weaker in its action. H. C. R.

**Chemotherapeutic Experiments with Chaulmoogra and Allied Preparations. II. Comparison of the Antiseptic Power of Chaulmoogra Oil with that of other Vegetable and Animal Oils.** O. SCHÖBL (*Philippine J. Sci.*, 1924, **24**, 23—27).—A series of 42 different oils, including vegetable oils, essential oils, and animal oils, was examined according to the technique previously described for their inhibitory effect on the growth of *Bacillus tuberculosis*, *Vibrio cholera*, and *Staphylococcus* in glycerol meat infusion agar culture. Certain vegetable oils other than those containing optically active fatty acids inhibited the growth of acid-fast bacteria *in vitro*. None of the vegetable oils proper that were investigated inhibited the growth of acid-fast bacteria at such a high dilution as do the chaulmoogra and *Hydnocarpus* oils, which contain optically active fatty acids. Certain essential oils and oils containing volatile constituents, such as cinnamon oil, show a very high selective inhibitory action on acid-fast bacteria. H. C. R.

**Toxins. I. Ricin.** P. KARRER, A. P. SMIRNOFF, H. EHRENSPERGER, J. VAN SLOOTEN, and M. KELLER (*Z. physiol. Chem.*, 1924, **135**, 129—166).—The purified products obtained by the fractionation of ricin, tested by intravenous injection into rabbits, showed an extraordinary constancy of toxicity, the lethal dose being 0.005 to 0.003 mg. per kg. live weight. Ricin is not adsorbed by kaolin; basic aluminium sulphate adsorbs the toxic constituents, whilst aluminium hydroxide adsorbs the less toxic constituents. Fractional precipitation with salts of heavy metals affects ricin preparations adversely. The destruction by trypsin of ricin, as measured by the toxicity of the digestion mixture and of the undigested residue at different stages, ran parallel to the protein hydrolysis, so that the toxic action of ricin appears to be a function

of the protein. It has not been possible to concentrate the toxic principle beyond a certain point, and yet such preparations are not single substances, since less toxic materials may be removed by adsorption and different preparations give different equivalents on titration in alcohol. A complete analysis by the Fischer and Dakin methods has been made of the amino-acids after hydrolysis of the protein. The original must be consulted for details.

E. M. C.

**Comparison of the Activities of Antiseptics on Bacteria and on Leucocytes.** A. FLEMING (*Proc. Roy. Soc.*, 1924, **B**, 96, 171—180).—Leucocytes have a rapid lethal action on bacteria, distinct from their phagocytic action. There is, for all common antiseptics, with the possible exception of flavine, a range of concentrations (below that at which bacteria are killed) within which the bactericidal power of leucocytes is destroyed ("antibactericidal zone"). Thus the presence in blood of an antiseptic in a concentration within this zone, so far from preventing the growth of bacteria, may actually favour it.

W. O. K.

**Mechanism of the Action of Bismuth Derivatives in Trypanosomiasis and Spirillosis.** C. LEVADITI and S. NICOLAU (*Ann. Inst. Pasteur*, 1924, **38**, 179—239).—A detailed account of work already published in brief (*Compt. rend.*, 1923, **176**, 1189).

W. O. K.

**Degradation of Starch by Animal Amylases.** O. HOLMBERGH (*Ark. Kemi, Min., Geol.*, 1923, **8**, No. 33, 1—5).—The author has investigated the action on 2% starch solution of glycerol extracts of dry, powdered liver, prepared by treating the minced liver with ether and acetone. As these preparations contain maltase as well as amylase, parallel experiments were made in all cases with substrates containing only maltose. The velocity of the amylolytic reaction is diminished to the extent of about 32 (75)% by the presence of 0.4 (3)% of maltose. Liver-amylase is far more sensitive to the influence of maltase than is malt-amylase. When the maltose formed is removed by either dialysis or fermentation, the hydrolysis of the starch is quantitative. In all the experiments the reaction of the medium was adjusted to  $p_H$  6.9, which is the optimum acidity for amylolytic changes.

Dialysis of 1% starch solution proceeds far more rapidly when the starch is prepared by Zulkowski's method (A., 1880, 865) than when Lintner's soluble starch is used.

T. H. P.

**Action of Potassium Iodide on the Saccharification of Starch by Various Amylases.** O. HOLMBERGH (*Biochem. Z.*, 1924, **145**, 244—248).—Potassium iodide inhibits the formation of maltose from starch by the action of malt-amylase, the action in this respect resembling that on liver-amylase (cf. Holmbergh, *Z. physiol. Chem.*, 1924, **134**, 68). It increases the similar actions of salivary and pancreatic amylases. The two latter amylases therefore differ from liver-amylase. The varying extents to which dextrins and maltose are formed by the action of liver-amylase on

starch have been investigated in concentrations of potassium iodide varying from 0.1*N* to 2.0*N*. The amount of maltose formed when the achromic point is reached diminishes with increasing concentrations of the iodide, but the rate of formation of the dextrins themselves is increased. J. P.

**Hydrolysis of Starch by Emulsin.** R. KUHN (*Z. physiol. Chem.*, 1924, **135**, 12—15).—Preparations of emulsin from both bitter and sweet almonds brought about a considerable hydrolysis of soluble potato starch, at an optimum acidity of  $p_H$  5.5. A specially purified sample of the enzyme converted the amylase of the starch grains quantitatively into maltose. E. M. C.

**Digestion of Gums by Organisms and Enzymes. Digestion of Cherry Tree Gum *in vitro*.** A. VOSKRESSENSKY (*Bull. Soc. Chim. biol.*, 1924, **6**, 226).—Experiments are recorded on the breaking down of cherry tree gum, as indicated by the production of reducing sugars, by the enzymes of various plants, micro-fungi, yeasts, and bacteria, and by enzymes contained in various animal organs. Several enzymes, of which some occur in the digestive tract of animals, can decompose the gum to some extent, but the amount of hydrolysis is much less than can be obtained with mineral acids.

Rats can live on a ration consisting largely of cherry tree gum but not on the gum alone. Various insects and molluscs refused to eat gum. C. T. G.

**Invertase.** V. R. WILLSTÄTTER and K. SCHNEIDER (*Z. physiol. Chem.*, 1924, **133**, 193—228).—In continuation of previous work (A., 1923, i, 69), it has been found that direct adsorption of invertase from yeast autolysates by kaolin can be brought about without preliminary adsorption by alumina, and without the considerable dilution formerly used, if the acidity of the solution is increased to the maximum limit (*e.g.* 10% acetic acid) consistent with the non-destruction of the enzyme.

Using the above improved method, several invertase preparations have been separated into easily and difficultly adsorbed fractions, and the former have been further subdivided by fractional elution. An examination of the various fractions so obtained, furnished evidence that the nitrogen content and the activity of the enzyme preparations were not proportional. Indeed, in certain cases active preparations which failed to give any protein reactions were obtained. Since in earlier work other preparations have been obtained which were free from carbohydrates, it is proved that invertase belongs neither to the proteins nor to the carbohydrates.

After a single adsorption by this method, a preparation of high activity was obtained. When the kaolin treatment was followed by adsorption by alumina, the activity was still further increased. The stability of the enzyme during adsorption varies considerably with the acidity.

The age of the autolysate and its previous purification both have a profound effect on the adsorptive value of kaolin. Whereas

with fresh autolysates preliminary precipitation with alcohol is essential for successful adsorption, this is not the case for old autolysates. O. O.

**Invertase as an Amphoteric Electrolyte and as a Colloid.** H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **133**, 279—297).—Using an invertase preparation of high purity ( $I_f = 240$ —242) the authors have obtained, by electrometric determination, values of  $4.3 \times 10^{-11}$  and  $5.5 \times 10^{-11}$  for  $K_b$ , and values of  $0.9 \times 10^{-11}$ ,  $0.32 \times 10^{-7}$ , and  $0.62 \times 10^{-8}$  for  $K_a$ . From the values for  $K_b$  it is calculated that the molecular weight of invertase cannot exceed 3900. Viscosity measurements showed the isoelectric point to lie between  $p_H = 4.5$  and 5; this is also the  $p_H$  for maximum adsorption of the enzyme by aluminium hydroxide. The results are discussed in the light of L. Michaelis' theory concerning enzyme action, and the conclusion is drawn that the theory is inadequate. O. O.

**Invertase.** E. CANALS (*Bull. Soc. chim.*, 1924, [iv], **35**, 213—217).—Hydrochloric and phosphoric acids increase the hydrolysing power of dialysed yeast invertase preparations to a slightly greater extent than when undialysed preparations are used, but with sulphuric acid the reverse is the case. E. E. T.

**Influence of Stereoisomeric Sugars, Non-hydrolysable Carbohydrates, and Glucosides on the Efficiency of Yeast Invertase. Specificity of Enzymes. VI.** R. KUHN (*Z. physiol. Chem.*, 1924, **135**, 1—11).—The  $\alpha$ - and  $\beta$ -forms of *d*-mannose and *l*-arabinose resemble those of *d*-fructose in slowing down the action of invertase on sucrose to the same extent.  $\beta$ -*d*-Galactose resembles  $\beta$ -*d*-glucose in being more active than the  $\alpha$ -form, although both forms of *d*-galactose are much more active than the other hexoses studied. The stereoisomeric forms of lactose, maltose, cellobiose, melibiose, gentiobiose, and trehalose are without perceptible effect. The inactivity of inulin suggests that there is no combination of inulin with the invertase. Salicin, helicin, and  $\beta$ -methylglucoside reduce the rate of inversion, but amygdalin is without effect. The  $\alpha$ -methylglucoside is many times as active as  $\beta$ -methylglucoside. These results are in agreement with the view that the activity of invertase is determined by its power of combination. E. M. C.

**Fermentation Co-enzyme (Co-zymase) of Yeast. II.** H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **133**, 260—278).—Using small quantities of material, fermentation has been followed in the presence of co-zymase with the following results: the fall in the rate of fermentation can be overcome by the addition of fructose diphosphate; an extract of germinating malt has no influence on the rate; glycerol has no effect, whilst toluene and alcohol exert a retardation; *l*ævulose and dextrose are identical in their action. Zymophosphate causes fermentation to start immediately, and it is suggested that yeast always contains sufficient of this substance to initiate the fermentation. In addition

to blood, milk at  $p_H$  5 increases the activity of the co-enzyme. The co-enzyme present in muscle is probably identical with that present in yeast, but it does not appear to bear any relation to the anti-neuritic or growth-promoting vitamins. O. O.

**Latent Fermenting Powers of Bacteria. I—III.** E. C. GREY (*Proc. Roy. Soc.*, 1924, **B**, **96**, 156—170).—The general course of the decomposition occurring during fermentation by *Bacillus coli* in the presence of formates is the same whether the substrate is dextrose or glycerol. In each case, about 25% and 40% of the substrate is converted into carbon dioxide and acetic acid, respectively, but the remaining 35% is mainly lactic acid when dextrose is used, and mainly ethyl alcohol when glycerol is used. In presence of formates, glycol and malonic acid are fermented by *B. coli* with the production of acetic and lactic acids, whilst citric, malic, and tartaric acids yield carbon dioxide, acetic acid, and succinic acid. The yield of succinic acid from dextrose is decreased by the presence of formates, and this is apparently due to the ability of the bacteria to ferment succinic acid under these conditions. On the basis of these and earlier results, the author outlines a simple theory of fermentation, for details of which the original must be consulted. W. O. K.

**Enzymic Transformation of Aldehydes. I. Acceleration of the Cannizzaro Reaction by Yeast.** K. JOSEPHSON and H. VON EULER (*Z. physiol. Chem.*, 1924, **135**, 49—60).—The authors emphasise the importance of acidity in controlling the yields of the different products of fermentation. Acetaldehyde is stable in solutions more acid than  $p_H$  8.5. In the presence of living yeast, removal of acetaldehyde occurs even in solutions as acid as  $p_H$  3—4. The reaction velocity is difficult to measure owing to the changes produced by the acetic acid formed, but in the early stages the acetaldehyde decomposition is only slightly less at  $p_H$  4 than at  $p_H$  7. A slight removal of acetaldehyde is caused by boiled yeast suspensions and is probably due to a combination with the proteins of the yeast. *iso*Valeraldehyde gives similar results to acetaldehyde, although the reaction is considerably slower. E. M. C.

**Metabolism of Pyruvic Acid in Bacteria.** E. AUBEL (*Bull. Soc. Chim. biol.*, 1924, **6**, 288).—A continuation of work previously published (Cambier and Aubel, *Compt. rend.*, 1922, **175**, 71). Sodium pyruvate serves as a source of carbon for bacteria. It gives rise in cultures to carbon dioxide, hydrogen, methane, lactic, glycollic, acetic, and formic acids. The energy relationships of the reactions taking place in the formation of these substances from pyruvic acid are discussed.

Working with a bacterium isolated from the Paris water supply, it was found that considerable quantities of dextrose were converted into pyruvic acid, which was then utilised; later, lactic acid made its appearance, but whether this was formed from pyruvic acid or was the product of a separate fermentation of dextrose is uncertain. C. T. G.

**Mechanism of the Production of  $\beta$ -Hydroxybutyric Acid by Biochemical Means.** LEMOIGNE (*Compt. rend.*, 1924, **178**, 1093—1095).—Continuing previous work (A., 1923, i, 881; this vol., i, 353), the author finds that a new insoluble, crystallisable product may be obtained from macerations of bacteria of the *Bacillus subtilis* group, by means of boiling alcohol. The structure of the pure substance, m. p. 118—119°, has not been determined, but alkaline hydrolysis gave 1 mol. of  $\alpha$ -crotonic acid, m. p. 72°, and 2 mols. of  $\beta$ -hydroxybutyric acid. The proportion of the two acids was calculated from the observed optical rotation of the alkaline mixture.

A. B. H.

**Yeast. V. Is Bios a Single Substance?** E. J. FULMER and V. E. NELSON (*Proc. Iowa Acad. Sci.*, 1922, **29**, 371; cf. A., 1921, i, 386; *J. Biol. Chem.*, 1922, **51**, 77).—Combination of the absolute alcohol extracts of lucerne with the water extract of the residue produced greater yeast growth than either extract alone. Bios is composed of at least two yeast-growth promoting materials.

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**Multiple Nature of Bios.** E. J. FULMER, W. W. DUECKER, and V. E. NELSON (*J. Amer. Chem. Soc.*, 1924, **46**, 723—726).—An aqueous extract of lucerne was fractionally precipitated with alcohol and the four resulting fractions were tested for "bios" in a medium containing ammonium chloride, dipotassium phosphate, calcium chloride and carbonate, and sucrose, which was inoculated with yeast. The results obtained showed that bios contains at least two different growth stimulants.

C. J. S.

**Pancreatic Enzymes. VI. Effect of Lipase on Different Substrates.** R. WILLSTÄTTER and F. MEMMEN (*Z. physiol. Chem.*, 1924, **133**, 229—246).—The hydrolysis of methyl butyrate by lipase is accelerated by calcium oleate, but much more so by a mixture of albumin, sodium oleate, and calcium chloride at  $p_H$  8.9. The addition of a large amount of glycerol (33%) still further accelerates the hydrolysis. Both the rate and degree of hydrolysis are directly proportional to the amount of the enzyme present.

In the hydrolysis of triacetin by lipase, the enzyme is activated by salts of bile acids and oleic acid. As in the case of tributyrin (A., 1923, ii, 704), the increase in hydrolysis due to calcium oleate is not further emphasised by the addition of albumin. In the course of the hydrolysis, the effect due to the enzyme diminishes, and this change is due to deterioration of the enzyme.

From a study of the rate of hydrolysis of various esters by various lipase preparations it is concluded that pancreatic lipase is not a mixture of enzymes, but one single enzyme which, however, shows a quantitative specificity as regards its rate of action on different substrates.

O. O.

**Pancreatic Enzymes. VII. Comparison of Gastric Lipase with Pancreatic Lipase.** R. WILLSTÄTTER and F. MEMMEN (*Z. physiol. Chem.*, 1924, **133**, 247—259).—Gastric lipase and pancreatic lipase, from the pig, differ in their behaviour towards

activators such as sodium oleate and bile salts, and towards the hydrogen-ion concentration. Further, different preparations of the one enzyme from the same source show inconsistent behaviour. These divergences can, however, be traced to contamination. When gastric lipase is purified by adsorption with kaolin and elution with ammoniacal phosphate solution containing glycerol, these differences disappear, and it is concluded that there is no difference between gastric lipase and pancreatic lipase. Lipase is not present in the organs as a zymogen. O. O.

**Enzyme Action. XXV. Comparative Lipase and Protease Actions of the Flexner-Jobling Rat Carcinoma and of different Rat Tissues. XXVI. Comparative Lipase and Protease Actions of different Beef Tissues. XXVII. Comparative Enzyme Actions of Tissue Mixtures and of Tumour-tissue Mixtures in Relation to the Comparative Enzyme Actions of Tumour Extracts Alone.** K. G. FALK, H. M. NOYES, and K. SUGIURA (*J. Biol. Chem.*, 1924, **59**, 183—212, 213—223, 225—235).—The activities of extracts of various tissues in hydrolysing phenyl acetate, glyceryl acetate, methyl butyrate, benzyl acetate, ethyl acetate, ethyl butyrate, methyl benzoate, ethyl benzoate, isobutyl acetate, and protein, were measured. By expressing the results graphically, characteristic differences between the action of the extracts from different tissues are brought out. For details, the original must be consulted. W. O. K.

**Protein Studies. III. Decomposition of Silk Fibroin by Fermentation.** F. WESSELY (*Z. physiol. Chem.*, 1924, **135**, 117—121).—Silk fibroin was dispersed by dissolving it rapidly in cold concentrated hydrochloric acid and neutralising with sodium hydroxide, with rapid cooling. The resulting solution was stable if it contained less than 1.5% of fibroin, but was flocculated by shaking or stirring. The fibroin could be reprecipitated quantitatively by alcohol and ether. On digestion with trypsin, about one-quarter of the fibroin separated as a jelly in 24 hours; the remaining liquid gave no precipitate with 50% alcohol, and contained little nitrogen as amino-acids or as compounds not precipitated by phosphotungstic acid. Similar evidence of decomposition by pepsin was obtained. E. M. C.

**Can Copper Salts Act Simultaneously as Oxydases and Peroxydases?** R. DUBOIS (*Compt. rend. Soc. Biol.*, 1923, **89**, 10—11; from *Chem. Zentr.*, 1924, i, 458).—Fehling's solution can act on luciferin, producing luminescence in the same manner as luciferase. The observations of Valdiguié (*Compt. rend. Soc. Biol.*, 1923, **88**, 1091) are confirmed. G. W. R.

**Effect on Phenols and their Derivatives of Oxydases of Melanotic Tumours in Chorioidea.** J. MAWAS (*Compt. rend. Soc. Biol.*, 1923, **88**, 263—265, 332—333; from *Chem. Zentr.*, 1924, i, 354).—The peroxydase from melanotic tumours in chorioidea has no effect on phenol, thymol, phloroglucinol, and naphthol.

With pyrocatechol a colour change with the formation of a precipitate is observed. Pyrogallol and hydroxyquinol are oxidised. A direct relationship appears to exist between the constitution of organic compounds and their ability to be oxidised by enzymes. For example, phenols are only attacked when the hydroxy groups are in the ortho position. The formation of a black pigment is not attributed to a tyrosinase or to the oxidation of tyrosine by a peroxydase.

G. W. R.

**Action of Laccase. Influence of Concentration of Guaiacol and Pressure of Oxygen.** P. FLEURY (*Compt. rend.*, 1924, 178, 1027—1030).—For concentrations of guaiacol below a certain value, the reaction velocity of laccase was proportional to the concentration of guaiacol, but at concentrations above that value it tended to become constant. Diminution of laccase concentration displaced this zone of inflection in the direction of lower guaiacol concentration. Variation of the oxygen content of the air current affected the reaction velocity only when it was decreased; a similar zone of inflection was observed, which was displaced in the direction of low oxygen concentration as the amount of laccase present decreased. The rate of diffusion of the oxygen into the solution also conditioned the activity of the laccase.

H. J. E.

**Liver Catalase.** S. HENNICH (S. HENNICHS (*Biochem. Z.*, 1924, 145, 286—305).—Denoting the “activity” of the catalase present by: (reaction constant)  $\div$  (dried residue in 1000 c.c. of the reaction mixture), it is shown that liver catalase preparations may be obtained with an “activity” of 532 by adsorption with kaolin and elution with a phosphate mixture of  $p_H$  7.6, by which means a quantitative recovery of the enzyme is achieved. Aluminium hydroxide is also used as an adsorbent ( $p_H$  5—7) and the elution carried out at  $p_H$  8. Two such treatments gave a preparation with an “activity” of 521. Previous preparations of liver and blood catalase by Madinaveitia (*Diss.*, Zurich, 1912) had “activities” of 66.8 and 34.9 respectively, and it is concluded that a considerable advance has been made in purifying the enzyme. The affinity constant of the system catalase—substrate is given as  $K_M$  22. The thermostability of catalase varies with the concentration, dilute solutions being much less stable at 60° than more concentrated solutions.

J. P.

**Relations between the Physico-chemical State and the Functioning of Protoplasm. Photosynthesis and Respiration.** C. FROMAGEOT (*Bull. Soc. Chim. biol.*, 1924, 6, 169—180).—Pieces of the alga *Ulva lactuca* kept in sea-water containing varying amounts of glycerol showed an output of oxygen which diminished as the concentration of glycerol was increased, and ceased when the latter reached 15%. This effect was reversible when the alga was removed from the glycerol solution provided its concentration had not exceeded 10%. The alga kept in the dark under the same conditions showed an increased absorption of oxygen up to glycerol



concentrations of 5%, above which the respiration diminished but did not cease even in concentrations of 40%. Saline solutions of the composition of sea-water and of the same  $p_H$ , but with varying concentrations, affected the photosynthetic activity markedly, the latter being at an optimum when the osmotic pressure of the solution was that of sea-water. A similar effect on respiration was not observed, but in very concentrated sea-water it was slightly diminished. It is concluded that physico-chemical alterations of the protoplasm do not affect photosynthesis and respiration in the same way, and that the former process is much more susceptible to such disturbances than is the latter. J. P.

**Feeding of Plants with Aldehydes. IV.** T. SABALITSCHKA. **Behaviour and Detection of Formaldehyde in Plants and Plant Substances.** T. SABALITSCHKA and H. RIESENBERG (*Biochem. Z.*, 1924, **145**, 373—378).—Fresh leaves of cress plants grown in an atmosphere containing formaldehyde (cf. this vol., i, 475) contained less than 0.5 mg. of formaldehyde per gram, whilst the same amount of leaves after drying contained 0.2 mg., and after extraction with water and alcohol 0.1 mg. The dry residue obtained from the aqueous extract of the leaves contained no formaldehyde. Formaldehyde added to fresh rhubarb or cress leaves made into a pulp with water was fixed wholly or in part. Its presence in fresh cress leaves or in the aqueous distillate from an extract of the leaves could not be demonstrated. J. P.

**Water Cultures containing Benzoic Acid. Assimilation of Benzoic Acid by Culture Plants.** T. BOKORNY (*Biochem. Z.*, 1924, **145**, 306—308).—Barley seedlings grown in a medium containing benzoic acid (0.016%) appeared to absorb the latter and to give increased growth. The presence of the acid in the plants could not be demonstrated, and it is concluded that it is assimilated and serves as a source of carbon. J. P.

**Nitrogenous Substances in Ripening Rye Ears.** A. KIESEL (*Z. physiol. Chem.*, 1924, **135**, 61—83).—The total nitrogen content of whole rye ears increased as ripening proceeded; the increase was chiefly in the protein nitrogen, with slight increases in the base and peptone nitrogen and in the amide nitrogen. The ammonia nitrogen remained constant, whilst the amino-acid nitrogen showed a pronounced minimum in one case. Asparagine was absent in each stage. The purine bases decreased markedly as the ripening proceeded. Xanthine, guanine, adenine, and hypoxanthine were separated from one sample. Histidine could be detected only in traces. Arginine was absent, but the arginine fraction contained guanidine, a base, probably agmatine, and an unidentified base. The lysine fraction from the above sample gave tetramethylenediamine, choline, aspartic acid, and phenylalanine. None of these was identified from the second fraction and only choline from the third. This is the first definite record of the isolation of aspartic acid from plants; the possibilities of its being derived from protein hydrolysis are discussed. E. M. C.

**Colloidal Properties of Winter Wheat Plants in Relation to Frost Resistance.** R. NEWTON (*J. Agric. Sci.*, 1924, **14**, 178—191).—The hardness of wheat plants was found to be related to the imbibition pressure of the leaves in the winter-hardened condition, but not in unhardened leaves. The quantity of hydrophilic colloids contained in the press juice of hardened leaves was directly proportional to hardness. A. G. P.

**Photoperiodism in Relation to Hydrogen-ion Concentration of the Cell Sap and the Carbohydrate Content of the Plant.** W. W. GARNER, C. W. BACON, and H. A. ALLARD (*J. Agric. Res.*, 1924, **27**, 119—156).—The variations which occur in the habit of plants exposed to different day lengths (*ibid.*, 1920, **18**, 553) extend to the acidity of the sap, the carbohydrate content, and the water content of the tissues. Short day plants exposed to long day illumination show a progressive increase in acidity, particularly at the growing point, until the upper parts are more acid than the lower parts. Exposure to short day illumination results in a transitory period of decreased acidity followed by a moderate increase which persists until flowering is initiated. In this case, the acidity in the upper parts is not as high as that found in the lower parts of the plant. The low acidity of the embryonic flower-bud increases to a maximum in the unfolded blossom, in contrast to the developing seed in which there is a decrease in acidity during active growth. Long day plants exposed to short day periods show a low level of acidity, which increases when the day length is increased. *Helianthus annuus*, which is intermediate between the long day and the short day groups, shows changes in acidity which may be typical of either group. Transfer of *Cosmos* plants from a long to a short day caused a marked increase in reducing sugar in the upper portion of the stem within 48 hours of the transfer. After 2 days the increased sugar was present as polysaccharide, but 12 days later, after the flower-buds appeared, the sugar was present as monosaccharide. At the same time, a considerable increase in the water content of the tissues had occurred. O. O.

**Changes in Hydrogen-ion Concentration Produced by Growing Seedlings in Acid Solutions.** J. DAVIDSON and E. T. WHERRY (*J. Agric. Res.*, 1924, **27**, 207—217).—Wheat seedlings, after growing for several days in tap-water or dilute nutrient solutions, were transferred to dilute solutions of nitric, phosphoric, sulphuric, or hydrochloric acid, and the changes in  $p_H$  values observed. The greatest reduction in acidity was with nitric acid for young seedlings and with phosphoric acid for older seedlings. The importance of these acids in plant nutrition suggests that the initial changes of reaction in culture media are due to absorption rather than to neutralisation of the acids by root excreta. The reduction of acidity was less for seedlings grown in nutrient solutions lacking the corresponding anion, owing, apparently, to functional disturbances. Large reductions of acidity in solutions of organic acids were ascribed to the action of micro-organisms. E. M. C.

**Insecticides. I. Isolation and Constitution of the Active Constituent of Dalmatian Insect Powder.** H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 177—201).—The insect powder obtained from the flowers of *Chrysanthemum cinerariifolium* Bocc., was investigated by Fujitani (A., 1909, ii, 825), who obtained from it a highly insecticidal, viscous oil which he termed pyrethrone. By alkaline hydrolysis of this he obtained an alcohol, pyrethrol, and an acid, both of which were inactive. Fujitani's viscous oil is found to contain about 50% of inactive substances, from which the pyrethrol is derived. There are two active constituents present in the oil, termed *pyrethrine I* and *II*, esters of a ketonic alcohol, *pyrethrolone*, combined with *chrysanthemumcarboxylic acid* and *chrysanthemumdicarboxylic acid*, respectively. The crude oil, the yield of which is 0.5% of the weight of the powder, forms a crystalline mixed semicarbazone, from which the *semicarbazone* of pyrethrine I can be obtained almost pure, m. p. 122—123°. By hydrolysis of the mixed semicarbazones, with methyl-alcoholic sodium hydroxide, the *semicarbazone* of pyrethrolone is obtained, m. p. 200° (decomp.), and by acid hydrolysis of this, the alcohol itself, *pyrethrolone*, a colourless, optically active liquid, b. p. 110—112°/0.1 mm. The acid of pyrethrine I, *chrysanthemumcarboxylic acid*, is an optically active liquid, b. p. 135°/12 mm., and that of pyrethrine II, *chrysanthemumdicarboxylic acid*, is a more viscous, optically active liquid, b. p. 120°/0.1 mm. Neither the alcohol nor the acids have insecticidal properties. The insect powder contains the two active substances, I and II, in the proportions of about 2 : 3; the former is the more active, killing moths at a dilution of 1 in 10,000 in 10 to 20 minutes, whilst the latter takes twice as long (cf. this vol., i, 510, 521, 522, 523). E. H. R.

**Phlobaphens.** M. DITTMAR (*J. Amer. Pharm. Assoc.*, 1923, 12, 680—688).—Phlobaphens can be salted out from solution, but if the salt be removed by osmosis the phlobaphen again enters into solution. The dark red solution of a phlobaphen in ethyl alcohol may be reduced by boiling with zinc dust, but the product gradually becomes coloured by atmospheric oxidation. The phlobaphens, which vary considerably in composition, yield oxalic acid when boiled with nitric acid, but when boiled with dilute sulphuric acid do not yield dextrose, although some colour changes result.

#### CHEMICAL ABSTRACTS.

**Essence of the Carnation.** M. L. S. GLICHITCH (*Bull. Soc. chim.*, 1924, [iv], 35, 205—207).—The essence extracted from the flowers (0.003% yield) by distillation in steam was a pale green solid of greasy taste and touch with an intense odour resembling that of certain aliphatic aldehydes; m. p. 35—37°;  $d_{40}^{20}$  0.869;  $[\alpha]_D^{20} -8.28^\circ$  ( $c=3.148$  in benzene). From it a branched chain heptacosane, m. p. 53—55°, was isolated in 31% yield. Other paraffins were also present. Inconclusive evidence of an acetylated compound and of a substance of aldehydic or ketonic nature was obtained. E. E. T.

## Organic Chemistry.

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**Pyrogenic Decomposition of Acyclic Hydrocarbons.** H. GAULT, F. A. HESSEL, and Y. ALTCHIDJIAN (*Compt. rend.*, 1924, **178**, 1562—1565).—An introductory paper to the systematic study of the pyrogenic decomposition of acyclic hydrocarbons containing at least 16 carbon atoms, with special reference to the effects of temperature, rate of flow of liquid, and period of heating. The apparatus and procedure to be used are described. The preparation of hexadecene by the distillation of cetyl palmitate and of hexadecane by catalytic hydrogenation of hexadecene (cf. Brochet, A., 1914, i, 1069) is described. J. W. B.

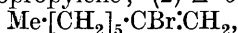
**Preparation of Acetylenic Hydrocarbons, their Sodium Derivatives, and the Corresponding Acetylenic Acids.** L. MEUNIER and E. DESPARMET (*Bull. Soc. chim.*, 1924, [iv], **35**, 481—484; cf. A., 1907, i, 186).—Chloro derivatives of aliphatic aldehydes and ketones react with sodamide, giving the sodium derivatives of the corresponding acetylenic hydrocarbons. Acetylenic hydrocarbons react quantitatively with sodamide to give the corresponding sodium derivatives. Allyl and disubstituted acetylenic hydrocarbons react quantitatively on heating with sodamide, giving the sodium derivatives of the corresponding acetylenes. Ether and similar solvents play no useful part in the absorption of carbon dioxide by the sodium derivatives to form acids. A. B. H.

**Partial Dehydration of Aldehydes and Ketones forming Acetylenic Hydrocarbons.** BOURGUEL (*Compt. rend.*, 1924, **178**, 1557—1560).—The dehydrating and chlorinating action of phosphorus pentachloride on methyl *n*-propyl ketone, diethyl ketone, dipropyl ketone, heptaldehyde, acetophenone, and ethyl phenyl ketone, resulting in the formation of acetylenic and ethylenic compounds, is described. Methyl *n*-propyl ketone (1 mol.) treated in the cold with phosphorus pentachloride (1 mol.) forms  $\Delta^2$ -pentinene,  $\text{C}_6\text{H}_{10}$  (0.005 mol.), together with the compounds  $\text{CH}_2\text{Et}\cdot\text{CClMe}$  (0.35 mol.), and  $\text{CH}_2\text{EtCl}\cdot\text{CHCl}\cdot\text{CH}_3$  (0.06 mol.), the latter being detected by conversion into  $\Delta^2$ -pentene by the action of zinc powder and alcohol; much hydrogen chloride is also evolved. It is assumed that it is the enolic form of the ketone which reacts with the phosphorus pentachloride. Diethyl ketone and dipropyl ketone yield the corresponding compounds, whilst heptaldehyde yields  $\Delta^2$ -heptinene,  $\text{C}_7\text{H}_{12}$ , and  $\text{C}_7\text{H}_{11}\cdot\text{C}(\text{OH})\cdot\text{CH}_3$ , and

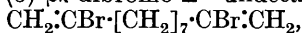
chlorinated compounds. Neither acetophenone nor ethyl phenyl ketone gives acetylenic hydrocarbons. J. W. B.

### Preparation of Two True Diacetylenic Hydrocarbons.

LESPIEAU (*Compt. rend.*, 1924, **178**, 1565—1567).—On addition of  $\alpha\beta$ -dibromopropylene in ether to the product of the interaction of pentamethylene dibromide and magnesium shavings suspended in ether, a brisk reaction occurs and from the product, on repeated fractionation, the following compounds have been isolated: (1) Unchanged dibromopropylene; (2)  $\Delta^{\alpha}$ -bromo-octene,



b. p. 60—61°/11 mm.,  $d^{20}_D$  1.158,  $n_D$  1.4715; (3) unchanged pentamethylene dibromide; (4) the alcohol,  $\text{CH}_2\cdot\text{CBr}\cdot[\text{CH}_2]_5\cdot\text{CH}_2\cdot\text{OH}$ , b. p. 120—121°/11 mm.,  $d^{21}_D$  1.272,  $n_D$  1.499 (*phenylurethane*, m. p. 52.5—53.5°); (5)  $\beta\kappa$ -dibromo- $\Delta^{\alpha\kappa}$ -undecadiene,



b. p. 150—151°/10 mm.,  $d^{25}_D$  1.359,  $n_D$  1.504; (6)  $\beta\sigma$ -dibromo- $\Delta^{\alpha\sigma}$ -hexadecadiene,  $\text{CH}_2\cdot\text{CBr}\cdot[\text{CH}_2]_{12}\cdot\text{CBr}\cdot\text{CH}_2$ , b. p. 200—202°/10 mm., m. p. —5°,  $d^{20}_D$  1.221,  $n_D$  1.497. By the action of sodamide on (2) the octinene is obtained in more than 70% yield. By the action of alcoholic potash at the temperature of a water-bath on (5)  $\Delta^{\alpha\kappa}$ -undecadi-inene,  $\text{CH}\cdot\text{C}\cdot[\text{CH}_2]_7\cdot\text{C}\cdot\text{CH}$ , a liquid with an orange-like odour, b. p. 82.5—83°/12 mm., m. p. —17°,  $d^{21}_D$  0.8182,  $n_D$  1.453, is obtained which yields a yellow precipitate with ammoniacal cuprous chloride and a white precipitate,  $\text{C}_{11}\text{H}_{14}\text{Ag}_2\cdot 2\text{AgNO}_3$ , with alcoholic silver nitrate. Similar treatment of (6) yields  $\Delta^{\alpha\sigma}$ -hexadecadi-inene,  $\text{CH}\cdot\text{C}\cdot[\text{CH}_2]_{12}\cdot\text{C}\cdot\text{CH}$ , brilliant laminæ, m. p. 44—45°, b. p. 152—155°/12 mm., giving corresponding copper and silver compounds. J. W. B.

### Action of Inorganic Iodides on $\alpha\beta$ -Dibromo Compounds.

I. Mechanism of the Reaction. C. F. VAN DUIN (*Réc. trav. chim.*, 1924, **43**, 341—358).—The velocity of the reaction between metallic iodides and  $\alpha\beta$ -dibromo compounds,  $\text{R}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{R}' + 2\text{M}'\text{I} = \text{R}\cdot\text{CH}\cdot\text{CHR}' + \text{I}_2 + 2\text{M}'\text{Br}$ , has been measured at 25° in the dark in an atmosphere of carbon dioxide, using potassium iodide as the metallic iodide with  $\alpha\beta$ -dibromopropionic acid and  $\alpha\beta$ -dibromo- $\beta$ -*p*-sulphophenylpropionic acid, respectively. The reaction appears to be termolecular, and it is probable that  $\alpha\beta$ -diiodo compounds occur as intermediate products which break down into ethylenic compounds and free iodine, with a velocity great compared with that of the substitution. Cations, except hydrogen ions, exert a strongly positive catalytic influence, and iodine ions act more rapidly than undissociated iodides. Light accelerates the reaction whilst iodine retards it. Calcium salts are slightly more active catalytically than potassium salts. E. H. R.

Spontaneous Combustion during Work with Dichloroethylene. H. THRON (*Chem.-Ztg.*, 1924, **48**, 142).—Spontaneous combustion due to chloroacetylene was observed during the distillation of a large quantity of alcohol containing about 0.25% of dichloroethylene, with sodium hydroxide. A. R. P.

**Preparation of Alcohols of the Formulæ  $R\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$  and  $R\cdot CR'H\cdot CH_2\cdot CH_2\cdot OH$  and the Corresponding Acids, starting with Aldehydes,  $R\cdot COH$ , and Ketones,  $R\cdot CO\cdot R'$ .**

A. VERLEY (*Bull. Soc. chim.*, 1924, [iv], 35, 487—488).—Condensation of an aldehyde and a ketone in presence of sodium ethoxide gives rise to an ester of the type  $R\cdot CH\text{---}CH\cdot CO_2Et$ ,

which, by reduction with sodium and alcohol, gives the alcohol,  $CH_2R\cdot CH_2\cdot CH_2\cdot OH$ , and by hydrolysis followed by reduction, the acid  $CH_2R\cdot CH_2\cdot CO_2H$ .

A. B. H.

**Catalytic Decomposition of Ethyl Alcohol in the Presence of Alumina.** J. E. GORIS (*Chim. et Ind.*, 1924, 11, 449—452).—

Ethyl alcohol is decomposed into ethylene and water when its vapour is passed over alumina heated at 430—450°; a small quantity of hydrogen (about 4.5% of the ethylene) is also produced, and the formation of hydrogen increases rapidly with increase of temperature above the limit mentioned. The volume of ethylene produced is a measure of the amount of alcohol, and the reaction may be used for the determination of alcohol in mixtures of alcohol and benzene, since the latter is not decomposed by the catalyst. To prepare the catalyst, a mixture of equal weights of aluminium hydroxide and pumice-stone is powdered and heated for 1 hour at 300°.

W. P. S.

**Chlorination of Ethyl Alcohol.** F. D. CHATTAWAY and O. G. BACKEBERG (*J. Chem. Soc.*, 1924, 125, 1097—1101).—The initial stage in the chlorination of ethyl alcohol consists in the formation of ethyl hypochlorite, which then reacts with the excess of alcohol to yield acetaldehyde. The latter undergoes a series of changes resulting in the successive formation of (*inter alia*) monochloroacetaldehyde alcoholate, trichloroethyl ether, dichloroacetaldehyde alcoholate, and finally chloral alcoholate.

C. J. S.

**Stepwise Oxidation of Citronellol and Geraniol.** A. KOTZ and T. STECHE (*J. pr. Chem.*, 1924, [ii], 107, 193—210; cf. Verley, A., 1919, i, 146).—The regulated oxidation of citronellol and geraniol yields formic acid, thus pointing to the presence of the group  $CH_2\cdot CMe-$ . Citronellol, treated with perbenzoic acid (Prileschaeff, A., 1912, i, 633), gives *oxidocitronellol*,  $C_{10}H_{20}O_2$ , an oil, b. p. 139—140°/13 mm.,  $d_4^{20}$  0.9439,  $n_D^{20}$  1.45519, in nearly theoretical yield. This product is rapidly hydrolysed by dilute sulphuric acid to dihydroxyhydrocitronellol, which, oxidised with ice-cold alkaline potassium permanganate solution, gives an oily substance, possibly  $\alpha$ -hydroxy- $\alpha$ -dimethylsuberic acid; the latter substance at 30° breaks up into formic acid and a heavy oil. Dihydroxyhydrocitronellol oxidised with cold chromic acid yields acetic acid, a little acetone, and  $\beta$ -methyladipic acid.

When geranyl acetate is oxidised in ice-cold solution with potassium permanganate, *dihydroxygeraniol oxide acetate*, m. p. 106—106.5°, is obtained, which is hydrolysed to *dihydroxygeraniol oxide*, m. p. 99°. The latter, treated with ice-cold potassium perman-

ganate, gives an oily acid, possibly  $\alpha\epsilon\zeta$ -trihydroxy- $\alpha\epsilon$ -dimethylsuberic acid, which at 30° rapidly breaks up into formic acid and a ketonic compound, yielding a *phenylhydrazone*, m. p. 166—167°. The same end-products were obtained by oxidising geraniol dioxide or geraniol itself in the same way.

W. A. S.

**Complex Compounds of Bivalent Platinum with Organic Disulphides and Polysulphides.** L. TSCHUGAEV and S. ILJIN [Edited by E. FRITZMANN] (*Z. anorg. Chem.*, 1924, **135**, 143—152).

— $\beta$ -Dimethyltrimethylene diethyl dithioether,  $\text{CMe}_2(\text{CH}_2\cdot\text{SEt})_2$ , prepared by the action of sodium mercaptide on pentaglycol, when shaken for 3 hours with an aqueous solution of potassium chloroplatinate, gives an insoluble rose-coloured powder,  $[\text{C}_9\text{H}_{20}] \begin{smallmatrix} \text{S} \\ \diagup \diagdown \\ \text{S} \end{smallmatrix} \text{PtCl}_2$ , which reacts with salts of Riesel's base; on heating, it yields a yellow form, m. p. 218—219°, soluble in alcohol, giving no reaction with Riesel's salts, to which the structure  $[(\text{C}_9\text{H}_{20}) \begin{smallmatrix} \text{S} \\ \diagup \diagdown \\ \text{S} \end{smallmatrix} \text{Pt} \begin{smallmatrix} \text{S} \\ \diagup \diagdown \\ \text{S} \end{smallmatrix} (\text{C}_9\text{H}_{20})] \text{PtCl}_4$  is assigned.

Pentaerythrityl ethyl thioether,  $\text{C}(\text{CH}_2\cdot\text{SEt})_4$ , b. p. 216—218°/14 mm., when shaken with the chloroplatinate solution in the cold yields a yellow insoluble compound,  $\text{PtCl}_2 \begin{smallmatrix} \text{SEt}\cdot\text{CH}_2 \\ \diagup \diagdown \\ \text{SEt}\cdot\text{CH}_2 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CH}_2\cdot\text{SEt} \\ \diagup \diagdown \\ \text{CH}_2\cdot\text{SEt} \end{smallmatrix}$ . If the reaction mixture is heated, a mixture is produced of this substance and a compound,  $(\text{PtCl}_2 \begin{smallmatrix} \text{SEt}\cdot\text{CH}_2 \\ \diagup \diagdown \\ \text{SEt}\cdot\text{CH}_2 \end{smallmatrix})_2 \text{C}$ .

Acetylene diethyl dithioether,  $\text{SEt}\cdot\text{CH}\cdot\text{CH}\cdot\text{SEt}$ , reacts very rapidly in the cold with potassium chloroplatinate solution, giving a rose-coloured powder which quickly changes to a yellow form.

S. I. L.

**Complex Compounds of Palladium with Organic Mono- and Di-sulphides.** L. TSCHUGAEV and C. IWANOV [Edited by E. FRITZMANN] (*Z. anorg. Chem.*, 1924, **135**, 153—160).—The additive compounds of diethyl sulphide with palladium dichloride have been re-examined, and the descriptions of Ardell (*ibid.*, 1897, **14**, 143) and of Phillips (A., 1901, i, 444) confirmed except in the following particulars:  $\text{PdCl}_2\cdot 2\text{Et}_2\text{S}$ , m. p. 82°;  $\text{PdBr}_2\cdot 2\text{Et}_2\text{S}$ , m. p. 100°;  $\text{PdI}_2\cdot 2\text{Et}_2\text{S}$ , m. p. 104°. The solubilities in isopentane at 25° have been determined.

With the ethylene diethyl dithioether,  $\text{SEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SEt}$ , an analogous series of compounds has been obtained. The *chloride*,  $\text{PdCl}_2\cdot\text{C}_6\text{H}_{14}\text{S}_2$ , m. p. 180°, *bromide*, m. p. 159°, and *iodide*, m. p. 154°, exist in one form only.

The action of carbon monoxide on complex palladium compounds has been examined; whilst the ammoniacal compounds are readily reduced, the sulphide compounds are less readily and the disulphide compounds only with difficulty reduced; the speed of reduction varies with the solubility.

S. I. L.

**Application of Thallium Compounds in Organic Chemistry.**

**I. Thallous Hydroxide.** R. C. MENZIES and E. M. WILKINS (*J. Chem. Soc.*, 1924, **125**, 1148—1152).—A standard solution of

thallous hydroxide may be used for the titration particularly of organic acids. The thallous salts of organic acids are considerably less soluble than those of the alkali metals, are readily crystallised, and hence can be used as a convenient means of isolation and purification. Several new thallous salts are described. The *palmitate* (feathery aggregates from ethyl alcohol) and the *oleate* (white needles) both behave as soaps in dilute aqueous solution. Normal *thallous adipate*, crystalline leaflets, *normal pimelate*, long needles, and *hydrogen pimelate*, prisms, m. p. 137—140°, have also been prepared. The *thallous* salt of ethyl acetonedicarboxylate forms minute needles, m. p. 125° (decomp.). Thallous hydroxide dissolves isatin and yields yellow needles of *thallous isatate*, decomp. 148°.

Thallous hydroxide gives coloured solutions when heated with reducing sugars, thus resembling sodium hydroxide; further heating causes reduction with the formation of thallium mirrors. Non-reducing sugars are not affected. C. J. S.

**Basic Zinc Acetate Analogous to the Beryllium Salt.** V. AUGER and (MLLE.) I. ROBIN (*Compt. rend.*, 1924, **178**, 1546—1548).—Whereas the distillation of zinc acetate under atmospheric pressure or in a moderate vacuum furnishes the normal salt mixed with decomposition products, distillation in a high vacuum gives, in a pure state, the *basic* salt,  $\text{Zn}_4\text{O}(\text{CH}_3\text{CO}_2)_6$ , which crystallises in transparent octahedra, m. p. 249—250°, decomposed by water and by absolute alcohol. Urbain and Lacombe (A., 1902, i, 132) obtained the corresponding salt of beryllium, and the formation of this volatile basic zinc salt demonstrates the close analogy between beryllium and zinc (cf. Lacombe, A., 1902, i, 418).

J. W. B.

**Heterogeneous Catalysis. I. Selective Action of the Nickel Catalyst in the Hydrogenation of certain Vegetable Oils.** A. S. RICHARDSON, C. A. KNUTH, and C. H. MILLIGAN (*Ind. Eng. Chem.*, 1924, **16**, 519—522).—The hydrogenation of cotton seed, arachis, and soya bean oils is characterised by the preferential conversion of linoleic acid to oleic acid and its isomerides. The selective hydrogenation of linoleic acid appears to be more marked when increasing amounts of the nickel catalyst are used and when the temperature is increased up to an optimum of about 200°. It appears to be well established that the normal course of hydrogenation of a single unsaturated component of a liquid mixture involves a constant rate of hydrogen absorption as long as the concentration of that component exceeds a fairly well-defined critical value. Owing to the selective action of the catalyst, a constant rate of hydrogen absorption is not uncommon, even when the reaction mixture contains a variety of unsaturated components. H. C. R.

**Catalytic Hydrogenation of Oleic Acid and Commercial Olein with Nickel as Catalyst.** DE ROUBAIX (*Bull. Soc. chim. Belg.*, 1924, **33**, 193—212).—Oleic acid and commercial olein may be completely hydrogenated, after purification by distillation under



diminished pressure, by means of a rapid current of hydrogen at atmospheric pressure in the presence of 4% of reduced nickel as catalyst, the temperature being between 160° and 230°. The catalyst should not be prepared within the material to be hydrogenated, as this leads to considerable formation of nickel oleate, which encloses the nickel particles and inhibits their action. The presence of sulphur in non-distilled olein poisons the catalyst. [Cf. *B.*, July 25th.] W. T. K. B.


**Preparation of Solutions of Acetoacetic Acid.** G. LJUNGREN (*Biochem. Z.*, 1924, **145**, 422—425).—A 2% excess of sodium hydroxide solution warmed to 25° is placed in a flask which has been blown out with air free from carbon dioxide, and a weighed quantity of methyl acetoacetate is added. Hydrolysis is complete in 250 minutes and the solution is then neutralised with hydrochloric acid or by passing a stream of carbon dioxide for 10 minutes. The solution is 0.3% less concentrated than theory demands. The methyl alcohol resulting from the hydrolysis may be removed by aëration in a vacuum with pure air. Under similar conditions, ethyl acetoacetate is hydrolysed in 375 minutes. Kept over ice, such solutions decrease in concentration by 0.15% *per diem*.

J. P.

**Pyrogenic Dissociation of Sodium Oxalate.** S. OTT (*Z. physikal. Chem.*, 1924, **109**, 1—33).—The thermal decomposition of sodium oxalate, obtained by heating sodium formate, into sodium carbonate and carbon monoxide has been studied. At all temperatures at which an appreciable decomposition takes place, even as low as 160°, there is a further reaction by which the carbon monoxide gives carbon dioxide and carbon, which accelerates the further evolution of gas. Hydrogen always appears in the residual gases, probably derived from traces of water which are difficult to remove from the oxalate. The equilibrium pressure has not been reached experimentally in a single case. Heating sodium carbonate under a pressure of 1100 atmospheres of carbon monoxide (which is greatly in excess of the calculated pressure) failed to reverse the process. This result seems to indicate that the decomposition of sodium oxalate by heat is still another example of an irreversible equilibrium.

M. S. B.

**Stereochemistry of Ruthenium.** R. CHARONNAT (*Compt. rend.*, 1924, **178**, 1279—1282).—Complex salts of ruthenium have been studied on the basis of the Werner theory of co-ordination. The compound  $2[\text{Ru}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot \text{KCl} \cdot 8\text{H}_2\text{O}$ , which is perfectly hexa-co-ordinated, was prepared by treating  $\text{RuCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$  with a slight excess of normal potassium oxalate for 2 hours at 130°. By recrystallisation from water, the salt,  $[\text{Ru}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot 4.5\text{H}_2\text{O}$ , was obtained. These compounds are isomorphous with corresponding compounds of iridium and rhodium. Resolution was attempted by crystallisation of the double salt with *d*-potassium iridiotrioxalate. The active ruthenotrioxalate, however, either racemised immediately on liberation or possessed nearly zero

rotatory power. The compound  $[\text{Ru}(\text{NO})\text{en}_2\text{I}]\text{I}_2 \cdot 2\text{H}_2\text{O}$  was transformed by prolonged heating into a salt of the same molecular composition, but crystallising in the anhydrous form. This compound and the series derived from it must possess the *cis* configuration if the series prepared by Werner and Smirnof (A., 1921, i, 13) possesses the *trans* configuration. A. B. H. 

**Stereochemistry of Ruthenium.** R. CHARONNAT (*Cmpt. rend.*, 1924, 178, 1423—1426; cf. preceding abstract).—The action of normal potassium oxalate (2 mols.) on Joly's salt,  $[\text{Ru}(\text{NO})\text{Cl}_5]\text{K}_2$ , yields a highly soluble *potassium ruthenochloronitrosodioxalate*,  $[\text{Ru}(\text{NO})\text{Cl}(\text{C}_2\text{O}_4)_2]\text{K}_2$ , which is prone to supersaturation and with alkaloids forms salts incapable of crystallising. The replacement of an atom of chlorine in the complex anion by a molecule of pyridine lowers the solubility and yields a more tractable compound. *Potassium ruthenonitrosopyridinodioxalate*,  $[\text{Ru}(\text{NO})\text{C}_5\text{H}_5\text{N}(\text{C}_2\text{O}_4)_2]\text{K}$ , prepared by the successive action of potassium oxalate and pyridine on  $[\text{Ru}(\text{NO})\text{Cl}_5]\text{K}_2$ , forms large, red, triclinic plates ( $+4\text{H}_2\text{O}$ ), and by hydrochloric acid at  $100^\circ$  is converted into the complex  $[\text{Ru}(\text{NO})\text{C}_5\text{H}_5\text{NCl}_4]$ . The latter, under the action of pyridine, gives the compound  $[\text{Ru}(\text{NO})(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2(\text{OH})]$ , and this yields the compound  $[\text{Ru}(\text{NO})(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_3]$  (I), when treated with hydrochloric acid. Compound (I) is obtained also by the action of hydrochloric acid on the compound  $[\text{Ru}(\text{NO})(\text{C}_5\text{H}_5\text{N})_2\text{Cl}(\text{C}_2\text{O}_4)]$ , which is another product of the action of potassium oxalate and pyridine on the salt  $[\text{Ru}(\text{NO})\text{Cl}_5]\text{K}_2$ . All these compounds are highly stable.

By double decomposition with quinine hydrochloride, potassium ruthenonitrosopyridinodioxalate yields two isomeric, pink quinine salts of different solubilities, the one dextro- and the other lævoro-rotatory; the quinidine salts behave similarly, but most of the alkaloids yield uncrystallisable salts. In aqueous solution, the corresponding ammonium salts have  $[\alpha]_D \pm 425^\circ$ , and from a solution containing a mixture of the two a crystalline racemic salt may be obtained. The active pyridine salts were also obtained crystalline. T. H. P.

**Condensation Reactions involving Elimination of Ester Groups.** L. SOUTHER (*J. Amer. Chem. Soc.*, 1924, 46, 1301—1305).—Methylene iodide condenses with methyl and ethyl phenylmalonates in presence of sodium methoxide with formation, respectively, of *methyl  $\alpha\gamma$ -diphenylglutarate*, b. p.  $205\text{--}210^\circ/6\text{ mm.}$ , and *ethyl  $\alpha\gamma$ -diphenylglutarate*, b. p.  $216\text{--}217^\circ/7\text{ mm.}$ , and elimination of methyl and ethyl carbonates. A new *isomeride* of  $\alpha\gamma$ -diphenylglutaric acid, m. p.  $185\text{--}186.5^\circ$ , together with the ordinary modification, was obtained by saponification of the methyl ester with sodium methoxide. With ethyl phenylcyanoacetate, methylene iodide yields similarly  $\alpha\gamma$ -diphenylglutaronitrile. F. G. W.

**Rotatory Dispersion of Tartaric Acid.** L. LONGCHAMON.—(See ii, 373.)

**Decomposition of Dihydroxymaleic Acid.** A. LOCKE (*J. Amer. Chem. Soc.*, 1924, **46**, 1246—1252).—An attempted synthesis of optically active sugars by the decomposition of the quinine salt and menthyl ester of dihydroxymaleic acid failed because the rate of polymerisation of the glycollaldehyde first formed was so slow in comparison with that of the decomposition of the dihydroxymaleic acid that the orientating effect of the quinine and menthol was lost. An attempt to catalyse the condensation of the aldehyde by means of alkalis showed that the sodium and potassium salts of dihydroxymaleic acid are relatively stable in solution, and that the addition of pyridine induces rapid decomposition of the otherwise stable solution of dihydroxymaleic acid in chloroform or benzene. The rates of decomposition of dihydroxymaleic acid and its disodium salt were measured in aqueous solution at 25°, by determining at intervals the glycollaldehyde produced. The experimental values for the unimolecular constant of the reaction are in accordance with the hypothesis that decomposition proceeds through the solvated, non-ionised, carboxyl group.

F. G. W.

**Biological Oxidation. I. Absorption of Oxygen by the System Linoleic Acid-SH Group.** A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1924, **146**, 245—253).—The product resulting from the catalytic oxidation of linoleic acid by thioglycollic acid in the presence of oxygen has been isolated as a dark yellow, viscous oil, which appears to be a compound of the ethylene oxide type, and not a peroxide, as supposed by Meyerhof (*Pflüger*, 1923, **199**, 531).

J. P.

**Biological Oxidation. II. Mechanism and Significance of SH-Catalysis.** A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1924, **146**, 254—258).—From a comparison of the oxidative action of thioglycollic acid and of ethyl peroxide on various aliphatic acids in the presence of air and an iron catalyst, it is concluded that thioglycollic acid combines with the oxygen of the air to form an active peroxide.

J. P.

**n- $\alpha$ -Sulphobutyric Acid and its Optically Active Components.** H. J. BACKER and J. H. DE BOER (*Rec. trav. chim.*, 1924, **43**, 297—315).—An extended account of work previously published in an abbreviated form (*A.*, 1923, i, 536). *Lead  $\alpha$ -sulphobutyrate* crystallises in small needles with 2H<sub>2</sub>O; a *basic salt* has the composition C<sub>4</sub>H<sub>6</sub>O<sub>5</sub>SPb<sub>2</sub>(OH)<sub>2</sub>. *Copper  $\alpha$ -sulphobutyrate* forms a pale blue crystalline powder containing 1H<sub>2</sub>O; the *copper hydrogen*, *nickel*, and *cobalt* salts are also described. Two *strychnine* salts are described, the *normal salt*, small, glistening needles, m. p. 226—227°, and the *hydrogen salt*, aggregates of small, white needles. The two corresponding *brucine* salts and the *normal quinine salt* were obtained. Both the strychnine and quinine salts were used for the resolution of  $\alpha$ -sulphobutyric acid, the former depositing first the salt of the *d*-acid, whilst the latter deposited the salt of the *l*-acid in excess. The pure components of  $\alpha$ -sulphobutyric acid

have  $[\alpha]_D \pm 7.8^\circ$  and the normal barium salts,  $\pm 29.6^\circ$ . The acid salts, in which the carboxyl group is probably free, have the same sign of rotation as the free acids, the value being about  $\pm 4^\circ$ . The rotation-dispersions of the acid and its salts are normal, except for the coloured salts in alcohol.

E. H. R.

**Condensation of Aldehydes with Ammonia in Presence of Alumina.** A. E. TSCHITSCHIBABIN (*J. pr. Chem.*, 1924, [ii], 107, 129—131).—Further details of work already published (this vol., i, 312).

W. A. S.

**Sodium Hydroxylaminesulphonate as a Reagent for the Preparation of Oximes.** W. L. SEMON and V. R. DAMERELL (*J. Amer. Chem. Soc.*, 1924, 46, 1290—1293).—Sodium hydroxylaminemonosulphonate forms a convenient reagent for the preparation of oximes in acid solution. The ketone is heated at  $70$ — $100^\circ$  with the theoretical quantity of the sodium monosulphonate in aqueous solution (1.29 mols. per litre), made alkaline in the cold, and the oxime extracted with a solvent. Negative results were obtained with benzil and quinonemonoxime.

F. G. W.

**Reduction of Citronellal.** H. RUPE and R. RINDERKNECHT (*Helv. Chim. Acta*, 1924, 7, 541—546).—Citronellal was reduced by von Braun and Kaiser (this vol., i, 3) to dihydrocitronellol ( $\gamma\eta$ -dimethyloctanol),  $[\alpha]_D + 2.38^\circ$ , a value only about one-half that of citronellol,  $[\alpha]_D + 4.17^\circ$ . This contradicts the authors' rule that a double bond so far removed from the asymmetric carbon atom as that in citronellol should have practically no effect on the rotation. The authors have therefore repeated the reduction of citronellal, using the nickel catalyst previously described (A., 1919, i, 29). The dihydrocitronellol had  $n_D 1.43417$ ,  $[\alpha]_D + 4.09^\circ$ , from which it is concluded that the preparation of von Braun and Kaiser, obtained by reduction under pressure at  $150^\circ$ , was impure. Both citronellol and dihydrocitronellol show slightly anomalous rotation dispersion.

E. H. R.

**Carbohydrates and Polysaccharides. IX. Synthesis of 2:3-Dimethylcyclopentenaldehyde.** R. R. READ and H. HIBBERT (*J. Amer. Chem. Soc.*, 1924, 46, 1281—1283).— $\beta$ -Bromobutaldehyde diethyl acetal,  $\text{CHMeBr}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ , a heavy, yellow, unstable oil, b. p.  $82$ — $85^\circ/12$ — $15$  mm., was obtained by the addition of crotonaldehyde to alcoholic hydrobromic acid. This was treated with magnesium in ether, and the product decomposed with dilute sulphuric acid. The oil obtained was identical with the 2:3-dimethylcyclopentenaldehyde obtained by the electrolytic reduction of crotonaldehyde (this vol., i, 613). Its formation is to be represented by the elimination of water from dimethyladipaldehyde, the acetal of which is formed by the elimination of bromine from two molecules of  $\beta$ -bromobutaldehyde diethyl acetal by the action of the magnesium. A similar synthesis could not be carried out with the corresponding chlorine compound.

F. G. W.

bb\*

**Carbohydrates and Polysaccharides. X. Synthesis and relative Stability of Cyclic Acetals from  $\alpha\beta$ - and  $\alpha\gamma$ -Glycols.** H. HIBBERT and J. A. TIMM (*J. Amer. Chem. Soc.*, 1924, **46**, 1283—1290).—The relative stability and ease of formation of 5- and 6-membered cyclic acetals were measured by allowing an  $\alpha\beta$ - and an  $\alpha\gamma$ -glycol to condense competitively with various aldehydes in presence of dilute sulphuric acid at 100°, and measuring the yields of the two cyclic acetals formed when equilibrium had been reached. In the cases examined, the end-product contained a preponderance of the 6-membered derivative, the preponderance being greater the higher the molecular weight of the aliphatic aldehyde employed. A mixture of ethylene and trimethylene glycols (1 mol. of each) condensed with 1 mol. of paracetaldehyde, *n*-butaldehyde, *n*-heptaldehyde, and benzaldehyde, respectively, to form the 5- and 6-membered cyclic acetals in the respective proportions 1:1.8, 1:6.6, 1:7.3, and 1:2.1. Similar partition experiments, using ethylene glycol (1 mol.) and a mixture of benzaldehyde (1 mol.) with paracetaldehyde, *n*-butaldehyde, or *n*-heptaldehyde (1 mol.) gave ratios of the yields of products from benzaldehyde to those from the aliphatic aldehydes of 1:3.6, 1:1.2, and 1:0.7, respectively. Using trimethylene glycol, the corresponding ratios were 1:6.2, 1:4.4, and 1:2.0, the stability of cyclic acetals from aliphatic aldehydes decreasing with increasing molecular weight. The *n*-butylidene ether, b. p. 132—136°, and benzylidene ether, b. p. 225°, of ethylene glycol and the *n*-butylidene ether, b. p. 154—157°, of trimethyleneglycol are described. The cyclic acetals are readily hydrolysed by water or dilute acids, are more stable to alkalis, and very resistant to permanganate in acetone.

F. G. W.

**Application of Azeotropy to the Preparation of Organic Compounds.** H. WUYTS (*Bull. Soc. chim. Belg.*, 1924, **33**, 167—192).—A general discussion of the vapour pressures and boiling points of liquid binary mixtures, and a recapitulation of previous work on esterification (*A.*, 1921, i, 494) and etherification (*A.*, 1923, i, 532). Similar methods are described for the preparation of formals. In each case, the lower members of the homologous series are obtained directly as the most volatile component or as the predominant constituent of a binary mixture. With the higher members, the separation is facilitated by the heterogeneity of the mixture, and water is eliminated in the form of a binary mixture with alcohol.

W. T. K. B.

**Preparation of Acetals from Aldehydes and Ketones.** B. HELFERICH and J. HAUSEN (*Ber.*, 1924, **57**, [B], 795—799).—Acetals may be obtained by the action of orthosilicic esters (1.1 mols.) on solutions of aldehydes or ketones (1 mol.) in the requisite anhydrous alcohol (2—3 mols.) in the presence of hydrogen chloride; the mixtures are preserved for some days at the atmospheric temperature or heated under a reflux condenser. Unchanged ester is removed, if necessary, by treating the products with potassium hydroxide. The new method is not more advantageous than

Fischer's process in those cases in which the latter gives good yields, but is superior to that involving orthoformic esters, since the materials are more readily prepared, and, in certain cases, it is possible to transform unsaturated aldehydes and ketones into acetals without addition of alcohol at the double bond. The following compounds are described: *lævulinaldehyde* (keto)-dimethylacetal, b. p. 76—80°/10 mm.,  $d_4^{20}$  0.9713,  $n_D^{20}$  1.4203; the derivatives of *cyclohexanone*: *dimethylacetal*, b. p. 54—56°/13 mm.,  $d_4^{19.2}$  0.9528,  $n_D^{19.2}$  1.4416; *diethylacetal*, b. p. 75—76°/13 mm.,  $d_4^{17.5}$  0.9156,  $n_D^{17.5}$  1.4452; *diallylacetal*, b. p. 106—108°/13 mm.,  $d_4^{17.5}$  0.9410,  $n_D^{17.5}$  1.4632; *diisobutylacetal*, b. p. 115—116°/13 mm.,  $d_4^{15}$  0.8927,  $n_D^{15}$  1.4413; *diisoamylacetal*, b. p. 138—140°/12 mm.,  $d_4^{18.5}$  0.9165,  $n_D^{18.5}$  1.4605; *benzaldehyde* *cetylacetal*; *crotonaldehyde* *dimethylacetal*, b. p. 124—128°/760 mm.,  $d_4^{18}$  0.8829,  $n_D^{18}$  1.4130; *methylheptenone* *dimethylacetal*, b. p. 80—83°/14 mm.,  $d_4^{18}$  0.8770,  $n_D^{18}$  1.4380.

The requisite orthosilicic esters are prepared by gradually adding silicon tetrachloride (1 mol.) to the well-cooled alcohol (4.4 mols.) and subsequently slowly heating the mixture to its boiling point if this does not exceed 150° and keeping it at this temperature until hydrogen chloride ceases to be evolved. The final traces of acid are removed by treatment of the product with a solution of sodium ethoxide in alcohol. The following new esters are described: *tetra-allyl orthosilicate*, b. p. 115—116°/13 mm.,  $d_4^{17}$  0.9842,  $n_D^{17}$  1.4347; *tetrabenzyl orthosilicate*, long needles, m. p. 32.5°, b. p. 305°/12 mm.; *tetracyclohexyl orthosilicate*, needles, m. p. 88.5°, b. p. 230—240°/11 mm.; *tetra-acetyl orthosilicate*, m. p. 46.5—48.5°. Tetramethyl, tetraethyl, tetraisobutyl, and tetraisoamyl orthosilicates have b. p. 25—27°/12 mm., 60—62°/12 mm., 129—131°/13 mm., and 173—176°/12 mm., respectively. *Methyl silico-orthoformate*, b. p. 104—106°/760 mm., is prepared in 66% yield from methyl alcohol and trichlorosilane.

H. W.

**Additive Products of Methyl Ethyl Ketone with Chloroform, Bromoform, and Iodoform.** B. EKELEY and C. J. KLEMME (*J. Amer. Chem. Soc.*, 1924, 46, 1252—1254).—Chloroform, bromoform, and iodoform (2 mols.) condense, respectively, with methyl ethyl ketone (1 mol.) in presence of dry, powdered potassium hydroxide, with formation of *trichloro-tert.-amyl alcohol*, b. p. 110—113°/620 mm. (decomp.),  $d_4^{20}$  1.2128,  $n_D^{20}$  1.4460,  $M_D$  42.107; *tribromo-tert.-amyl alcohol*, b. p. 130—135°/40 mm. (decomp.),  $d_4^{20}$  1.8788,  $n_D^{20}$  1.5130, and *tri-iodo-tert.-amyl alcohol*,  $d_4^{20}$  2.1438,  $n_D^{20}$  1.5680. The products are yellow, pungent liquids, which produce a numbing sensation when placed on the tongue. The first two, but not the last, are fairly stable in the dark, and they are all less stable than the corresponding trihalogeno-*tert.*-butyl alcohols.

F. G. W.

**Comparison of Hydrogen Ion and Enzyme Catalysis of certain Sugars and Glucosides.** R. KUHN and H. SOBOTKA (*Z. physikal. Chem.*, 1924, 109, 65—76).—In the enzymic hydrolysis of sugar derivatives an enzyme-sugar compound is formed as an intermediate product (cf. Kuhn, A., 1923, i, 1033). It has been

found (unpublished work) that the rates of enzyme hydrolysis of  $\alpha$ -phenylglucoside,  $\alpha$ -methylglucoside, and maltose vary as the corresponding rates of acid hydrolysis, and similar relations hold for raffinose and sucrose, but not for helicin, salicin, and  $\beta$ -methyl- and  $\beta$ -phenyl-glucosides. Various reasons are suggested to account for the difference, including the possibility that it may be due to the large differences between the acid dissociation constants of the different glucosides. Experiments have therefore been made to determine the influence of the hydrogen-ion concentration on the dissociation constant of the emulsin-salicin compound in the hydrolysis of salicin by emulsin. The maximum activity of the enzyme is obtained at  $p_H$  4.4, and falls to half value at  $p_H$  6.8. The concentration of salicin at which the activity is half the maximum, increases from 0.035*N* for  $p_H$  4.4 to 0.047*N* for  $p_H$  6.8. According to Michaelis and Rothstein (A., 1920, i, 896), it should, on the contrary, fall to half. The salicin-emulsin compound is to be regarded as half dissociated at these concentrations of salicin, that is, the dissociation constants are 0.035 at  $p_H$  4.4 and 0.047 at  $p_H$  6.8.

The acid dissociation constants of a number of sugars and glucosides have also been determined, and several differ to a rather large extent from those found by Michaelis and Rona (A., 1913, ii, 379).

M. S. B.

**Stepwise Oxidation of Dextrose.** M. HÖNIG and F. TEMPUS (*Ber.*, 1924, 57, [B], 787—791).—Cautious oxidation of dextrose by means of cold barium hypobromite, in presence of a slight excess of barium hydroxide, effects a stepwise oxidation in which the chief products are gluconic acid,  $\beta$ -ketogluconic acid, and arabonic acid, using 1, 2, or 3 equivalents of oxygen, respectively. Further oxidation affords a complex mixture of various substances such as arabonic, saccharic, tartaric, formic, and acetic acids. The constitution of ketogluconic acid was shown by its degradation by carboxylase to *d*-arabinose. Ketogluconic acid was identified by its *calcium* salt,  $[\alpha] -9.56^\circ$ , and *osazone*, bright yellow needles, m. p.  $174^\circ$ .

F. A. M.

**Polysaccharides. XXVI. Cleavage of Lichenin into Dextrose.** P. KARRER and M. STAUB (*Helv. Chim. Acta*, 1924, 7, 518—519).—The quantitative conversion of lichenin (reserve cellulose) into dextrose by lichenase (cf. A., 1923, i, 1182) has been confirmed by the preparation of the crystalline sugar in almost quantitative yield from the fermented lichenin solution.

E. H. R.

**Acetone [*iso*Propylidene] Compounds of the Mercaptals of certain Monosaccharides. I. Acetone Compounds of *d*-Glucosedibenzylmercaptal.** E. PACSU (*Ber.*, 1924, 57, [B], 849—853).—*d*-Glucosedibenzylmercaptal,  $[\alpha]_D^{15} -98.37^\circ$  in pyridine, m. p.  $139^\circ$  (Lawrence, A., 1896, i, 272, gives m. p.  $133^\circ$ ), condenses with acetone to form a brown syrup which was separated by means of chloroform and light petroleum into the crystalline

*monoacetone-d-glucosedibenzylmercaptal*, m. p.  $94^{\circ}$ ,  $[\alpha]_D^{25} -16.44^{\circ}$  (in tetrachloroethane), and the yellow, syrupy *diacetone-d-glucosedibenzylmercaptal*, which was treated with *p*-toluenesulphonyl chloride in pyridine to give *p*-toluenesulphonyldiacetone-d-glucosedibenzylmercaptal, colourless needles, m. p.  $114^{\circ}$ ,  $[\alpha]_D^{25} -51.89^{\circ}$  (in tetrachloroethane). The crude mixture of isopropylidene dimercaptal was converted by methylation and subsequent hydrolysis of the product into *monomethyl-d-glucosedibenzylmercaptal*, colourless needles, m. p.  $190-191^{\circ}$ ,  $[\alpha]_D^{25} -109.02^{\circ}$  in pyridine, and *trimethyl-d-glucosedibenzylmercaptal*,  $C_6H_5(OH)_4(OMe)(S \cdot CH_2Ph)_2$ , hexagonal platelets, m. p.  $73-74^{\circ}$ ,  $[\alpha]_D^{25} -63.12^{\circ}$  in pyridine. F. A. M.

**Synthetic Action of  $\alpha$ -D-Mannosidase in the Presence of some Monohydric Alcohols.** H. HÉRISSEY and J. CHEYMOL (*Bull. Soc. Chim. biol.*, 1924, **6**, 186—189).—The action on mannose of  $\alpha$ -D-mannosidase from lucerne grains (A., 1913, i, 497) in the presence of ethyl, propyl, isopropyl, or *n*-butyl alcohol results in the synthesis of the corresponding  $\alpha$ -mannoside. J. P.

**Isolation of Sucrose from Mixtures of Dextrose, Lævulose, and Sucrose.** S. KOMATSU and M. TANIMURA (*Mem. Coll. Sci., Kyōto*, 1924, **7**, 161—163).—Sucrose was isolated in the crystalline state from mixtures with lævulose and dextrose after transforming the reducing sugars into the sugar acids by oxidation with yellow mercuric oxide in the presence of calcium carbonate. The solution was kept neutral in order to reduce the hydrolysis of the sucrose. The sucrose was then crystallised from glacial acetic acid.

H. C. R.

**Oxidation of Lævulose in Phosphate Solutions.** O. WARBURG and M. YABUSOE (*Biochem. Z.*, 1924, **146**, 380—386).—In the presence of phosphates lævulose, but not dextrose, is oxidised by molecular oxygen with the formation of  $\frac{1}{3}$  mol. of carbon dioxide per mol. of oxygen absorbed. The rate of oxidation, which is most rapid during the first few hours, then slowly decreases; it increases with increasing  $p_H$ , and with the phosphate and lævulose concentration, other factors being kept constant. The phosphate cannot be replaced by other salts, and its action is regarded as specific.

J. P.

**Reaction of Acetohalogen-sugars with Tertiary Bases.** P. KARRER, A. WIDMER, and J. STAUB (*Helv. Chim. Acta*, 1924, **7**, 519—527; cf. A., 1921, i, 766).—By the action of trimethylamine on acetobromocellobiose a substance is obtained having the composition  $C_{12}H_{14}O_{10}Ac_6$ , long, white needles, m. p.  $206^{\circ}$ ,  $[\alpha]_D -11.3^{\circ}$ , to which the name *cellal acetate* is given. It cannot be hexa-acetyl-anhydrocellobiose, since it reduces Fehling's solution (in presence of alcohol or pyridine as solvent) and is quite stable to acids. By vigorous treatment with acetic anhydride and sodium acetate, it gives octa-acetylcellobiose. Unlike the latter compound, it is not converted into aceto- $\alpha$ -D-bromoglucose by phosphorus pentabromide.



The tetra-acetylglucosidopyridinium bromide of Fischer and Raske is hydrolysed by dilute hydrobromic acid to *glucosidopyridinium bromide*, m. p.  $179^{\circ}$ ,  $[\alpha]_D +41.4^{\circ}$ ; the corresponding *chloride* has m. p.  $177^{\circ}$ ,  $[\alpha]_D +49.2^{\circ}$ , the *iodide*, m. p.  $183^{\circ}$ , and the *perchlorate*, m. p.  $170^{\circ}$ . The fact that the pyridinium salt does not give lævoglucozan when hydrolysed with alkali, and that the acetyl compound has a negative rotation, suggests that the pyridinium salt has an  $\alpha$ -configuration, whilst tetra-acetylglucosidotrimethylammonium salts (A., 1921, i, 766) have the  $\beta$ -configuration.

When  $\xi$ -bromotriacetyl- $\beta$ -methylglucoside is heated with trimethylamine, *methylglucosidotrimethylammonium bromide*, white crystals which darken at  $240^{\circ}$ , m. p.  $263$ — $266^{\circ}$  (decomp.), is obtained; the *chloride* has m. p.  $274$ — $275^{\circ}$  (decomp.); *perchlorate*, broad needles, m. p.  $125^{\circ}$ ; *picrate*, microcrystalline; *chloroaurate*, m. p.  $136^{\circ}$ . Extensive decomposition occurs when the salts are heated with alkali.

E. H. R.

**Absorptive Power of Starch for Gases and its Action on Magnesium Alkyl Derivatives.** D. COSTA (*Gazzetta*, 1924, 54, 207—211).—The action of magnesium ethyl bromide on starch in ethereal solution and in complete absence of moisture (cf. A., 1923, i, 186) yields a grey, granular compound,  $C_6H_9O_5 \cdot MgBr \cdot Et_2O$ .

Under similar conditions, starch absorbs about twice as much hydrogen chloride (above 18.55%) as does cellulose (cf. Oddo, A., 1920, i, 16) and undergoes transformation into a black substance completely soluble in water. Ammonia and sulphur dioxide also are absorbed by starch in the proportion of approximately 1 mol. per  $C_6H_{10}O_5$ , the starch undergoing no apparent change. Starch absorbs about 0.675% (or 0.065%) of its weight of carbon dioxide (or oxygen).

T. H. P.

**Starch. IX. Constitution of the Polyamyloses.** H. PRINGSHEIM and J. LEIBOWITZ (*Ber.*, 1924, 57, [B], 884—887; cf. A., 1923, i, 899).—By treatment of  $\alpha$ -tetra-amylose or  $\beta$ -hexa-amylose with cold concentrated hydrochloric acid according to the method of A. and J. Pictet (A., 1923, i, 755) the authors have obtained a new disaccharide, termed *amylobiose*,  $C_{12}H_{22}O_{11}$ , which retains in its molecule the second bond of the glucose portion of diamylose, contrary to the views of Karrer and co-workers (A., 1922, i, 435). It is a pure white powder,  $[\alpha]_D^{20} +138^{\circ}$  in water (*osazone*, m. p.  $189^{\circ}$ ). Amylobiose remained unattacked by maltase or emulsin, but was fermented by amylase; it is suggested that amylobiose is a glucosido- $\gamma$ -glucose.

F. A. M.

**Starch. X. Different Structures of the Two Constituents of Starch.** H. PRINGSHEIM and K. WOLFSOHN (*Ber.*, 1924, 57, [B], 887—891; cf. A., 1923, i, 899, and preceding abstract).—The view of Pringsheim and Goldstein (A., 1923, i, 899) that the content- and integument-substances of the starch granule contain respectively a disaccharide and a trisaccharide has now been confirmed directly. Starch paste was separated into amylose and amylopectin, by the method of Ling and Nanji (T., 1923, 123,

2666) and the two substances were depolymerised separately by acetylation (cf. Pringsheim and Eissler, A., 1913, i, 1156) and by heating to 200—210° in glycerol (cf. Pictet and Jahn, A., 1922, i, 987), with the addition of a small quantity of phosphoric acid. Acetylation of amylopectin with acetic anhydride and sulphuric acid gave an *acetate*,  $C_{36}H_{48}O_{24}$ ,  $[\alpha]_D^{20} + 143.6$ — $144.2^\circ$  in tetrachloroethane, whilst the *acetate* of *amylose*,  $C_{24}H_{32}O_{16}$ , had  $[\alpha]_D^{20} + 142.4$ — $142.8^\circ$  in tetrachloroethane. Depolymerisation of amylopectin in glycerol gave a *trihexosan*,  $C_{16}H_{30}O_{15}$ ,  $[\alpha]_D^{20} + 165.2$ — $167.5^\circ$  in water, whilst amylose gave a *dihexosan*,  $C_{12}H_{20}O_{10}$ ,  $[\alpha]_D^{20} + 153.9$ — $154.8^\circ$  in water. The product obtained by Pictet and Jahn (*loc. cit.*) of  $[\alpha]_D + 162.2^\circ$  was therefore a mixture of trihexosan and dihexosan.

F. A. M.

**Behaviour of Cellulose and Lignin during Decay.** F. FISCHER (*Brennstoff-Chem.*, 1924, 5, 132—133).—The work of Bray and Andrews (*Ind. Eng. Chem.*, 1924, 16, 137) on the chemical processes during the bacterial decay of wood is cited in support of the author's hypothesis that the origin of coal is not principally the cellulose of dead vegetation but the lignin. Those authors showed that in the space of three years the cellulose calculated on the original wood had decreased down to 6.05%, whereas the lignin had practically resisted. Schwalbe's experiments whereby he prepared a substance resembling coal by the action of powerful dehydrating agents on cellulose are not held to be valid in determining the origin of coal because the conditions were so different from those prevailing in nature. It is far more probable that dead vegetation would be rapidly attacked by bacterial decay, with consequent destruction of the cellulose, than that it should be preserved and converted into coal by the accidental occurrence of powerful dehydrating conditions.

J. F. B.

**Conversion of Ligneous Plant Substances into Coal. II. Chemical Composition and Properties of Coal-like Substances from Cellulose.** C. G. SCHWALBE and R. SCHEPP (*Ber.*, 1924, 57, [B], 881—883; cf. this vol., i, 377).—Analytical figures are given for the composition of the coal-like substances obtained by heating wood-cellulose with concentrated solutions of salts during various periods. The artificial product appears to be more closely related to the lignites than to ordinary coal or to the humic acids, which was shown by analysis and by the behaviour both with alkalis and with nitric acid; there are, however, also very distinct differences in general behaviour between lignite and the artificial coal.

F. A. M.

**Isomorphism of the Amides and Substituted Amides of Dichloro- and Chloriodo-acetic Acids, and of Chlorobromo- and Chloriodo-acetic Acids.** [Miss] P. V. McKIE (*J. Chem. Soc.*, 1924, 125, 1075—1079).—The fusion mixtures of corresponding pairs of the amides and substituted amides of dichloro- and chloriodo- and of chlorobromo- and chloriodo-acetic acids show isomorphism (cf. T., 1923, 123, 2213). In the corresponding series of

derivatives of dichloro- and chlorobromo-acetic acids the melting-point curve approximates to a straight line joining the melting points of the two components of each system, whereas the curves of pairs of derivatives of chlorobromo- and chloriodo-acetic acids diverge from the straight line, the effect being very marked with derivatives of dichloro- and chloriodo-acetic acids. The following compounds were prepared by methods similar to those previously employed (*loc. cit.*): *Chloroiodoacetomethylamide*, m. p. 117.5°; *chloroiodoacetoethylamide*, m. p. 79.4°; *chloroiodoacetobenzylamide*, m. p. 120.5°; *chloroiodoacetomethylanilide*, m. p. 88.0°; *chloroiodoacetoethylanilide*, m. p. 92.3°. C. J. S.

**Alkylchloromalonamides. Influence of Homology on Taste.** A. W. DOX and B. HOUSTON (*J. Amer. Chem. Soc.*, 1924, **46**, 1278—1281).—Ethylchloromalonamide was obtained by the action of sulphuryl chloride on ethylmalonamide. Dichloromalonamide and the following alkylchloromalonamides were prepared by the action of chlorine on the appropriate malonamides in glacial acetic acid solution. *Methyl-*, m. p. 224—225°; *ethyl-*, m. p. 135°; *n-propyl-*, m. p. 150°; *n-butyl-*, m. p. 136°; *isobutyl-*, m. p. 132°; *isoamyl-*, m. p. 157°; *n-hexyl-*, m. p. 130°; and *benzylchloro-malonamide*, m. p. 183—185°. *isoPropylmalonamide* could not be chlorinated directly, and *isopropylchloromalonamide*, m. p. 177°, was obtained by the action of ammonia on *methyl isopropylchloromalonate*, a colourless oil, b. p. 110—112°/37 mm., 221—222°/757 mm., prepared by the chlorination of *methyl isopropylmalonate*. All the *n*-alkylchloroamides, as well as mono- and di-chloromalonamides, are sweeter than sucrose, the *n*-butyl derivative being at the same time bitter. The *isoalkyl* derivatives are bitter. Constant differences in sweetness between succeeding members of the series could not be established. F. G. W.

**Derivatives of Semioxamazide. II.** F. J. WILSON and E. C. PICKERING (*J. Chem. Soc.*, 1924, **125**, 1152—1156).—In addition to the ketonic semioxamazones previously described (T., 1923, **123**, 394) others have been obtained by the same method. *Methyl n-hexyl ketone semioxamazone*,  $C_6H_{13} \cdot CMe:N \cdot NH \cdot CO \cdot CO \cdot NH_2$ , forms small, colourless needles, m. p. 115—116°. *Benzil monosemioxamazone*, long, colourless prisms, m. p. 181—182°. *Benzil disemioxamazone* is a white powder, m. p. 275—278° (decomp.). *Dibenzyl ketone semioxamazone* is dimorphic, colourless prisms, m. p. 195—196°, being deposited from alcohol above 40°, whilst at temperatures below this, and from more dilute solutions, it crystallises in colourless needles, m. p. 187—189°.

Benzylamine and semioxamazide interact on heating to form *s*-dibenzylloxamide hydrazone, hydrazine, and ammonia. Benzylamine and acetophenone semioxamazone, when heated at 150°, gave *s*-dibenzylloxamide, methylphenylketazine, m. p. 129—130°, hydrazine, and ammonia. Benzylamine and dibenzyl ketone semioxamazone react similarly to give *s*-dibenzylloxamide and *dibenzylketazine*, m. p. 95—96°, which has also been synthesised by heating dibenzyl ketone and hydrazine hydrate in a sealed tube at

100°. By the interaction of piperidine and acetophenone semi-oxamazone there results *acetophenone piperidino-oxalylhydrazone*, a white, microcrystalline powder, m. p. 174—175°, which is hydrolysed to *piperidino-oxalylhydrazine*, colourless, transparent plates, m. p. 77—79° (*hydrochloride*, m. p. 180°; *benzylidene derivative*, m. p. 201—202°).  
C. J. S.

**Preparation and Hydrolysis of Substituted Cyanamides : Di-*n*-butylcyanamide and Diallylcyanamide.** E. B. VLIET (*J. Amer. Chem. Soc.*, 1924, **46**, 1305—1308).—*Di-n-butylcyanamide*, a clear, slightly viscous liquid, b. p. 147—151°/35 mm., 187—191°/190 mm., and *diallylcyanamide*, a colourless liquid, b. p. 105—110°/18 mm., 140—145°/90 mm., are obtained by the action of *n*-butyl and allyl bromides, respectively, on a solution of sodium cyanamide obtained by the action of cold sodium hydroxide on an aqueous suspension of commercial calcium cyanamide, the reaction being facilitated by the addition of alcohol. The above cyanamides are hydrolysed to di-*n*-butylamine and diallylamine on boiling with 25% sulphuric acid.  
F. G. W.

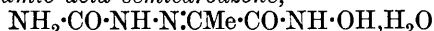
**Production of Thiocyanogen by Electrolysis of Alkali Thiocyanates.** H. KERSTEIN and R. HOFFMANN (*Ber.*, 1924, **57**, [B], 491—496).—Thiocyanogen, first obtained by Söderbäck (*A.*, 1920, i, 219) by the action of bromine on a suspension of silver thiocyanate in carbon disulphide, can be obtained by the electrolysis of alkali thiocyanates in aqueous or alcoholic solutions, using a platinum-gauze anode and a silver cathode. By evaporating the methyl-alcoholic solution at very low pressure, the thiocyanogen was left as a viscous oil which became solid at -70° and gradually crystallised. The thiocyanogen united with thiocyanates to form trithiocyanates,  $M(SCN)_3$  (cf. tri-iodides), which behaved precisely like free thiocyanogen except for their smaller sensitiveness towards water.  
F. A. M.

**Reduction of Pyruvylhydroxamic Acid Phenylhydrazone.** V. C. GASTALDI (*Gazzetta*, 1924, **54**, 212—213).—Reduction of pyruvylhydroxamic acid phenylhydrazone by means of sodium amalgam at 0° (cf. *A.*, 1923, i, 1236) proceeds in accordance with the scheme:  $NHPh \cdot N : CMe \cdot CO \cdot NH \cdot OH \xrightarrow{-O} NHPh \cdot N : CMe \cdot CO \cdot NH_2 \xrightarrow{+2H} NHPh \cdot NH \cdot CHMe \cdot CO \cdot NH_2 \xrightarrow{+H_2O} NHPh \cdot NH \cdot CHMe \cdot CO_2H + NH_3$ . The intermediate products obtained are thus: (1)  $\alpha(\beta$ -phenylhydrazido)-propionamide,  $NHPh \cdot NH \cdot CHMe \cdot CO \cdot NH_2$ , m. p. 124° (cf. Reissert, *A.*, 1884, 1152; Miller and Plöchl, *A.*, 1892, 1196), and (2) *pyruvamide phenylhydrazone*,  $NHPh \cdot N : CMe \cdot CO \cdot NH_2$ , which crystallises in nacreous, white laminæ, m. p. 144°, and may be obtained also by dehydrogenating compound (1) by treatment with the alkaline tartrate solution used in preparing Fehling's solution.  
T. H. P.

**Derivatives of Pyruvylhydroxamic Acid. VI.** C. GASTALDI (*Gazzetta*, 1924, **54**, 214—220).—Pyruvylhydroxamic acid phenyl-

hydrazone and its acetyl derivative, prepared as described by Pickard (T., 1902, **81**, 1573), melt at 178—179° and 142°, respectively, not at 148° and 113°, as stated by this author. Further, the oxime of this acid has m. p. 161° and not 143° as given by Whiteley (T., 1900, **77**, 1046).

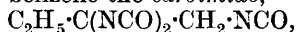
*Pyruvylhydroxamic acid semicarbazone*,



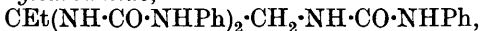
or  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{NOH}\cdot\text{H}_2\text{O}$ , colourless needles, m. p. 200° (decomp.), gives a deep violet-red coloration with ferric chloride in aqueous solution; its *acetyl* derivative forms colourless prisms, m. p. 170° (decomp.). The *thiosemicarbazone*,  $3\text{C}_4\text{H}_8\text{O}_2\text{N}_4\text{S}\cdot 2\text{H}_2\text{O}$ , m. p. 185° (decomp.), forms a silver mirror when heated with ammoniacal silver nitrate. The  $\beta$ -*naphthylhydrazone*,  $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}_3$ , forms lustrous, orange laminæ or slender needles, m. p. 182° (decomp.), dissolves in concentrated sulphuric acid to a deep yellow solution, and in alcoholic solution gives a dark green coloration with aqueous ferric chloride; its *sodium* salt forms chestnut-red prisms and explodes violently when heated, and its *acetyl* derivative crystallises in orange prisms, m. p. 147—148° (decomp.), and on fusion is converted into 5-*hydroxy*-1- $\beta$ -*naphthyl*-3-*methyl*-1 : 2 : 4-*triazole*, yellowish-brown prisms, m. p. 199°.

1- $\beta$ -*Naphthyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*,  $\text{C}_{14}\text{H}_{13}\text{N}_3$ , obtained when pyruvylhydroxamic acid  $\beta$ -*naphthylhydrazone* is fused with acetic anhydride, separates in yellow prisms, m. p. 105—106°; its *hydrochloride*, prisms, has m. p. 257°. T. H. P.

**Conversion of *n*-Butane- $\alpha\beta\beta$ -tricarboxylic Acid into its Triazide and into Aminomethyl Ethyl Ketone.** T. CURTIUS and R. GUND (*J. pr. Chem.*, 1924, [ii], **107**, 177—192).—Ethyl butane- $\alpha\beta\beta$ -tricarboxylate (cf. Bischoff, A., 1890, 742), b. p. 153—155°/9 mm., treated with hydrazine hydrate gives the *trihydrazide*,  $\text{C}_2\text{H}_5\cdot\text{C}(\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , needles, m. p. 167°. This is not converted into a hydrazihydrazide by the action of iodine but only into the original acid and hydrazine dihydriodide. The *tribenzylidene* compound, m. p. 244° (decomp.); *derivatives* with salicylaldehyde, m. p. 212°; *p*-tolualdehyde, m. p. 249° (decomp.); *o*-chlorobenzaldehyde, m. p. 262°; *o*-nitrobenzaldehyde, m. p. 303°; acetone, m. p. 156°; and benzophenone, m. p. 162°; the *triacetyl* compound, m. p. 222°; *tribenzoyl* compound, m. p. 236°; *hydrochloride*, m. p. 185°, and *picrate*, m. p. 185°, are described. When treated as hydrochloride with sodium nitrite the trihydrazide is converted into the *triazide*, an explosive lachrymatory oil, decomposing even in ethereal solution at 0°. Treated with aniline in the cold, this gives *butane- $\alpha\beta\beta$ -tricarboxyanilide*, needles, m. p. 217°; the corresponding *tri-p-toluidide* forms prisms, m. p. 186°. With alcohol, the *urethane*,  $\text{CEt}(\text{NH}\cdot\text{CO}_2\text{Et})_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , an oil, is formed, and when this substance is hydrolysed with hydrochloric acid at 80°, the hydrochloride of  $\alpha$ -amino- $\beta$ -ketobutane (Kolshorn, A., 1904, i, 675) is produced. When the triazide is decomposed by heating its solution in benzene the *carbimide*,



is formed. This substance, an oil, interacts with aniline to yield *butenyltri-phenylcarbamide*,



white crystals soon turning yellow, m. p.  $225^\circ$ , which may be hydrolysed giving the above aminoketone, aniline, carbon dioxide, and ammonia.

W. A. S.

**Rubidium and Cæsium Creatinine Picrates.** I. GREENWALD and J. GROSS (*J. Biol. Chem.*, 1924, **59**, 613—614).—The double picrates of creatinine with rubidium and with cæsium, m. p.  $256\text{--}257^\circ$  and  $255^\circ$ , respectively, were prepared by mixing hot solutions of creatinine, picric acid, and the sulphate or chloride of the metal.

C. R. H.

**Ultra-violet Absorption Spectrum of Naphthalene Vapour.** V. HENRI and H. DE LÁSZLÓ.—(See ii, 367.)

**Methylnaphthalenes.** I.  $\alpha$ -Methylnaphthalenesulphonic Acids. K. ELBS and B. CHRIST (*J. pr. Chem.*, 1923, [ii], **106**, 17—24).— $\alpha$ -Methylnaphthalene (b. p.  $241^\circ$ , picrate, m. p.  $141^\circ$ ) was converted by the action of sulphuric acid at the ordinary temperature into *1-methylnaphthalene-4-sulphonic acid*, which was separated by means of its barium salt, a small amount of an isomeric barium salt being found in the mother-liquors. The free acid is deliquescent, exceedingly soluble in water, and readily soluble in concentrated sulphuric acid. The barium salt ( $+1\text{H}_2\text{O}$ ) crystallises in colourless plates, the copper salt ( $+4\text{H}_2\text{O}$ ) in small, pale green crystals. Attempts to oxidise the methyl group to the carboxyl group by means of potassium permanganate under varying conditions were unsuccessful. The sulphochloride,  $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{SO}_2\text{Cl}$ , m. p.  $81^\circ$ ; sulphonamide, m. p.  $174^\circ$ ; sulphonhydrazide, m. p.  $124\text{--}125^\circ$  (decomp.); acetyl derivative of the hydrazide, m. p.  $220\text{--}222^\circ$  (decomp.); sulphanilide, m. p.  $158^\circ$ ; the methyl ester, m. p.  $107^\circ$ , and the ethyl ester, m. p.  $98^\circ$ , are described. *1-Methylnaphthalene-4-sulphinic acid*, obtained by reduction of the sulphochloride with zinc dust, crystallises in needles, m. p.  $114\text{--}115^\circ$ ; the sodium salt ( $+3\text{H}_2\text{O}$ ) and the copper salt are described. *4-Thiol-1-methylnaphthalene*,  $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{SH}$ , results in an impure form on reduction of the sulphochloride with iron turnings and hydrochloric acid; it is a yellow oil distilling between  $168^\circ$  and  $178^\circ/25\text{ mm.}$  The lead and mercury mercaptides form yellow precipitates. *1:1'-Dimethyldinaphthyl 4:4'-disulphide*,  $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{S}\cdot\text{S}\cdot\text{C}_{10}\text{H}_6\text{Me}$ , obtained by the action of alcoholic ammonia on the thionaphthol, is a colourless, crystalline solid, m. p.  $114^\circ$ . *4-Methyl- $\alpha$ -naphthol* is obtained from the acid by the ordinary method.

F. G. P.

**Course of Reaction in the Gattermann Synthesis of Diphenyl and the Formation of Para Chains of Benzene Rings.** O. GERNGROSS, L. SCHACHNOW, and R. JONAS (*Ber.*, 1924, **57**, [B], 747—750).—In the Gattermann synthesis of diphenyl (A., 1890, 970) a small amount of *p*-phenyldiphenyl is produced simultaneously. The yield of diphenyl diminishes with decrease in alcohol concen-

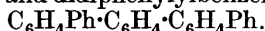
tration, owing to the diminished solubility of the intermediately formed benzene, which is thus prevented from reacting with fresh diazonium salt. When diphenyldiazonium sulphate was treated with benzene and copper powder in a mixture of acetic, formic, and sulphuric acids, diphenyl (1 g.), *p*-phenyldiphenyl (0.3 g.) and *pp'*-diphenyldiphenyl (0.02 g.), were obtained. The mechanism of the reaction is therefore  $C_6H_4Ph \cdot N_2Cl + C_6H_6 = Ph \cdot C_6H_4 \cdot Ph + N_2 + HCl$ . By a modification of the usual Gattermann synthesis from aniline (31 g.), diphenyl (4.2 g.), *p*-phenyldiphenyl (1.8 g.), *pp'*-diphenyldiphenyl (1.0 g.), and didiphenylbenzene (0.11 g.) were isolated. (Cf. also *infra*) F. A. M.

**Studies in the Anthracene Series. IX.** E. DE B. BARNETT and J. W. COOK (*J. Chem. Soc.*, 1924, 125, 1084—1087).—The reaction between anthracene and bromine is reversible (cf. T., 1923, 123, 1994), and by treatment of the anthracene dibromide with dilute hydriodic acid or compounds such as phenol which readily take up bromine, anthracene is regenerated. By the decomposition of anthracene dibromide on warming, dibromoanthracene is formed in addition to 9-bromoanthracene, but the formation of the dibromo compound is inhibited by phenol. The action of chlorine on 9-bromoanthracene is more rapid than on anthracene, but the only product isolated was 9-*chloro*-10-bromoanthracene, lemon-yellow needles, m. p. 207°. The same product was obtained by the action of sulphuryl chloride. On treatment with nitric acid in glacial acetic acid, 9-bromoanthracene yields 9:10-dibromoanthracene, 9-nitroanthrone, and probably a little bromonitroanthracene. The mechanism of the reaction is discussed. R. B.

**Reduction of Organic Halogen Compounds. VII. 3-Phenyl-1-diphenylmethylene-indene.** K. BRAND and L. W. BERLIN (*Ber.*, 1924, 57, [B], 846—847; cf. A., 1921, i, 783).—The constitution of the hydrocarbon, m. p. 207—208°, obtained from  $\beta\gamma$ -dichloro- $\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^2$ -butene has now been proved by its synthesis from 3-phenylindene and benzophenone in presence of sodium ethoxide, and the formula previously ascribed,  $C_6H_4 < \begin{smallmatrix} \text{---CPh} \\ \text{C}(\text{CPh}_2) \end{smallmatrix} > CH$ , is therefore correct. The synthesis also confirms the structure assigned to the substance  $C_{32}H_{28}O_4$ , m. p. 173° (A., 1921, i, 787), obtained by the reduction of  $\beta\gamma$ -dichloro- $\alpha\alpha\delta\delta$ -tetra-*p*-anisyl- $\Delta^2$ -butene, and proves that compounds of the tetra-arylbutane series are easily converted into indene derivatives. R. B.

**A Para Linking of the Benzene Ring ; Extension of the Gattermann Diphenyl Synthesis and Quinquephenyl [Didiphenyl]benzene], a Straight Chain of Five Benzene Nuclei.** O. GERNGROSS and M. DUNKEL (*Ber.*, 1924, 57, [B], 739—746).—Aniline was diazotised in a mixture of concentrated sulphuric acid and glacial acetic acid, by amyl nitrite; glacial formic acid was added and then copper powder by degrees at 0—2°. On steam

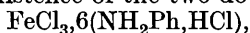
distillation diphenyl was obtained in the distillate (10.3%); 24.8% of the non-volatile, insoluble residue sublimed in a vacuum, at 135° to 400°/30 mm. This product was separated into *p*-phenyldiphenyl, *pp'*-diphenyldiphenyl, and didiphenylbenzene,



The *p*-phenyldiphenyl had m. p. 209.5°, as compared with 207.5° when made from benzenediazonium chloride diphenyl, and aluminium chloride, and its other properties differ slightly from those given in the literature. The *pp'*-diphenyldiphenyl had m. p. 320°, in agreement with Ullmann's figure (A., 1904, i, 725). *Didiphenylbenzene* is a faintly yellow substance, m. p. 388.5°, very sparingly soluble in all organic solvents; it was also prepared by Pummerer's method (A., 1922, i, 24, 1196) from *p*-iodophenyldiphenyl, *p*-iododiphenyl, and silver powder. F. A. M.

**Specific Heats of certain Organic Liquids at Elevated Temperatures.** J. W. WILLIAMS and F. DANIELS.—(See ii, 450.)

**Equilibrium of the System Ferric Chloride—Aniline Hydrochloride—Hydrogen Chloride—Water at 25°.** Y. OSAKA, G. SHIMA, and R. YOSHIDA (*Mem. Coll. Sci. Kyōtō*, 1924, 7, 69—76).—Investigation of this system from the point of view of the phase theory indicates the existence of the two double salts:



in yellowish crystals, and  $\text{FeCl}_3\cdot 2(\text{NH}_2\text{Ph}\cdot\text{HCl})$  in bluish-green, acicular crystals. The two hydrated salts obtained by McKenzie (A., 1913, i, 1321) were not formed under the conditions employed.

T. H. P.

**The Imino Residue.** K. F. SCHMIDT (*Ber.*, 1924, 57, [B], 704—706).—Azoimide is converted by concentrated sulphuric acid partly into hydroxylamine, some oxidation also occurring. At the atmospheric temperature, azoimide dissolved in benzene is transformed by concentrated sulphuric acid mainly into hydrazine, hydroxylamine and aniline being produced in small amount; at 60°, the main product is aniline sulphate, very little hydrazine being formed. Addition of carbonyl derivatives greatly accelerates the decomposition of azoimide by concentrated sulphuric acid and causes the immediate withdrawal of the liberated radical, NH, from the oxidising action of the acid, so that it is possible to convert  $\text{N}_3\text{H}$  quantitatively into NH. Ketones yield acid amides,  $\text{R}\cdot\text{CO}\cdot\text{R} + \text{NH} \rightarrow \text{R}\cdot\text{CO}\cdot\text{NHR}$ , whereas aldehydes give nitriles or substituted formamides.  $\alpha$ -Ketonic acids are converted into  $\alpha$ -amino acids, the yields being 80—98% of the theoretical (glycine,  $\alpha$ -aminobutyric acid, leucine,  $\alpha$ -amino- $\delta$ -methylhexoic acid, phenylalanine, aspartic acid, and  $\alpha$ -aminodibenzylacetic acid are thus prepared).

*cyclo*Hexanone gives  $\epsilon$ -leucyl-lactam,  $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2\text{---CH}_2\text{---CO} \end{array} > \text{NH}$ , or with

an excess of azoimide the tetrazole,  $\text{N} < \begin{array}{c} \text{N}\cdot\text{N} \\ | \\ \text{N}\cdot\text{C} \end{array} > [\text{CH}_2]_5$ . Acyclic ketones likewise yield tetrazoles with an excess of azoimide, acetone



giving the compound  $\text{CMe} \begin{smallmatrix} \text{N} - \text{N} \\ \text{NMe} \cdot \text{N} \end{smallmatrix}$ , whereas benzophenone gives 5-anilino-1-phenyl-1 : 2-dihydropyrazole. H. W.

**Nitrogen Chlorides derived from Nitro-substituted Acetanilides.** F. D. CHATTAWAY and H. J. DOWDEN (*J. Chem. Soc.*, 1924, 125, 1195—1197).—*N*-Chloro derivatives of polynitroacetanilides are not transformed into chloronitroacetanilides, but are hydrolysed and decomposed, or the original nitroacetanilide is regenerated. The transformation of *N*-chloro-2- and -3-nitroacet-*p*-toluidides is also inhibited by the presence of the nitro group. *N*-Chloro-2 : 4-dinitroacetanilide, m. p. 54—55°, is obtained by the action of chlorine on 2 : 4-dinitroacetanilide in acetic acid solution. 6-Chloro-2 : 4-dinitroacetanilide, m. p. 221°, on treatment with hypochlorous acid in chloroform yields *N* : 6-dichloro-2 : 4-dinitroacetanilide, m. p. 68·5°. 2 : 4 : 6-Trinitroacetanilide is not attacked by chlorine in acetic acid solution, but in sodium hydroxide solution it yields *N*-chloro-2 : 4 : 6-trinitroacetanilide, m. p. 127·5°. *N*-Chloro-2-nitroacet-*p*-toluidide, m. p. 125—126°, is obtained by the action of hypochlorous acid on 2-nitroacet-*p*-toluidide in chloroform. *N*-Chloro-3-nitroacet-*p*-toluidide, m. p. 51·5°, is similarly prepared from the 3-nitrotoluidide. R. B.

**Preparation of Anilides of Glycine.** P. KARRER and W. T. HAEBLER (*Helv. Chim. Acta*, 1924, 7, 534—536).—Glycineanilide is simply prepared by reducing Sandmeyer's oximinoacetanilide (A., 1919, i, 318) either electrolytically or with zinc dust and acetic acid. *Glycylanthranilic acid*,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH}_2$ , obtained by reduction of oximinoacetylanthranilic acid, has m. p. 233—234°; *sulphate*, white crystals. *Glycyl-p*-phenetidine (phenocoll) is obtained similarly from oximinoacetyl-*p*-phenetidine.

E. H. R.

**Naphthol AS [2-Hydroxy-3-naphthoanilide] Derivatives.** M. BATTEGAY, C. LANGJAHR, and P. RETTIG (*Chim. et Ind.*, 1924, 11, 453—455).— $\beta$ -Naphthaquinone-1-oxime-3-carboxyanilide, obtained by the action of nitrous acid on Naphthol AS, forms red needles which decompose at 200° without melting, soluble in warm sodium hydroxide solution. The sodium compound, when treated with sodium hydrogen sulphite solution, yields a hydrogen sulphite compound which dyes cotton better than does the corresponding  $\beta$ -naphthol derivative. 1-Amino-2-hydroxynaphthalene-3-carboxyanilide, obtained by the reduction of the quinoneoxime, crystallises in fine needles, m. p. 180°.  $\beta$ -Naphthaquinone-3-carboxyanilide, brick-red crystals, m. p. 204°, yields a red solution in sulphuric acid. The *Meldola-blue*, prepared from Naphthol AS instead of  $\beta$ -naphthol, is insoluble in water but soluble in acetic acid; it dyes cotton a duller shade than does ordinary Meldola-blue.

W. P. S.

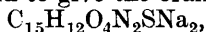
**Reactions of Tetryl [2 : 4 : 6-Trinitrophenylmethylnitroamine].** T. L. DAVIS and C. F. H. ALLEN (*J. Amer. Chem. Soc.*, 1924, 46, 1063—1065).—Commercial samples of tetryl often contain occluded acid. When tetryl is heated with hexyl or *n*-butyl

alcohol, methylpicramide (picrylmethylamine) is formed in small quantities (cf. Mertens, A., 1886, 1022). Tetryl is not affected by prolonged boiling with dilute sulphuric acid, but with aqueous chromic acid it yields picric acid. In the presence of glacial acetic acid, tetryl is destroyed by chromic acid. It is rapidly dissolved by concentrated sulphuric acid at 100°, forming a red solution, and is reprecipitated on pouring this solution on to ice. If the solution is allowed to stand for some days and then poured on to ice, a gummy material is precipitated which dissolves in warm alcohol. The solution deposits 20% of the theoretical yield of picrylmethylamine. As picrylmethylamine yields tetryl on nitration, the reaction is reversible. [Cf. B., 1924, 539.] A. C.

**Colour Tests for Nitro Derivatives of Diphenylamine.** T. L. DAVIS and A. A. ASHDOWN (*J. Amer. Chem. Soc.*, 1924, 46, 1051—1054).—Such nitro derivatives as were likely to be found in smokeless powder which has been stored for some time, were prepared in a state of high purity (detailed methods are given), and their colour reactions with alcoholic solutions of sodium hydroxide, ammonia, and sodium cyanide, as well as with sulphuric acid, were examined under standardised conditions. The derivatives examined were *o*-, *m*-, and *p*-nitrodiphenylamine; 2:4-, 2:4', 4:4'-dinitro-; 2:4:6- and 2:4:4'-trinitro-; 2:4:2':4'- and 2:4:6:4'-tetranitro-diphenylamines, together with diphenylnitrosoamine. The colours are compared according to the standard colour chart of Mulliken ("Identification of Pure Organic Compounds," Vol. I). An attempt to prepare *o*- and *p*-nitrodiphenylnitrosoamines by nitrating diphenylnitrosoamine in glacial acetic acid at 15° led to the formation of *p*-nitrosodiphenylamine (Fischer-Hepp rearrangement) and nitrodiphenylamines with nitro groups in the para-position. Derivatives with melting points higher than previously recorded were: 4:4'-dinitro-, 216—216.5°; 2:4'-dinitro-, 220—221.5°; and 2:4:2':4'-tetranitro-diphenylamine, 201—201.5°. A. C.

**Hydrindene.** II. W. BORSCHÉ and G. JOHN (*Ber.*, 1924, 57, [B], 656—662; cf. Borsche and Pommer, A., 1921, i, 168).—5-Aminohydrindene, coarse needles, m. p. 37—38°, b. p. 247—249°/745 mm., is prepared by the action of phosphorus pentachloride on an ethereal solution of 5-acetylhydrindeneoxime or of bromine and sodium hydroxide solution on hydrindene-5-carboxamide. When diazotised and coupled with  $\beta$ -naphthol or 5-hydroxyhydrindene, it yields 5'-hydrindeneazo- $\beta$ -naphthol, carmine-red leaflets, m. p. 156—157°, or 5'-hydrindene-4(?) -azo-5-hydroxyhydrindene, brown needles, decomp. 175°.

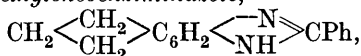
5-Hydroxyhydrindene, m. p. 55°, is obtained in moderate yield from 5-aminohydrindene through the diazo compound, or more readily by fusing sodium hydrindene-5-sulphonate with sodium hydroxide at 280—290°; the corresponding benzoate forms colourless leaflets, m. p. 106—107°. The phenol couples with diazobenzene-*p*-sulphonic acid to give the orange-red dye,



which is converted by sodium hyposulphite into 4(?)-amino-5-hydroxyhydrindene, m. p. 183—184°. 4:6-Dinitro-5-hydroxyhydrindene forms dark yellow leaflets or needles, m. p. 106—107°. 5-Hydroxyhydrindene is converted by bromine in glacial acetic acid solution into a colourless, crystalline substance, m. p. 40—41°, which loses hydrogen bromide when kept and passes into dibromo-5-hydroxyhydrindene, a colourless liquid (*benzoate*, leaflets, m. p. 139°).

5:5'-Dihydrindyl ketone,  $C_{19}H_{18}O$ , m. p. 117—118°, b. p. 245—250°/15 mm., is prepared from hydrindene-5-carboxylic chloride and hydrindene in the presence of carbon disulphide and aluminium chloride; the corresponding *oxime*, colourless needles, m. p. 173°, is isomerised to *hydrindene-5-carboxy-5'-hydrindylamide*, colourless needles, m. p. 173°, which is also obtained from hydrindene-5-carboxylic chloride and 5-aminohydrindene in the presence of pyridine.

5-Acetylhydrindene is converted successively into 4-nitro-5-acetylhydrindene, long, colourless needles, m. p. 51—52°, and 4-nitro-5-acetylhydrindeneoxime, colourless needles, m. p. 153—154°. The latter substance is transformed by successive treatment with phosphorus pentachloride and boiling hydrochloric acid (20%) into 4-nitro-5-aminohydrindene, orange-red needles, m. p. 92—93°. 4-Nitro-5-benzoylaminohydrindene, yellow crystals, m. p. 118—119°, is reduced by tin and fuming hydrochloric acid to 2-phenyl-4:5-trimethylenebenziminazole,



b. p. about 280°/50 mm., m. p. 224—226° (decomp.). De-amination of 4-nitro-5-aminohydrindene in the usual manner gives 4-nitrohydrindene, a yellow liquid, which is reduced by iron and acetic acid to 4-aminohydrindene, a colourless liquid, b. p. 235°/754 mm. (*benzoyl* derivative, colourless leaflets, m. p. 135—136°; *azo* dye, obtained with  $\beta$ -naphthol, long, red needles, m. p. 141—142°). The base is also obtained by converting hydrindene-5-carboxylic acid into *nitrohydrindene-5-carboxylic acid*, m. p. about 140° (*amide*, colourless leaflets, decomp. 194°), reduction of the acid with tin and hydrochloric acid, and distillation of the crude amino-acid with potassium hydroxide.

H. W.

**Condensation of Cyclic Hexenes with Phenol. (Chemical Structure of Lignin.)** W. SCHRAUTH and K. QUASEBARTH (*Ber.*, 1924, 57, [B], 854—858).—By condensing phenol with cyclohexene in the presence of sulphuric and acetic acids (cf. Koenigs, A., 1891, i, 208, 571) *p*-cyclohexylphenol, m. p. 130°, identical with that previously prepared from phenol and cyclohexanol (A., 1923, i, 1084) is obtained. Condensation in the presence of concentrated hydrochloric acid gives the same product in poorer yield, with some *phenyl cyclohexyl ether*, b. p. 125—127°/10 mm. In the absence of a catalyst, no condensation takes place. Similar results were obtained with the methylcyclohexenes. Condensation of phenol with the methylcyclohexenes prepared from 3-methyl-, 4-methyl-, 2-methyl-, and 1-methylcyclohexan-1-ol by Koenigs' method yielded in all cases *p*-methylcyclohexylphenol, felted needles, m. p. 112.5°,

whilst condensation with hydrochloric acid gave the same product in poorer yield, together with phenyl methylcyclohexyl ether, b. p. 129—130°/8.5 mm.,  $d_4^{20}$  0.9857. 1 : 3-Dimethyl- $\Delta^5$ -cyclohexene and phenol in the presence of hydrochloric acid yielded *dimethylcyclohexylphenol*, fine needles, m. p. 68—73°, which gives the Liebermann reaction; octahydronaphthalene similarly yields *decahydronaphthylphenol*, fine needles, m. p. 127—128°. The alkali salts of these two phenols possess lathering properties. Similar products were obtained from pinene and limonene by condensation in the presence of hydrochloric acid, but the products could not be satisfactorily purified. All the condensation products are readily soluble in organic solvents.

The property of reacting in this way with phenol appears to be characteristic of the tetrahydrobenzene ring carrying side-chains or other ring systems, and in conjunction with the observation that lignin dissolves in phenol in the presence of traces of mineral acid, supports the view that lignin possesses an unsaturated hydroaromatic structure (cf. A., 1923, i, 443; ii, 502). R. B.

**cycloHexyl Ether.** W. SCHRAUTH and W. WEGE (*Ber.*, 1924, 57, [B], 858).—Phenyl cyclohexyl ether (cf. preceding abstract) in the presence of active nickel at 165—170° and under 10—15 atm., is readily converted into cyclohexyl ether, (C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>O, a mobile, colourless liquid, b. p. 239—240°,  $d_4^{20}$  0.9241, identical with the product described by Willstätter and Hatt (A., 1912, i, 544). The discrepancy in the results obtained by Ipatiev (A., 1908, i, 342) is attributed to the high temperature and pressure employed by him (cf. A., 1923, i, 204). R. B.

**Action of Chloropicrin on Phenol.** S. BERLINGOZZI and P. BADOLATO (*Atti R. Accad. Lincei*, 1924, [v], 33, i, 290—292).—The interaction of chloropicrin and phenol in presence of potassium hydroxide results in elimination of the nitro group, which effects oxidation and is itself reduced to ammonia. The principal products are *o*- and *p*-hydroxybenzaldehydes and the corresponding acids, and considerable quantities of pararosolic acid are formed, probably by condensation of the phenol with the hydroxybenzaldehyde.

T. H. P.

**Tautomerism with Respect to Nitrosophenols.** H. H. HODGSON (*J. Soc. Dyers and Col.*, 1924, 40, 167—174).—No conclusion can be drawn from the work of previous investigators (cf. Bridge, A., 1894, i, 25) as to the existence of nitrosophenols as such, since the conditions employed in preparing derivatives all favour conversion into the quinone-oxime form before or during reaction. Similar causes are responsible for the poor yield and impure product obtained in nitrosating phenol in the usual way. If the nitrosation be carried out by dissolving the phenol in dilute sodium hydroxide solution, adding an excess of sodium nitrite, and then running dilute sulphuric acid in gradually, a clean product of m. p. 133° is obtained. When *m*-chlorophenol is

nitrosated in this way it gives 60% of the theoretical yield of *m*-chloro-*p*-nitrosophenol, needles, m. p. 135·8°, affording *m*-chloro-*p*-nitrophenol on oxidation. When boiled with dilute hydrochloric acid, the nitroso compound is converted into *syn*(?)-2-chlorobenzoquinonemonoxime, orange crystals, m. p. 172° (decomp.), and this is further converted into the *anti*(?) form, yellow needles, m. p. 178°, by solution in dilute sodium hydroxide and reprecipitation. A mixture of the two substances melts at 170·6°. The reverse change is brought about by treatment with hot dilute acid. *Anti*(?)-2-chlorobenzoquinonemonoxime may also be obtained directly from the true nitrosophenol by dissolving the latter in a saturated solution of sodium carbonate and reprecipitating it with acid. Alkali hydroxide causes further changes, impure products being obtained. W. A. S.

**Reactions of Strongly Electropositive Metals with Organic Substances in Liquid Ammonia Solution. V. Syntheses of Oxygen and Sulphur Ethers and of Alkyl Derivatives of Ammono Acids.** G. F. WHITE, A. B. MORRISON, and E. G. E. ANDERSON (*J. Amer. Chem. Soc.*, 1924, **46**, 961—968).—A number of organic compounds, containing hydroxyl, thiol, amino, or imino groups, which possess acidic character, react with the alkali metals or with alkali amides in liquid ammonia. The salts formed are more or less soluble in the liquid ammonia, and many of them react in that medium with organic halides and form compounds in which the hydrocarbon radical of the halide has replaced the metal atom of the salt. The latter reaction is often quantitative, particularly in cases where there is no action between the halide and liquid ammonia. The speed of the reaction depends largely on the solubility of the salt formed. The reactions approach the ionic type, being completed within 5 minutes at -33°. Methyl iodide reacts vigorously with liquid ammonia, producing tetramethylammonium iodide, and is therefore not suitable for these reactions. Ethyl iodide and benzyl chloride have only a slight action, whilst *n*-butyl bromide, ethylene bromide, and iodobenzene do not react at all. Aliphatic ethers were synthesised by dissolving an atomic proportion of potassium (or sodium) in liquid ammonia, adding a molecular proportion of an alcohol (when the alkoxide was partly or wholly precipitated) followed by the halide. The ether was isolated after distilling off the ammonia under water. Its yield depended largely on the solubility of the alkoxide. The yield of ethyl ether was 71% of theory, ethyl *n*-butyl ether 19%, benzyl ethyl ether 81%, benzyl ether 55%. The phenoxides of the alkali metals are more soluble in liquid ammonia and react readily with alkyl halides. Anisole was obtained in 42% yield by passing gaseous methyl chloride into a solution of sodium phenoxide in liquid ammonia. Phenetole was obtained in 59·5% yield, using ethyl bromide. A small amount of phenetole is obtained when ethyl iodide is allowed to stand with phenol in liquid ammonia in the absence of a metal. Phenyl *n*-butyl ether was obtained in 28% yield. Neither ethylene bromide nor chloride reacts with

sodium phenoxide to form diphenyl ethylene ether.  $\alpha$ -Naphthol reacts with sodium in liquid ammonia, giving a clear solution, but no hydrogen is given off, the naphthol being partly reduced to tetrahydronaphthol. A mixture of the ethers of naphthol and tetrahydronaphthol was obtained on adding an alkyl halide.  $\beta$ -Naphthyl ethyl ether was obtained in this way using ethyl iodide; yield 61% of theory. Resorcinol and ethyl iodide gave small yields of the mono- and di-ethyl ethers. Thiophenols are more reactive, and evidence of the formation of an ammonium phenyl sulphide was obtained. Thiophenol added to ethyl bromide in liquid ammonia resulted in 76% of the theoretical yield of the thio-ether, the preparation of a metal compound being unnecessary. Phenyl *n*-propyl sulphide and diphenyl ethylene disulphide were prepared in 86 and 98% yields, respectively. Certain amino and imino compounds of acidic character form metallic amides which react with alkyl (not aryl) halides. Thus acetamide forms potassium acetamide which reacts with ethyl bromide to form acetethylamide (34% yield). Diphenylamine gives a soluble potassium compound which with ethyl bromide leads to a quantitative yield of diphenylethylamine. Acetethylanilide (40% yield) and ethylphthalimide (small yield) were similarly prepared. A. C.

***o*-Nitrotoluene-*p*-sulphon-*p*-anisidide and its Nitration Products.** F. REVERDIN (*Helv. Chim. Acta*, 1924, 7, 567—574).—The following nitro derivatives of *o*-nitrotoluene-*p*-sulphon-*p*-anisidide were prepared to investigate the formation by such compounds of molecular compounds and substitution products with aliphatic and aromatic amines. Nitration of *o*-nitrotoluene-*p*-sulphon-*p*-anisidide in acetic acid solution with nitric acid, *d* 1.38, at about 0° gives a high yield of *o*-nitrotoluene-*p*-sulphon-3-nitro-*p*-anisidide, lemon-yellow crystals, m. p. 135°. It gave no definite compounds with amines. Nitration of a paste of the anisidide with glacial acetic acid at 0°, using nitric acid *d* 1.51, gave as principal product *o*-nitrotoluene-*p*-sulphon-2 : 3-dinitro-*p*-anisidide, pale yellow, transparent prisms, m. p. 178—179°. This forms a compound, m. p. 158°, with ethylamine, and a particularly stable compound with diethylamine,  $C_{14}H_{12}O_9N_4S.NH_2Et$ , lemon-yellow needles, m. p. 194°. As a by-product of the second method of nitration there is formed *o*-nitrotoluene-*p*-sulphon-2 : 5-dinitro-*p*-anisidide, lemon-yellow needles, m. p. 152°. By further nitrating the above 3-nitro-*p*-anisidide, *o*-nitrotoluene-*p*-sulphon-3 : 5-dinitro-*p*-anisidide was obtained, pale yellow needles, m. p. 147°. By heating 2 : 3-dinitro-*p*-anisidide with nitric acid, *d* 1.4, at 70—80°, *o*-nitrotoluene-*p*-sulphon-2 : 3 : 5-trinitro-*p*-anisidide is formed, small, white prisms, m. p. 188—189°. This forms compounds with ethylamine,  $C_{14}H_{11}O_{11}N_5S.NH_2Et$ , orange prisms, m. p. indistinct, near 149°, and with diethylamine,  $C_{14}H_{11}O_{11}N_5S.NH_2Et$ , lemon-yellow prisms, m. p. about 168—169°. With aniline it forms a substitution compound,  $C_{20}H_{17}O_9N_5S$ , yellow needles, m. p. 210°. The 2 : 3-dinitro-*p*-anisidide also forms a substitution compound with aniline,  $C_{20}H_{18}O_7N_4S$ , red needles, m. p. 175—176°. E. H. R.

**Sulphur Phenyl Chloride [Chlorothiolbenzene].** H. LECHER and F. HOLSCHNEIDER (*Ber.*, 1924, **57**, [B], 755—758; cf. Zincke and Baeumer, A., 1918, i, 537).—The simplest member of the series of sulphur aryl chlorides discovered by Zincke (cf. A., 1912, i, 763) has been obtained by converting phenylthiol thiocyanate (A., 1922, i, 641) with diethylamine in ethereal solution into *diethylaminothiolbenzene* (*benzenesulphendiethylamide*),  $\text{SPh}\cdot\text{Net}_2$ , colourless fluid, b. p.  $90^\circ/3.5$  mm., which on treatment with hydrogen chloride in absolute ether yields *chlorothiolbenzene*,  $\text{PhSCl}$ , a red, fuming liquid, b. p.  $73\text{--}75^\circ/9$  mm. Chlorothiolbenzene can also be obtained by the action of chlorine on thiophenol or diphenyl disulphide in carbon tetrachloride solution. Chlorothiolbenzene closely resembles sulphur dichloride both in odour and in absorption spectrum. Its constitution follows from its reaction with diethylamine to give diethylaminothiolbenzene, with zinc dust giving diphenyl disulphide, and with  $\beta$ -thionaphthol yielding phenyl  $\beta$ -naphthyl disulphide.

R. B.

**Interconversion of some Isomeric Cyclic *cis*- and *trans*-1 : 2-Glycols.** P. H. HERMANS (*Ber.*, 1924, **57**, [B], 824—827).—During the investigation of the equilibrium proportions of the *cis*- and *trans*-isomerides of certain glycols, viz., hydrindene-1 : 2-diol, tetrahydronaphthalene-1 : 2-diol and -2 : 3-diol, by the acetone method (cf. A., 1921, i, 663), it was found that equilibrium constants could not be obtained, the *cis*-diol obtained by hydrolysing the acetone compound with boiling dilute acid being partly converted into, and therefore contaminated with, the *trans*-isomeride. The reverse transformation occurs on boiling the pure *trans*-diol with dilute acid, and in boiling dilute acid solution the three 1 : 2-glycols named give equilibrium mixtures of the *cis*- and *trans*-forms. The pure *cis*-isomerides are obtained when the hydrolysis of the acetone compound is carried out with 1.5% sulphuric acid in aqueous acetone below  $50^\circ$ . From the fact that isomerisation does not occur during the formation or hydrolysis of the acetone compound, it is deduced that in these reactions only the O—H linkings of the glycol are concerned and not the C—O linkings, an observation which has some significance for the mechanism of the mutarotation of sugars. The isomerisation was not observed in the case of *cyclohexane*-1 : 2-diol.

R. B.

**Derivatives of *iso*- $\alpha$ -Naphthyl-1 : 4-dihydroxy- $\beta$ -naphthylsulphone. II.** O. HINSBERG (*Ber.*, 1924, **57**, [B], 838—840; cf. A., 1919, i, 202).—By crystallising  $\alpha$ -naphthyl-1 : 4-dihydroxy- $\beta$ -naphthylsulphone twice from acetic acid the yield of *iso*- $\alpha$ -naphthyl-2- $\alpha$ -naphthaquinonylsulphoxide is considerably improved and the by-product melting at  $225^\circ$  is not formed. The sulphoxide is also formed when the dihydroxysulphone is boiled in acetic acid solution for 6 hours. By reduction with zinc dust and sodium hydroxide in the presence of ammonia, the sulphoxide yields a grey substance, changing to bright yellow crystals, m. p.  $110^\circ$ . Reduction of the *iso*- $\alpha$ -naphthyl-2- $\alpha$ -naphthaquinonylsulphone (obtained by oxidation of the sulphoxide, A., 1919, i, 202), with

sulphurous acid and hydriodic acid in acetic acid solution, regenerates the *isosulphoxide*. The sulphoxide and sulphone are distinguished by their behaviour with ammoniacal methyl alcohol. The sulphone dissolves readily and the solution remains clear on dilution, whilst the sulphoxide only partly dissolves on boiling, and the bright yellow solution becomes turbid on adding water. Sodium hydroxide converts the sulphone into a *substance*,  $C_{20}H_{11}O_5Sn_2 \cdot 0.5H_2O$ , bright yellow needles, probably the sodium salt of *iso*- $\alpha$ -naphthyl-2- $\alpha$ -hydroxynaphthaquinonylsulphone,  $C_{10}H_7 \cdot SO_2 \cdot C_{10}H_4O_2(OH)$ . Compounds of the *iso*-series crystallise from chloroform with 0.5 mol. of solvent. R. B.

**Configuration of the Hydrobenzoin in Connexion with the Situation of the Hydroxyl Groups in Space.** J. BÖESEKEN and P. H. HERMANS (*Proc. K. Akad. Wetensch.*, 1924, **27**, 178—183).—Substitution of hydrogen atoms attached to the  $\alpha$ -carbon atom of  $\alpha$ -hydroxy acids by alkyl or phenyl groups renders the two hydroxyl groups more readily accessible to boric acid. That this substitution also favours the formation of cyclic acetone compounds is indicated by Willstätter and Königsberger's observations (A., 1923, i, 1172).

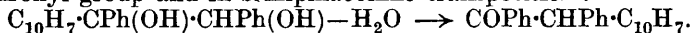
The effects of inactive and racemic hydrobenzoin on the conductivity of boric acid are analogous to those produced by esters of tartaric acid, from which it is concluded that the mutual repulsion of the phenyl groups exceeds that of the hydroxyl groups, and the hydroxyl groups in racemic hydrobenzoin are consequently strongly inclined towards each other. These results are discussed in their relationship to those previously obtained. T. H. P.

**Semipinacolinic Transformation of Arylhydrobenzoin. Comparative Migratory Tendencies of Naphthyl and Phenyl Radicals.** A. ORÉKHOFF and M. TIFFENEAU (*Compt. rend.*, 1924, **178**, 1619—1621).—In the pinacolinic transposition, the naphthyl radical, like all substituted phenyl radicals, tends to migrate more readily than the phenyl group itself. To ascertain if this is the case also in the semipinacolinic conversion, the authors have investigated the two reactions: (I)  $C_{10}H_7 \cdot CPh(OH) \cdot CHR \xrightarrow[+ AgNO_3]{- HI}$   $C_{10}H_7 \cdot CPh(O \cdot) \cdot CHR \cdot$ , and (II)  $C_{10}H_7 \cdot CPh(OH) \cdot CHR \cdot OH \xrightarrow[+ H_2O]{- H_2SO_4}$   $C_{10}H_7 \cdot CPh(O \cdot) \cdot CHR \cdot$ .

Reaction (I) yielded no useful result since, in each of the instances examined, the action of silver nitrate causes loss, not of HI, but of HOI, the hydrocarbon used for preparing the iodohydrin being regenerated. As regards reaction (II), concentrated sulphuric acid converts  $\alpha\beta$ -dihydroxy- $\alpha\beta$ -diphenyl- $\beta$ ( $\alpha$ -naphthyl)ethane into  $\alpha$ -naphthyldeoxybenzoin, m. p. 108—109°. This ketone was obtained by McKenzie and Roger (T., 1924, **125**, 845), who did not, however, fix its constitution; the latter is evident from the fact that it yields benzoic acid and phenyl- $\alpha$ -naphthylmethane when treated with alcoholic potassium hydroxide. Evidently the



action of the sulphuric acid results in elimination of the secondary hydroxyl group and in semipinacolinic transposition :



That the reaction takes place in this manner is rendered more probable by the fact that McKenzie and Richardson (T., 1923, 123, 79) obtained the same ketone by the action of nitrous acid on the amino-alcohol corresponding with  $\alpha\beta$ -dihydroxy- $\alpha\beta$ -diphenyl- $\beta$ -( $\alpha$ -naphthyl)ethane, by so-called "semipinacolinic de-amination."

T. H. P.

**Insecticides. VII. Syntheses of Chrysanthemumic Acid and other *cyclo*Propanecarboxylic Acids with Unsaturated Side Chains.** H. STAUDINGER, O. MUNTWYLER, L. RUZICKA, and S. SEIBT (*Helv. Chim. Acta*, 1924, 7, 390—406).—The monocarboxylic acid obtained from pyrethrine I, one of the active constituents of insect powder (this vol., i, 510), and identified as 2 : 2-dimethyl-3-isobutenylcyclopropane-1-carboxylic acid, has been synthesised by condensing  $\beta\epsilon$ -dimethyl- $\Delta^{88}$ -hexadiene with ethyl diazoacetate. (The hexadiene was obtained in a novel manner by distilling  $\beta\epsilon$ -dichloro- $\beta\epsilon$ -dimethylhexane with soda-lime.) A mixture of *cis*- and *trans*-acids was thus obtained, forming a colourless oil, b. p. 140—145°/12 mm., from which on cooling the *cis*-isomeride gradually separated, m. p. 115—116°. The *trans*-isomeride was only obtained in an impure form, b. p. 145—146°/13 mm. By the action of ozone, the two isomerides give, respectively, *cis*- and *trans*-caronic acid. Both acids give insecticidal esters with pyrethrolone, that from the *trans*-acid being the more active. The natural ester is from the *d-trans*-acid, but the synthetic acid has not yet been resolved. A number of related acids were also synthesised, using other butadiene derivatives, but only those from  $\beta\gamma$ -dimethylbutadiene and isoprene gave insecticidal esters with pyrethrolone, and these were weaker than the true pyrethrins. Purely aliphatic acids of similar structure but without the *cyclo*propane ring, such as  $\beta\zeta$ -dimethyl- $\Delta^c$ -heptene- $\gamma$ -carboxylic acid,  $\text{CHMe}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CH}:\text{CMe}_2$ , do not form insecticidal esters.

By the action of ethyl diazoacetate on  $\beta\delta$ -dimethyl- $\Delta^{88}$ -hexadiene an ester was obtained which on hydrolysis gave an acid,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ , b. p. 140—145°/13 mm., which appeared to be a mixture of isomerides. Using  $\beta$ -methyl- $\Delta^{88}$ -hexadiene and  $\beta\delta$ -dimethyl- $\Delta^{\alpha\gamma}$ -penta-diene, mixed products were also obtained. From ethyl diazoacetate and  $\beta\gamma$ -dimethylbutadiene, 2-methyl-2-isopropenylcyclopropanecarboxylic acid, b. p. 122—123°/15 mm., was obtained; chloride, b. p. 90°/11 mm. By oxidation with ozone followed by permanganate, the acid gave a methylcyclopropanedicarboxylic acid, m. p. 168—169°. Ethyl diazoacetate and  $\Delta^{88}$ -hexadiene give 2-methyl-3-propenylcyclopropanecarboxylic acid, a liquid, b. p. 126°/9 mm.; chloride, b. p. 86°/9 mm. Isoprene and ethyl diazoacetate give *trans*-2-isopropenylcyclopropanecarboxylic acid, a colourless oil, b. p. 115—119°/12 mm.; chloride, b. p. 62—64°/13 mm. From its ozonide was obtained 2-acetylcyclopropanecarboxylic acid, crystals, m. p. 52—54° (*semicarbazone*, m. p. 177—179°). Further oxidation

with permanganate gives *trans*-cyclopropane-1 : 2-dicarboxylic acid. Hydrocarbons of the terpene series also condense with ethyl diazoacetate to give cyclopropanecarboxylic acid derivatives of uncertain constitution.

By condensing ethyl methylmalonate with dimethylallyl bromide,  $\alpha\delta$ -dimethyl- $\Delta^7$ -hexenoic acid was obtained, b. p. 125°/15 mm.; chloride, b. p. 80—85°/12 mm.  $\beta\zeta$ -Dimethyl- $\Delta^6$ -heptene- $\gamma$ -carboxylic acid, from dimethylallyl bromide and ethyl isopropylmalonate, is a colourless oil, b. p. 140—145°/12 mm.; chloride, b. p. 115°/10 mm.  $\beta$ -Methyl- $\Delta^{8,9}$ -octadiene- $\epsilon$ -carboxylic acid,

$\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ ,  
colourless oil, b. p. 137—138°/10 mm., is obtained from dimethylallyl bromide and ethyl allylmalonate; chloride, b. p. 84°/10 mm.  
E. H. R.

**Modification of the Sandmeyer Synthesis of Nitriles.** H. T. CLARKE and R. R. READ (*J. Amer. Chem. Soc.*, 1924, **46**, 1001—1003).—A method of preparing nitriles which avoids the evolution of hydrogen cyanide is described. The diazonium solution is neutralised by means of sodium carbonate at 0—4° and poured into a similarly cooled solution of sodium cuprocyanide, the surface of which is first covered with a layer of benzene. With good stirring, the benzene (in which the nitrile is soluble) is drawn beneath the surface and a rise in temperature prevented. Yields of nitriles up to 60—70% of the theoretical were obtained using aniline, *o*-toluidine, *p*-toluidine, and other amines. In the absence of the benzene, the reaction product comes to the surface as a dark brown oil, in which, after a few moments, a vigorous action is set up and fumes smelling of phenylcarbylamine are given off. A. C.

**Electrochemical Reductions in Acid Solution.** K. KINDLER, O. GIESE, and A. ISBERG (*Ber.*, 1924, **57**, [B], 773—775).—An examination of the reduction of phenylacetamide, phenylthioacetamide, and their *N*-alkyl derivatives shows that the more *N*-methyl groups there are present the more rapid is the electrochemical reduction and the slower the reduction by aluminium amalgam. The figures in brackets give the percentage of the theoretical yield of amine formed by reduction of the corresponding amide. (I) Electrochemical reduction (cf. A., 1923, i, 568, 1090):  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}_2$  (<1%);  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NHMe}$  (80%);  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NMe}_2$  (92%);  $\text{CH}_2\text{Ph}\cdot\text{CS}\cdot\text{NHMe}$  (80%);  $\text{CH}_2\text{Ph}\cdot\text{CS}\cdot\text{NMe}_2$  (100%). No phenylacetaldehyde was observed as a by-product. (II) Reduction with aluminium amalgam:  $\text{CH}_2\text{Ph}\cdot\text{CS}\cdot\text{NH}_2$  (74%);  $\text{CH}_2\text{Ph}\cdot\text{CS}\cdot\text{NHMe}$  (2%);  $\text{CH}_2\text{Ph}\cdot\text{CS}\cdot\text{NMe}_2$  (<1%). During the electrolysis of an aqueous-alcoholic hydrochloric acid solution of phenylacetdimethylamide, its concentration around the cathode increased, whereas with phenylacetamide no such increase was noted. It is suggested that during electrolysis of the strongly acid solution the first stage is the addition of acid to form the ammonium or oxonium salts, the cations of which, after giving up their charge, are converted into free radicals which then readily undergo reduction at the cathode.  
F. A. M.

**Syntheses by means of Sodamide. Preparation of Benzyl Phenylalkylacetates and the Corresponding Acids.** (MME.) RAMART and A. HALLER (*Compt. rend.*, 1924, **178**, 1583—1587; cf. this vol., i, 171, 286).—At the ordinary temperature, the action of sodamide on phenyl formate yields sodium phenoxide, ammonia, and carbon monoxide, and on phenyl acetate, sodium phenoxide and acetamide. Treatment of benzyl isobutyrate in xylene solution with sodamide and then with benzyl chloride yields *N*-benzylisobutyramide and another compound, m. p. 65—66°, of unknown constitution.

With benzyl phenylacetate, a similar reaction occurs, the temperature gradually rising and phenylacetamide and phenylacetbenzylamide being formed. If, however, the reaction is carried out at 0° and the flask is connected through a reflux condenser with a vacuum pump so as to facilitate the disengagement of ammonia, little amide is formed but instead the sodium derivative of the ester,  $C_7H_7 \cdot O \cdot CO \cdot CHPhNa$  or  $C_7H_7 \cdot O \cdot C(ONa) \cdot CHPh$ ; when the evolution of ammonia becomes very slight, the alkyl or benzyl halide is added gradually, the product being finally treated with water and the mixture of esters rectified in a vacuum.

Benzyl  $\alpha$ -phenylpropionate (hydratropate), formed under these conditions, could not be separated from the benzyl phenylacetate, but is readily separated as acid (cf. Fittig and Würster, A., 1879, 379). *Benzyl phenylallylacetate*, similarly obtained, forms an oil, b. p. 210—212°/25 mm. (cf. Buddeberg, A., 1890, 1142). *Benzyl benzylphenylacetate* is a yellow, oily liquid, b. p. 250—255°/18 mm.

T. H. P.

**Higher Terpene Compounds. XXII. l-Pimaric Acid.** L. RUZICKA, F. BALAS, and F. VILIM (*Helv. Chim. Acta*, 1924, **7**, 458—471).—Improved methods for obtaining *l*-pimaric acid from galipot are described, consisting in fractionally crystallising the resinic acids from acetone, a procedure which may be preceded by fractional crystallisation of the sodium salts (cf. Dupont, A., 1921, i, 510). *l*-Pimaric acid is more stable in the form of its sodium salt than *d*-pimaric acid. Hydrogenation experiments show that *l*-pimaric, like abietic acid, has two double bonds (cf. A., 1923, i, 818). *Dihydro-l-pimaric acid* is obtained by hydrogenation of *l*-pimaric acid with colloidal platinum and hydrogen in ethyl acetate; it consists apparently of a mixture of isomerides, the first fraction of which, from alcohol, forms crystals, m. p. 142—144°,  $[\alpha]_D +24^\circ$  in 1% alcoholic solution. More energetic hydrogenation by the method of Willstätter and Waldschmidt-Leitz (A., 1921, ii, 185) resulted in the formation of *tetrahydro-l-pimaric acid*, a mixture of isomerides, m. p. 120—160°. The molecular refractions of the esters of *l*-pimaric acid also indicate the presence of two double bonds; the *methyl* ester is a viscous oil, b. p. 166—169°/0.5 mm.,  $[\alpha]_D -190.36^\circ$  in 5% alcoholic solution,  $d_4^{25} 1.0312$ ;  $n_D^{25} 1.5232$ ; when kept, the oil formed long crystals, m. p. 57°; the *ethyl* ester is a viscous oil, b. p. 175—177°/0.5 mm.,  $[\alpha]_D -170.9^\circ$  in 6% alcoholic solution,  $d_4^{25} 1.0124$ ;  $n_D^{25} 1.5153$ .

When *l*-pimaric acid is heated in boiling acetic acid, an isomeride is formed, m. p. 167—168°,  $[\alpha]_D -103.7^\circ$ , corresponding in crystal-line form with abietic acids from various sources, whilst by heating at 300° it is converted into an isomeride, m. p. 175—176°,  $[\alpha]_D +22.3^\circ$ , corresponding with abietic acid from American colophony, m. p. 178—179°,  $[\alpha]_D +3^\circ$  (A., 1922, i, 547). It is concluded, therefore, that *l*-pimaric acid belongs to the group of spatially isomeric abietic acids. *d*-Pimaric acid is a structural isomeride and does not belong to the abietic acid group. In agreement with this view, *l*-pimaric acid gives retene when dehydrogenated with sulphur, and resembles abietic acid in other respects. E. H. R.

**isoFenchocarboxylic Acid.** S. NAMETKIN and A. RUSCH-ENTZEV (*J. pr. Chem.*, 1923, **106**, 39—40).—The acid is prepared by passing dry carbon dioxide into a cold solution of isofenchone in ether in the presence of sodium wire. After the vigorous reaction has subsided, the mixture is heated for 3 days. The ether is then evaporated, excess of sodium removed, and the residue decomposed by water. The viscid residual mass is washed with ether, acidified with sulphuric acid, and the acid purified through its sodium salt. It melts at 87—88° with evolution of carbon dioxide. With ferric chloride, it yields a dark blue coloration, rapidly turning dirty green. The acid decomposes rapidly, even in the dark, yielding isofenchone and a white solid, m. p. 230—231°. F. G. P.

**Action of Sodium Hydrogen Sulphite on Chlorides of the Hydroximic Acids.** VII. C. GASTALDI (*Gazzetta*, 1924, **54**, 220—226).—The ready replacement of the chlorine atom by hydroxyl observed when chloroximinoacetone is treated with sodium hydrogen sulphite (cf. A., 1923, i, 1236) occurs also in other similar cases and furnishes a means of preparing hydroxamic acids not obtainable by the ordinary methods.

*Benzoylformhydroxamic acid*,  $\text{COPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$  or  $\text{OH}\cdot\text{CBz}\cdot\text{NOH}$ ,

prepared from  $\alpha$ -chloro- $\alpha$ -oximinoacetophenone, forms stable, colourless prisms or pink laminæ, m. p. 117° (decomp.), and forms two oximes: (1) the  $\alpha$ -modification,  $\text{NOH}\cdot\text{CPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$  or  $\text{NOH}\cdot\text{CPh}\cdot\text{C}(\text{OH})\cdot\text{NOH}$ , crystallises in colourless prisms, m. p. 177° (decomp.), and in aqueous solution gives with nickel acetate and ammonia a green precipitate soluble in dilute acetic acid; (2) the  $\beta$ -modification, prepared by the action of sodium hydrogen sulphite on benzoylformhydroximic chloride oxime (chlorophenylglyoxime) (cf. Ponzio and Avogadro, A., 1923, i, 472), forms pale yellow laminæ, m. p. 189° (decomp.), and differs from the  $\alpha$ -form in giving with nickel acetate a brick-red precipitate insoluble in dilute acetic acid or ammonia solution. *Benzoylformhydroxamic acid phenylhydrazone*,  $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}_3$ , crystallises in yellow needles, m. p. 127°. T. H. P.

**3:4:5-Trihydroxycinnamic Acid and the Mechanism of Knoevenagel's Cinnamic Acid Synthesis.** K. W. ROSENMUND and T. BOEHM (*Annalen*, 1924, **437**, 125—147).—Gallaldehyde on warming with one or two mols. of aniline and malonic acid in

alcoholic solution yields a yellow solid which on heating at 155—160° melts with evolution of carbon dioxide. Treatment with hydrochloric acid converts the substance into the known hydrochloride of gallaldehyde-aniline, an additive compound, not a Schiff's base. The yellow solid proves to be a normal malonate of the aldehyde-aniline,  $[C_6H_2(OH)_3 \cdot CH(OH) \cdot NPh]_2 \cdot CH_2(CO_2H)_2$ , and the expected trihydroxycinnamic acid could not be obtained from this reaction. Protocatechualdehyde behaves similarly, and these results suggest that the primary product in the reaction is not a benzylidenemalonic acid, as Knoevenagel suggested (A., 1899, i, 144), but a benzylideneaniline (cf. Dimroth and Zoepprit, A., 1902, i, 292). These additive products form stable salts with strong acids (cf. Dimroth, A., 1902, i, 292), and do not react with malonic acid to give substituted acrylic acids. The Schiff's bases do not form stable salts, but react with malonic acid, yielding substituted acrylic acids. The formation of acrylic acid derivatives is thus conditional on the existence of a double bond between carbon and nitrogen, and it is suggested that the malonic acid attacks the molecule at this point:  $CHPh \cdot NPh + CH_2(CO_2H)_2 \rightarrow NPh \cdot CHPh \cdot CH(CO_2H)_2$ . The resulting  $\beta$ -anilindicarboxylic acid is unstable (cf. Goldstein, A., 1895, i, 470; 1896, i, 435) and easily loses carbon dioxide, yielding a  $\beta$ -substituted  $\beta$ -anilino-propionic acid, e.g.,  $NPh \cdot CHPh \cdot CH_2 \cdot CO_2H$ , which is decomposed by mineral acid, yielding aniline and the corresponding acrylic acid. On this theory, the failure of attempts to prepare trihydroxycinnamic acid from gallaldehyde, aniline, and malonic acid is attributed to the weakly basic character of aniline as opposed to the relatively acidic gallaldehyde. When instead of aniline, the stronger base piperidine was used, 3:4:5-trihydroxycinnamic acid was obtained in good yield.

Attempts were also made to prepare trihydroxycinnamic acid by condensing gallaldehyde with malonic acid derivatives. Ethyl malonate and cyanoacetic acid gave no result, but with malononitrile gallaldehyde yields  $\beta\beta$ -dicyano-3:4:5-trihydroxystyrene,  $C_6H_2(OH)_3 \cdot CH:C(CN)_2$ , m. p. 250° (decomp.), which by acid hydrolysis is converted into  $\alpha$ -cyano-3:4:5-trihydroxycinnamamide,  $C_6H_2(OH)_3 \cdot CH:C(CN) \cdot CO \cdot NH_2$ . On further hydrolysis, this yields  $\alpha$ -cyano-3:4:5-trihydroxycinnamic acid, but the hydrolysis of the second cyano group could not be effected. Condensation of gallaldehyde with rhodanine gave a trihydroxybenzylidenerrhodanine,  $C_6H_2(OH)_3 \cdot CH:C \begin{smallmatrix} S-CH \\ | \\ CO-NH \end{smallmatrix}$ , but attempts to prepare from

this  $\alpha$ -thioltrihydroxycinnamic acid were unsuccessful.

$\beta\beta$ -Dicyano-3:4:5-triacetoxystyrene (from triacetyl-gallaldehyde and malononitrile) has m. p. 139—140°.  $\beta\beta$ -Dicyano-3:4-dihydroxystyrene forms yellow needles, m. p. 221° (decomp.); acetyl derivative, m. p. 110—111°. Hydrolysis with 38% hydrochloric acid converts the dicyanotrihydroxystyrene into  $\alpha$ -cyano-3:4:5-trihydroxycinnamamide, reddish-yellow needles, m. p. 268° (decomp.), which was also obtained by condensation of gallaldehyde with cyanoacetamide; triacetyl derivative, m. p. 210—211°.  $\alpha$ -Cyano-3:4-di-

*acetoxycinnamamide* has m. p. 196—198°. Condensation of gallaldehyde with ethyl cyanoacetate in the presence of sodium ethoxide yields *ethyl α-cyano-3:4:5-trihydroxycinnamate*, yellow needles, m. p. 201—202° (*triacetyl* derivative, m. p. 142°), which on careful hydrolysis with dilute sodium hydroxide yields *α-cyano-3:4:5-trihydroxycinnamic acid*, small, pale yellow plates, m. p. 210—212° (decomp.); *triacetyl* derivative, m. p. 180°. Protocatechualdehyde similarly yields *ethyl α-cyano-3:4-dihydroxycinnamate*, yellow needles, m. p. 168° (*diacetyl* derivative, m. p. 97°), which by alkaline hydrolysis gives *α-cyano-3:4-dihydroxycinnamic acid* (*α-cyano-caffeic acid*), yellow plates, m. p. 224—225° (decomp.); *diacetyl* derivative, m. p. 195—196°.

Gallaldehyde condensed with rhodanine in the presence of sodium hydroxide yields amorphous *3:4:5-trihydroxybenzylidenerhodanine*, which gives a crystalline *triacetyl* compound, m. p. 222—223°. Similarly, protocatechualdehyde and rhodanine (in alcoholic sulphuric acid) yield *3:4-dihydroxybenzylidenerhodanine*, small, yellowish-brown tablets, m. p. 270—280° (decomp.); *diacetyl* derivative, m. p. 217—218°. Phenylrhodanine gives *phenyl-*

*3:4-dihydroxybenzylidenerhodanine*, 
$$\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}:\text{C} \begin{array}{l} \text{<S—CS} \\ \text{CO—NPh} \end{array}$$

dense yellow lances, m. p. 268—270° (decomp.); *diacetyl* derivative, m. p. 195°. Gallaldehyde and aniline in alcoholic solution give with hydrogen chloride a yellow precipitate of *gallaldehydeaniline hydrochloride* (*hydroxy-3:4:5-trihydroxyphenylmethylaniline hydrochloride*,  $\text{C}_6\text{H}_2(\text{OH})_3\cdot\text{CH}(\text{OH})\cdot\text{NHPH}\cdot\text{HCl}$ , m. p. 226°, which does not lose water at 130°. The free base crystallises in yellow needles (+1H<sub>2</sub>O), which lose water at 80° and melt at 190—192°, yielding the Schiff's base, *3:4:5-trihydroxybenzylideneaniline*, which on warming with hydrochloric acid is reconverted into the gallaldehydeaniline hydrochloride. The *malonate* (*supra*) forms yellow needles, m. p. 171°. *Protocatechualdehydeaniline hydrochloride* forms fine, yellowish-brown needles, m. p. 231—232°; *malonate*, m. p. 173°.

*3:4:5-Trihydroxycinnamic acid* forms colourless needles (+1H<sub>2</sub>O), m. p. 207—208°; the water is lost at 120°; *triacetyl* derivative, needles, m. p. 168°. The acid is distinguished from gallic acid and gallaldehyde by its ferric chloride reaction (dark green coloration, changing to clear yellow on dilution) and by the fine carmine-red to violet coloration produced with potassium cyanide. With bromine (2 mols.) in acetic acid solution, the trihydroxycinnamic acid yields a *dibromo* derivative,  $\text{C}_9\text{H}_6\text{O}_5\text{Br}_2$ , colourless needles, m. p. 186—187°, probably 2:6-dibromo-3:4:5-trihydroxycinnamic acid. The *triacetyl* derivative similarly yields the corresponding *dibromotriacetoxycinnamic acid*,  $\text{C}_{15}\text{H}_{12}\text{O}_8\text{Br}_2$ , long tablets, m. p. 183°. R. B.

**Preparation of *p*-isopropylphenylacetaldehyde and some of its Isomerides and Homologues.** P. CHUIT and J. BOLLE (*Bull. Soc. chim.*, 1924, [iv], **35**, 200—205).—*p*-isopropylphenylacetaldehyde (cf. A., 1923, i, 1101) may be prepared as a colourless liquid, b. p. 116.5—117°/11 mm.,  $d^{15}_4$  0.980,  $n^{20}_D$  1.51071, by con-

densing cumaldehyde with ethyl chloroacetate in presence of sodium ethoxide. The product is hydrolysed and then steam-distilled in presence of excess of oxalic acid solution. The semicarbazone melts at  $172^{\circ}$ , not at  $181^{\circ}$  (cf. Bert, *loc. cit.*). The aldehyde polymerises to a viscous oil on standing. In a similar manner, from 2:4:6-trimethylbenzaldehyde, 2:4:6-trimethylphenylacetaldehyde is obtained, m. p.  $61^{\circ}$ , b. p.  $137-140^{\circ}/13$  mm., having a faint disagreeable odour. 3:4:6-Trimethylphenylacetaldehyde is a colourless liquid, b. p.  $127-129^{\circ}/15$  mm.,  $d^{15}_4$  0.998,  $n^{15}_D$  1.5311; semicarbazone, m. p.  $191^{\circ}$ .

By the condensation of ethyl chloroglyoxylate with *p*-cymene in presence of aluminium chloride, ethyl cymylglyoxylate is formed (b. p.  $175-180^{\circ}/12$  mm.) which, on conversion into the acid and boiling with excess of aniline, forms the phenylimide (b. p.  $200-202^{\circ}/14$  mm.). By warming the latter with dilute hydrochloric acid, 6-methyl-3-isopropylbenzaldehyde is obtained, a colourless liquid, b. p.  $121-121.3^{\circ}/14$  mm.,  $d^{15}_4$  0.978,  $n^{15}_D$  1.5108. Condensation of this with chloroacetic acid as above yields 2-*p*-cymylacetaldehyde, b. p.  $128.5-129^{\circ}/13$  mm.,  $d^{15}_4$  0.967,  $n^{15}_D$  1.5175; semicarbazone, m. p.  $160^{\circ}$ .

Poor yields of *m*-cymylaldehyde (2-methyl-4-isopropylbenzaldehyde) are obtained from *m*-cymene by Gattermann's synthesis. It is a liquid, b. p.  $115-118^{\circ}/13$  mm.,  $d^{15}_4$  0.972; semicarbazone, m. p.  $198-199^{\circ}$ . It oxidises in air to a steam-volatile cymylcarboxylic acid, m. p.  $77.5^{\circ}$ , which is also one product of oxidation by boiling dilute nitric acid. The other product is 3-methylterephthalic acid, the formation of which proves the constitution of the original compound. 2-*m*-Cymylacetaldehyde, prepared by the above general method, is a colourless liquid, b. p.  $123-126^{\circ}/12$  mm.,  $d^{15}_4$  0.973,  $n^{15}_D$  1.5203, semicarbazone, m. p.  $158-159^{\circ}$ . E. E. T.

### Isomerisation of Nitroaldehydes by Chemical Means.

G. HELLER (*J. pr. Chem.*, 1923, **106**, 1-16).—*o*-Nitrobenzaldehyde on exposure to light in indifferent solvents is converted into *o*-nitrosobenzoic acid, in alcoholic solution into the related esters. Similarly, on exposure to light in absolute hydrocyanic acid, the nitrosobenzoic acid results, whilst *o*-nitromandelonitrile under the same conditions loses hydrogen cyanide and gives the acid. The question whether oxygen can be thus transferred from the nitro to the aldehyde group by chemical methods has not been satisfactorily settled. It has been found that potassium cyanide reacts with an aqueous-alcoholic solution of *o*-nitrobenzaldehyde readily in the cold, necessitating external cooling, *o*-nitrosobenzoic acid being found in the reaction product, and ammonium *o*-nitrosobenzoate is obtained by dissolving *o*-nitromandelonitrile in alcoholic ammonia. The conversion of *o*-nitrobenzaldehyde into the nitrosobenzoic acid without isolating the nitromandelonitrile is best accomplished by the action of a solution of potassium cyanide and ammonium acetate in concentrated ammonia on an alcoholic solution of the nitrobenzaldehyde, almost pure ammonium nitrosobenzoate being precipitated. *o*-Nitromandelonitrile is probably

first produced by the action of potassium cyanide, and loses hydrogen cyanide, forming *o*-nitrosobenzoic acid at the same time. Ekecrantz and Ahlqvist (A., 1908, i, 347) by the action of potassium cyanide on a hot alcoholic solution of the *o*-nitroaldehyde obtained azoxybenzoic acid and nitrosobenzoic acid, but since alkali does not act so smoothly on *o*-nitromandelonitrile as ammonia does, their investigation could not lead to a homogeneous result. By altering the conditions, it is found that small quantities of azoxybenzoic acid may be obtained. *o*-Nitropiperonal can be converted into the mandelonitrile by the action of potassium cyanide on its hydrogen sulphite compound, the nitrile produced yielding the nitroso-acid on treatment with alcoholic ammonia, or by the direct action of the alcoholic ammoniacal ammonium cyanide solution on the nitroaldehyde. The ammonium cyanide acts as an oxygen carrier since less than 1 mol. is sufficient. 2-Nitro-5-chlorobenzaldehyde and the corresponding 5-bromoaldehyde are readily converted into the nitroso-acids. Nitrohydroxyaldehydes give only resinous products, as do *o*-nitrovanillin and nitroterephthalaldehyde. In all these cases also, no cyanohydrin could be obtained from the aldehyde. 2:4-Dinitrobenzaldehyde reacts normally with ammonium cyanide to give 4-nitro-2-nitrosobenzoic acid, but by the action of potassium cyanide in glacial acetic acid solution yields 2-nitro-4-nitrosobenzoic acid. No analogous compounds were obtained from trinitrobenzaldehyde. Attempts to carry out the reaction with such substances as  $\beta$ -*o*-nitrophenyl-lactonitrile,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\text{CN}$ , and  $\gamma$ -*o*-nitrocinnamylglycollonitrile,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{OH})\text{CN}$ , gave negative results either with the nitriles themselves or with the parent nitroaldehydes. Oxygen is therefore not capable of migrating into the side chain from a neighbouring nitro group. *o*-Nitrophenyl-lactonitrile has been converted into the acid amide by hydrolysis with 75% sulphuric acid, and the amide into the acid by heating with concentrated sulphuric acid and glacial acetic acid. By reduction of the acid with zinc dust and hydrochloric acid, 3-hydroxycarbostyrl is produced.

*m*-Nitroaldehydes behave quite differently, yielding only amorphous products. 2-Chloro-5-nitrobenzaldehyde in glacial acetic acid solution yields a cyanohydrin, but from this only a compound of complex type was obtained by the use of the alcoholic ammoniacal ammonium cyanide solution. With *p*-nitrobenzaldehyde, an amorphous product was obtained.

A repetition of the work of Ekecrantz and Ahlqvist (*loc. cit.*) showed that *o*-nitrobenzaldehyde in the presence of a small quantity of potassium cyanide does not yield azoxybenzoic acid, but that *o*-nitrosobenzoic acid and a compound,  $\text{C}_{14}\text{H}_8\text{O}_6\text{N}_2$  (in very small yield), m. p. 162—163°, are produced. On the other hand, by increasing the amount of potassium cyanide, *o*-nitrosobenzoic acid, the compound  $\text{C}_{14}\text{H}_8\text{O}_6\text{N}_2$ , and azoxybenzoic acid are obtained.

[With H. KRETZSCHMANN.]—*o*-Nitropiperonalcyanohydrin,  $\text{C}_9\text{H}_6\text{O}_5\text{N}_2$ , crystallises in pale yellow needles, m. p. 119°. *o*-Nitrosopiperonylic acid,  $\text{C}_8\text{H}_5\text{O}_5\text{N}$ , a yellow, crystalline powder, sinters at 160—165°, and melts at about 198°.



[With H. GRUNDMANN.]—5-Bromo-2-nitrosobenzoic acid crystallises in pale brown needles, m. p. 173°. 4-Nitro-2-nitrosobenzoic acid,  $C_7H_4O_5N_2$ , from 2:4-dinitrobenzaldehyde, has m. p. above 300°; its methyl ester crystallises in silky needles, m. p. 137° to a green liquid. 2-Nitro-4-nitrosobenzoic acid is a yellow, crystalline solid, m. p. about 230°. On oxidation with fuming nitric acid, it yields dinitrobenzoic acid. Its methyl ester crystallises in yellow needles, m. p. 141° to a green liquid.  $\beta$ -o-Nitrophenyl-lactonitrile,  $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH(OH)CN$ , from the hydrogen sulphite compound of o-nitrophenylacetaldehyde, crystallises in plates, m. p. 70–71°. On hydrolysis with 75% sulphuric acid, it is converted into the lactamide,  $C_9H_{10}O_4N_2$ , needle aggregates, m. p. 195°. By heating the lactamide in glacial acetic acid with excess of concentrated sulphuric acid, o-nitrophenyl-lactic acid is obtained, nearly colourless needles, m. p. 72°.

[With H. JÜRGENS.]—o-Nitrocinnamylglycollonitrile,  $C_{10}H_8O_3N_2$ , obtained by the action of absolute hydrocyanic acid on o-nitrocinnamaldehyde, has m. p. 79°. By the action of alcoholic ammonia, hydrocyanic acid is eliminated and tarry products are obtained. Dilute solutions of sodium hydroxide regenerate the aldehyde.

[With K. MÜLLER-BARDOFF.]—2-Chloro-5-nitromandelonitrile, obtained by the action of potassium cyanide on a glacial acetic acid solution of the corresponding aldehyde, crystallises in scales, m. p. 124°. Alcoholic ammonia converts it into a complex, crystalline substance, m. p. 303°, containing 15.4% N, insoluble in acids and alkalis and scarcely soluble in any of the organic solvents.

F. G. P.

**Mercuration of Nitrohydroxybenzaldehydes.** T. A. HENRY and T. M. SHARP (*J. Chem. Soc.*, 1924, **125**, 1049–1060; cf. A., 1923, i, 726).—The previously described *m*-hydroxyacetoxymercuribenzenaldehyde (T., 1922, **121**, 1059) is now shown to be the 2-acetoxymercuri compound, from its conversion into 2-nitro-3-hydroxybenzaldehyde and into an iodo-*m*-hydroxybenzaldehyde yielding 2:3-dihydroxybenzoic acid on heating with sodium hydroxide.

The work has been extended to the nitrobenzaldehydes, which did not yield mercury derivatives, and to the nitrohydroxybenzaldehydes. The mercuration is effected by boiling with mercuric acetate and a small amount of acetic acid in 50% alcoholic solution. The dimercuri compounds obtained from 6-nitro-, 4-nitro-, and 2-nitro-3-hydroxybenzaldehyde on treatment with bromine all yield 2:4-dibromo-6-nitro-3-hydroxybenzaldehyde, the nitro groups in the 2 and 4 positions changing places with the bromine atom, which replaces mercury in position 6. The reaction with iodine is normal.

Mercuration of 3-nitro-4-hydroxybenzaldehyde yields only 3-nitro-4-hydroxy-5-hydroxymercuribenzenaldehyde, small orange plates, darkening at 285°, but not melting at 300°, which by solution in sodium hydroxide and precipitation with hydrochloric acid is

converted into 3-nitro-4-hydroxy-5-chloromercuribenzenaldehyde, colourless needles, m. p.  $226^{\circ}$  (decomp.), and on crystallisation from acetic acid yields 3-nitro-4-hydroxy-5-acetoxymmercuribenzenaldehyde, colourless prisms, darkening at  $250^{\circ}$ . With iodine in potassium iodide solution, the hydroxymmercuri compound yields 5-iodo-3-nitro-4-hydroxybenzenaldehyde, yellow plates, m. p.  $171-172^{\circ}$ . Similarly, 6-nitro-3-hydroxybenzenaldehyde yields first an orange solid, apparently a mixture of the diacetoxymmercuri and dihydroxymmercuri compounds, whilst from the mother-liquors mixtures of mono- and di-mercurated products are obtained. The orange solid by crystallisation from propionic acid is converted into 6-nitro-3-hydroxy-2:4-dipropoxydimmercuribenzenaldehyde, orange-yellow needles, exploding at  $235^{\circ}$ . Its solution in sodium hydroxide on treatment with hydrochloric acid precipitates 6-nitro-3-hydroxy-2:4-dichlorodimmercuribenzenaldehyde, colourless needles. The pale yellow 6-nitro-3-hydroxychloromercuribenzenaldehyde obtained from the more soluble fractions decomposes at  $198^{\circ}$ , and with iodine solution yields an iodo-6-nitro-3-hydroxybenzenaldehyde, yellow prisms, m. p.  $206^{\circ}$  (decomp.), and a small quantity of 2:4-di-iodo-6-nitro-3-hydroxybenzenaldehyde, yellow prisms or needles, m. p.  $142^{\circ}$  (decomp.); semicarbazone, m. p.  $214^{\circ}$  (decomp.); oxime, m. p.  $207-208^{\circ}$  (decomp.). The di-iodo compound is formed almost quantitatively by the action of iodine on the dimmercuri compound, a small quantity of a mercuric iodide additive compound,  $2C_7H_3O_4NI_2 \cdot HgI_2$ , m. p.  $184^{\circ}$  (decomp.), being also sometimes formed, and this on decomposition with hydrogen sulphide yields mercuric sulphide and 2:4-di-iodo-6-nitro-3-hydroxybenzenaldehyde. The dimmercurated compound on treatment with bromine in alcoholic solution yields 2:4-dibromo-6-nitro-3-hydroxybenzenaldehyde, colourless prisms, m. p.  $152.5^{\circ}$  (decomp.), which on oxidation with alkaline permanganate is converted into 2:4-dibromo-6-nitro-3-hydroxybenzoic acid, colourless needles, m. p.  $230^{\circ}$  (decomp.), identical with the acid obtained by oxidising 2:4-dibromo-6-nitro-m-cresol.

4-Nitro-3-hydroxybenzenaldehyde on mercuration yields an orange-coloured 4-nitro-3-hydroxy-hydroxymmercuriacetoxymmercuribenzenaldehyde, which on crystallisation from formic acid is converted into 4-nitro-3-hydroxy-2:6-diformoxydimmercuribenzenaldehyde, pale yellow needles, darkening at  $120^{\circ}$ , exploding at  $257^{\circ}$ . From its solution in potassium hydroxide, hydrochloric acid precipitates 4-nitro-3-hydroxy-2:6-dichlorodimmercuribenzenaldehyde, pale yellow needles ( $+1H_2O$ ), darkening at  $240^{\circ}$  (the anhydrous substance decomposes at  $282^{\circ}$ ) and carbon dioxide precipitates 2:3-anhydro-4-nitro-3-hydroxy-2:6-dihydroxymmercuribenzenaldehyde. From the more soluble fractions of the mercuration product, by extraction with formic acid, 4-nitro-3-hydroxyformoxymmercuribenzenaldehyde, m. p.  $233-235^{\circ}$ , is obtained. The 4-nitro-3-hydroxypropoxymmercuribenzenaldehyde, pale orange needles, and the 4-nitro-3-hydroxychloromercuribenzenaldehyde, yellow powder, decomposing at  $187^{\circ}$ , were also prepared. Treatment with iodine converts the mono-mercurated compound into an iodo-4-nitro-3-hydroxybenzenaldehyde, yellow needles, m. p.  $185^{\circ}$ . The dimmercurated compound, on

treatment with bromine, yields the 2 : 4-dibromo-6-nitro-3-hydroxybenzaldehyde previously obtained from the dimercuri-6-nitro-hydroxybenzaldehyde. 2 : 6-Dibromo-4-nitro-3-hydroxybenzoic acid, m. p. 209°, was obtained, together with 4 : 6-dibromo-2-nitrophenol, by the oxidation of 2 : 6-dibromo-4-nitro-*m*-cresol with alkaline potassium ferricyanide. On treatment with iodine solution, the dimercurated substance yields a *di*-iodo-4-nitro-3-hydroxybenzaldehyde, yellow needles, m. p. 122°, which on oxidation gives a *di*-iodo-4-nitro-3-hydroxybenzoic acid, yellow prisms, m. p. 249° (decomp.). This acid is identical with that obtained by oxidising with alkaline potassium ferricyanide the *di*-iodo-4-nitro-*m*-cresol (which by analogy should be the 2 : 6-di-iodo derivative) prepared by treating 4-nitro-*m*-cresol with iodine and mercuric oxide.

The mercuration of 2-nitro-3-hydroxybenzaldehyde similarly yields at first mainly 2-nitro-3-hydroxyhydroxymercuriacetoxymercuribenzenaldehyde, yellow amorphous, and then 2-nitro-3-hydroxydiacetoxydimercuribenzenaldehyde, pale yellow needles, from which the 2-nitro-3-hydroxydichlorodimercuribenzenaldehyde, pale green, gelatinous substance, decomp. at 236°, is obtained. From the mother-liquors by fractional crystallisation from acetic acid, 2-nitro-3-hydroxyacetoxymercuribenzenaldehyde, microscopic needles, was obtained. 2-Nitro-3-hydroxychloromercuribenzenaldehyde, yellow powder, decomposes at 207°. On treatment with bromine, the dimercurated substance gives 2 : 4-dibromo-6-nitro-3-hydroxybenzaldehyde, and on shaking with excess of iodine solution a *di*-iodo compound is obtained, bright yellow needles, m. p. 154·5°, which is probably 4 : 6-di-iodo-2-nitro-3-hydroxybenzaldehyde. The crude monomercurated product similarly yields an iodo compound, m. p. about 110°, probably iodo-2-nitro-3-hydroxybenzaldehyde, together with some *di*-iodo compound, m. p. 154·5°.

The bactericidal action of the new substances has been investigated. R. B.

### Isomerism of the Oximes. XVII. Some Bromo- and Nitro-substituted Mono- and Di-methoxybenzaldoximes.

O. L. BRADY and L. B. MANJUNATH (*J. Chem. Soc.*, 1924, 125, 1060—1068; cf. T., 1916, 109, 650; 1920, 117, 1040; 1923, 123, 2434).—A continuation of previous work on the influence of negative groups on the stability of isomeric benzaldoximes. Ciusa's work (A., 1907, i, 137) on 3-nitro-*p*-methoxybenzantialdoxime and its *syn*-isomeride has been confirmed. The conversion of the *anti*-isomeride into the *syn*-compound was effected by pouring a suspension of the *anti*-oxime in hydrochloric acid into sodium carbonate solution. The m. p. of the *anti*-oxime is 166° and of the *syn*-oxime 164—166°. Acetyl-3-nitro-*p*-methoxybenzsynaldoxime, colourless needles, m. p. 115°, on decomposition with sodium hydroxide yields 3-nitro-*p*-methoxybenzonitrile. The *N*-benzyl ether melts at 203° (cf. Ciusa, *loc. cit.*). The *N*-methyl ether, yellow prisms, m. p. 180°, the *O*-methyl ether of the *anti*-oxime, m. p. 120°, carb-anilino-3-nitro-*p*-methoxybenzantialdoxime, m. p. 128° (decomp.), and carbanilino-3-nitro-*p*-methoxybenzsynaldoxime, m. p. 117° (de-

comp.), are described. On hydrolysis with sodium hydroxide, the carbanilino derivative of the *anti*-oxime yields the original oxime, whereas the isomeric carbanilino derivative yields aniline and 3-nitro-*p*-methoxybenzonitrile on warming, and on prolonged boiling, ammonia and 3-nitro-*p*-methoxybenzoic acid with a little 3-nitro-*p*-methoxybenzantialdoxime.

3-Bromo-*p*-methoxybenzaldehyde, obtained by bromination of *p*-methoxybenzaldehyde in acetic acid solution in the presence of iodine, readily yields 3-bromo-*p*-methoxybenzantialdoxime, m. p. 118° (*acetyl* derivative, m. p. 82°, hydrolysed to the sodium salt of the original oxime with sodium hydroxide), which on boiling with excess of acetic anhydride is converted into 3-bromo-*p*-methoxybenzonitrile, m. p. 122°. The following derivatives of 3-bromo-*p*-methoxybenzantialdoxime were prepared: *O*-benzyl ether, m. p. 82°; *O*-methyl ether, m. p. 76°; phenylcarbimide derivative, m. p. 92°, hydrolysed mainly to the original oxime, some diphenylcarbamide being also formed. The *anti*-oxime is readily converted by the hydrochloric acid method (*supra*) into 3-bromo-*p*-methoxybenzsynaldoxime, m. p. 134° [*N*-benzyl ether, m. p. 151°; *N*-methyl ether, m. p. 108°; phenylcarbimide derivative, m. p. 104° (decomp.)], yielding ammonia and 3-bromo-*p*-methoxybenzoic acid on hydrolysis], which with cold acetic anhydride and sodium carbonate solution is converted into 3-bromo-*p*-methoxybenzonitrile. The 5-nitro-*o*-methoxybenzaldoxime, m. p. 183°, prepared by Schnell (A., 1884, 1164), is shown to be the *anti*-oxime, its *acetyl* derivative, m. p. 160°, yielding the original oxime on hydrolysis. In a similar manner, 6-nitro-3:4-dimethoxybenzaldoxime (A., 1900, i, 178) (*acetyl* derivative, yellow leaflets, m. p. 152°) is shown to be the *anti*-oxime. 5-Nitro-3:4-dimethoxybenzaldehyde, obtained from 5-nitrovanillin by methylation with diazomethane (excess of the reagent yields 5-nitro-3:4-dimethoxyacetophenone, m. p. 89°), or by treatment of the silver salt with methyl iodide, yields 5-nitro-3:4-dimethoxybenzantialdoxime, m. p. 151° (*acetyl* derivative, m. p. 115°, yielding the oxime on hydrolysis). 6-Bromo-3:4-dimethoxybenzaldoxime (Pschorr, A., 1912, i, 775) yields an *acetyl* derivative, m. p. 140°, regenerating the original oxime on hydrolysis and accordingly has the *anti*-structure. Attempts to prepare *syn*-isomerides from 5-nitro-*o*-methoxybenzantialdoxime, 6-nitro-, 6-bromo-, and 5-nitro-3:4-dimethoxybenzantialdoximes were unsuccessful, and in all these cases solutions of the oximes in organic solvents yielded no hydrochloride on treatment with hydrogen chloride (cf. T., 1923, 123, 1783).

R. B.

**Isomerism of the Oximes. XVIII. Action of Chloro-2:4-dinitrobenzene on some Isomeric Aldoximes.** O. L. BRADY and R. TRUSZKOWSKI (*J. Chem. Soc.*, 1924, 125, 1087—1096; cf. T., 1922, 121, 2106).—Chloro-2:4-dinitrobenzene reacts readily in alcoholic solution with the sodium salts of substituted benzantialdoximes yielding dinitrophenyl ethers, to which the *syn*-configuration is assigned (cf. Werner, A., 1894, i, 461), since on warming with alcoholic potassium hydroxide they are readily

hydrolysed with formation of sodium dinitrophenoxide and the corresponding nitrile:  $R \cdot CH \cdot N \cdot O \cdot C_6H_3(NO_2)_2 \rightarrow RCN + (NO_2)_2C_6H_3 \cdot OH$  (cf. T., 1923, **123**, 1190). The ethers obtained from *o*-methoxy- and *p*-hydroxy-benzantialdioximes behave in this way, although previously no *syn*-derivatives of these oximes had been prepared. 3-Bromo-*p*-dimethylamino- and *o*-hydroxybenzantialdioximes do not react in this way, but in the former case a dinitrophenyl ether was obtained by another method. The reaction has also been studied in the case of the sodium salts of the following *syn*-oximes: benzaldoxime, *p*-methoxybenzaldoxime, cinnamaldoxime, acetaldoxime, and heptaldoxime. A complicated reaction occurs but the only products isolated were sodium dinitrophenoxide and the corresponding aldehyde. The binary fusion curves of the *anti*-oximes and chlorodinitrobenzene indicate that in certain cases, e.g., benzantialdoxime and *p*-methoxybenzantialdoxime, well-defined additive compounds are formed containing equimolecular quantities of the two components. *o*-Methoxy- and *o*-hydroxybenzantialdioximes gave no indication of such an equimolecular compound, although in the former case there is some evidence of the formation of an unstable compound of chlorodinitrobenzene (2 mols.) and oxime (1 mol.). That stable additive compounds with chlorodinitrobenzene are characteristic of those oximes which are readily converted into *syn*-isomerides affords some support for the view that the formation of additive compounds precedes isomeric change in the oximes. 2:4-Dinitrophenyl ethers were prepared from the following: *p*-methoxybenzsynaldoxime, m. p. 174° (decomp.); *o*-aminobenzsynaldoxime, m. p. 177° (decomp.); 5-bromo-3:4-dimethoxybenzsynaldoxime, m. p. 199° (decomp.); 3:4-methylenedioxybenzsynaldoxime, m. p. 194° (decomp.); *o*-nitrobenzsynaldoxime, m. p. 184° (decomp.); *p*-nitrobenzsynaldoxime, m. p. 210° (decomp.); *p*-dimethylaminobenzsynaldoxime, m. p. 185° (decomp.); 3-nitro-*p*-dimethylaminobenzsynaldoxime, m. p. 179° (decomp.); 3:4-dimethoxybenzsynaldoxime, m. p. 176° (decomp.); *o*-methoxybenzsynaldoxime, m. p. 184° (decomp.). The monodinitrophenyl ether of *p*-hydroxybenzsynaldoxime melts at 185° (decomp.). The 2:4-dinitrophenyl ether of 3-bromo-*p*-dimethylaminobenzsynaldoxime, m. p. 181° (decomp.), was obtained by the action of sodium hydroxide solution on the powdered fusion of the *anti*-oxime (1 mol.) with chloro-2:4-dinitrobenzene (1 mol.). The additive compound of chloro-2:4-dinitrobenzene with benzantialdoxime has m. p. 32–33°, and with *p*-methoxybenzantialdoxime, m. p. 65°.

R. B.

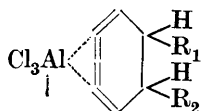
**Secondary Valency of the Hydroxyl Group in Complex Salts of Protocatechualdehyde.** H. REIHLEIN and A. SAFFER. —(See ii, 384.)

**Purification and Physical Constants of Acetophenone.** J. L. R. MORGAN and O. M. LAMMERT (*J. Amer. Chem. Soc.*, 1924, **46**, 881–888).—Pure acetophenone has been prepared by a method involving slow recrystallisation in the dark and in the absence of moisture, and the following constants have been determined:

freezing point  $19.655^{\circ} \pm 0.002^{\circ}$ ; specific conductance  $k^{25} 6.43 \times 10^{-9}$  mho;  $d_4^{25} 1.02382 \pm 0.002\%$ . The freezing-point curve of acetophenone with small quantities of water has been determined.

W. H.-R.

**Explanation of the Catalytic Action in Friedel-Crafts' Syntheses.** A. SCHAARSCHMIDT (*Z. angew. Chem.*, 1924, **37**, 286—288).—Unpublished experimental results (covered by patents) lead the author to conclude that the aluminium chloride (or ferric chloride) in a Friedel-Crafts reaction "activates" the benzene, or benzene derivative, in forming an additive compound.

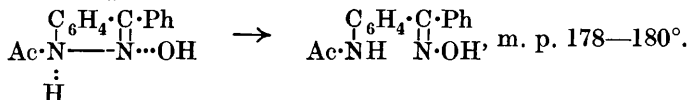


the intermediate compound formed by the three reagents he ascribes the annexed formula, in which  $R_1$  and  $R_2$  may be alike, as in halogenation, or unlike, as in the synthesis of acetophenone. If this compound be stable, as in the acetophenone

synthesis, then a molecular proportion of aluminium chloride is needed. If it be unstable, then the aluminium chloride behaves as a true catalyst. But if one of the end-products can react with the aluminium chloride then the reaction, although really catalytic, needs for completion a molecular proportion of the agent. The presence of reactive substituent groups in the benzene derivative may likewise influence the course of the reaction.

W. A. S.

**Oximes of *o*-Aminobenzophenone and the Beckmann Transformation.** K. v. AUWERS and O. JORDAN (*Ber.*, 1924, **57**, [B], 800—808; cf. Meisenheimer and Meis, this vol., i, 433).—The configuration of the two oximes of *o*-aminobenzophenone has been deduced from their behaviour on diazotisation (A., 1893, i, 587), and is supported by the hydrolysis of 1-acetyl-3-phenylindazole with sodium hydroxide to the *N*-acetyl derivative of the *n*-oxime, m. p.  $127^{\circ}$ :



Both oximes are transformed by acetic acid saturated with hydrochloric acid into phenylindazole in approximately equal yields, the transformation being slightly quicker with the *h*-oxime, m. p.  $156^{\circ}$ . On boiling with acetic acid, the *n*-oxime yields exclusively its acetyl derivative, m. p.  $178-180^{\circ}$ , whereas the *h*-oxime is converted mainly into 1-acetyl-3-phenylindazole, a small quantity of the acetyl compound, m. p.  $178-180^{\circ}$ , being also formed. Both oximes on heating with alcohol at  $160^{\circ}$  in the presence of a trace of hydrochloric acid yield benzenylphenyleneamidine (2-phenylbenziminazole), m. p.  $291^{\circ}$  (A., 1891, 1378), but the *n*-oxime yields a purer product. A similar result was obtained with 4—5% formic acid at  $140^{\circ}$ , both oximes yielding a little *o*-aminobenzophenone and the iminazole, the *n*-oxime again giving the purer product. At  $120^{\circ}$ , the *h*-oxime was largely converted into *o*-aminobenzophenone, whereas the *n*-oxime gave mainly the iminazole. On boiling with concentrated formic acid, both oximes are converted

into the *N*-formyl derivative of the *n*-oxime, fine needles, m. p. 165°, the *h*-oxime yielding also a small quantity of 1-formyl-3-phenylindazole. The hydrochlorides of both oximes undergo the Beckmann transformation on heating, yielding the hydrochloride of 2-phenylbenziminazole, m. p. 325—328°, the transformation being more rapid and without sintering in the case of the *n*-oxime. The *N*-acetyl derivative of the *h*-oxime, m. p. 154—155°, was obtained, together with a little of the *N*-acetate, by treating the oxime in ether-pyridine solution with acetyl chloride. The *N*-benzoyl derivative of the *h*-oxime has m. p. 175—176°, and of the *n*-oxime, m. p. 201°. Both oximes on benzylation by the Schotten-Baumann process also yield the same *dibenzoyl* compound, m. p. 165—166°, which on hydrolysis gives only the *N*-benzoate of the *n*-oxime. Treatment with methyl sulphate converts the *N*-benzoate, m. p. 201°, into its *methyl ether*, m. p. 142—143°, but from the isomeric *N*-benzoate of m. p. 175—176° only resinous products were obtained.

The great tendency to form derivatives of the *n*-oxime and the fact that both oximes give the same diacetyl and dibenzoyl compounds contrast with the behaviour of the benzildioximes, where all three series of diacyl derivatives are known. It is suggested

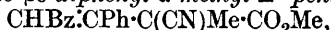
that the *syn*-oxime has a configuration such as  $\text{Ph} \cdot \overset{\text{HO} \cdot \text{N}}{\underset{\text{N} \cdot \text{OH}}{\text{C}}} \text{---} \overset{\text{N}}{\underset{\text{N}}{\text{C}}} \cdot \text{Ph}$ ,

comparable with those suggested for the stereoisomeric substituted diphenyl derivatives (T., 1922, **121**, 614; 1923, **123**, 2047).

R. B.

**Addition Reactions of Benzoylphenylacetylene.** E. P. KOHLER and G. R. BARRETT (*J. Amer. Chem. Soc.*, 1924, **46**, 747—753).—In the presence of a little sodium methoxide in methyl-alcoholic solution, benzoylphenylacetylene and methyl cyanoacetate combine readily with the production of an intense red colour, and formation of a termolecular condensation product *methyl γ-cyano-αε-dibenzoyl-βδ-diphenyl-Δ<sup>αδ</sup>-pentadiene-γ-carboxylate*,  $\text{CHBz} \cdot \text{CPh} \cdot \text{C}(\text{CN})(\text{CO}_2\text{Me}) \cdot \text{CPh} \cdot \text{CHBz}$ , yellow needles, m. p. 209°. Methyl α-cyanopropionate combines somewhat less readily with benzoylphenylacetylene. When one equivalent of sodium methoxide was used two products were obtained, *phenyl γ-cyano-β-phenylbutenyl ketone*,  $\text{CHMe}(\text{CN}) \cdot \text{CPh} \cdot \text{CH} \cdot \text{COPh}$ , colourless prisms, m. p. 129°; and a yellow solid, from which a substance was obtained as greenish-yellow needles turning red at about 260°, m. p. 264°. The latter substance dissolved in boiling methyl alcohol gave, on evaporation of the solvent, sodium chloride and a yellow substance from which hot methyl alcohol extracted 4 : 6-*diphenyl-3-methyl-1 : 2-pyrone*, stout yellow needles, m. p. 113°.

In presence of a smaller quantity of the condensing agent, methyl α-cyanopropionate and benzoylphenylacetylene condense to form *methyl α-cyano-δ-keto-βδ-diphenyl-α-methyl-Δ<sup>β</sup>-pentenoate*,



colourless needles, m. p. 70°.

When a benzene solution of benzoylphenylacetylene was added to a suspension of the sodium derivative of benzyl cyanide, a crimson condensation *product* separated which, when decomposed with dilute hydrochloric acid, formed *phenyl  $\gamma$ -cyano- $\beta$ - $\gamma$ -diphenyl-propenyl ketone*,  $\text{COPh}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CHPh}\cdot\text{CN}$ , colourless needles, m. p.  $137^\circ$ ; the compound reduces permanganate in acetone, readily forms a *hydrazone*, m. p.  $150$ — $151^\circ$ , and regenerates the crimson sodium compound when treated with sodium methoxide.

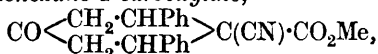
Equimolecular proportions of benzoylphenylacetylene and toluene-*p*-sulphinic acid, in the presence of a condensing agent, react to form *phenyl  $\beta$ -toluene-*p*-sulphonylstyryl ketone*,



colourless, 6-sided plates, m. p.  $141^\circ$ , and smaller quantities of a *stereoisomeride* (yellow needles, m. p.  $157^\circ$ ). The yellow compound is readily obtained from its colourless stereoisomeride, when a suspension of this in methyl alcohol is treated with a trace of sodium alkoxide. Both sulphones gave, on reduction,  $\beta$ -toluene-*p*-sulphonyl- $\beta$ -phenylpropiophenone, and a *substance* which crystallises in fine needles, m. p.  $249^\circ$ .  
C. J. S.

**Addition Reactions of certain Pentadienones.** E. P. KOHLER and R. W. HELMKAMP (*J. Amer. Chem. Soc.*, 1924, **46**, 1018—1024).

—Methyl cyanoacetate combines readily with distyryl ketone and other pentadienones in presence of sodium methoxide or hydroxide to form *cyclohexanone* derivatives. The closing of the ring takes place much more rapidly than the addition of a second molecule of cyanoacetate. No open-chain compounds are formed as is the case with malonic and acetoacetic esters. The products do not reduce permanganate. They are extracted from ethereal solution by sodium hydrogen sulphite, and form acetals with surprising ease. The *cyclohexanones* occur in two stereoisomeric forms; that first formed is transformed into a second, more stable to alkali, by treatment with sodium hydroxide. *Methyl 1-cyano-4-keto-2 : 6-diphenylcyclohexane-1-carboxylate*,



white filaments, m. p.  $137$ — $138^\circ$ , is obtained on adding a few drops of a sodium methoxide solution to a hot saturated solution of distyryl ketone in methyl alcohol containing a little more than one equivalent of methyl cyanoacetate. Using aqueous sodium hydroxide, the isomeride is obtained in stout prisms, m. p.  $146^\circ$ ; *oxime*, m. p.  $190^\circ$ ; *methyl acetal*, by passing dry hydrogen chloride into a solution of the *cyclohexanone* derivative in dry, cooled methyl alcohol, m. p.  $181^\circ$ . The *ethyl acetal*, m. p.  $151$ — $152^\circ$ , was made as above and also by the Claisen method. The melting point may drop as low as  $135$ — $145^\circ$  after standing some hours, but after one recrystallisation it is again  $151$ — $152^\circ$ . Bromination gave a product containing 1—2% more bromine than required for a dibromo derivative. *1-Cyano-4-keto-2 : 6-diphenylcyclohexane-1-carboxylic acid* forms needles or large, colourless prisms containing 1 mol. of acetone. On heating at  $180$ — $190^\circ$ , the acetone is driven



off, followed by a mol. of carbon dioxide, giving *4-cyano-3:5-diphenylcyclohexan-1-one*, minute prisms, m. p. 81—83° (decomp.); *semicarbazone*, minute prisms, m. p. 194—196° (decomp.). *Methyl 4-keto-2:6-diphenylcyclohexane-1-carboxylate*, prisms, m. p. 104.5—106°, is formed by heating the above nitrile in methyl-alcoholic hydrochloric acid. Dimethoxystyryl ketone reacts with methyl cyanoacetate in presence of a little sodium methoxide at room temperature to give a mixture of stereoisomerides of which the m. p. varies with the solvent used for crystallisation. *Methyl 1-cyano-4-keto-2:6-dianisylcyclohexane-1-carboxylate* is obtained as the more stable isomeride on boiling with sodium methoxide, needles, m. p. 208—209°; *methyl acetal*, m. p. 175.5—176°. Ethyl cyanoacetate condenses similarly with dimethoxystyryl ketone, and the condensation product gave the *ethyl acetal* of the above, m. p. 132—134°. A. C.

**Addition Reactions of certain Pentadienones. II.**  
**Addition of Malonic Esters.** E. P. KOHLER and C. S. DEWEY (*J. Amer. Chem. Soc.*, 1924, **46**, 1267—1278).—The condensation of methyl malonate with distyryl ketone in presence of bases leads to an equilibrium mixture of the three products

$\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Me})_2$  (I),  
 $\text{CO}[\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Me})_2]_2$  (II), and *dimethyl 4-keto-2:6-diphenylcyclohexane-1:1-dicarboxylate* (III), from which either may be isolated by inoculation or suitable variation of conditions. Compound (III), produced in presence of sodium methoxide, forms white, irregular prisms, m. p. 135°, from which the free acid,  $\text{C}_{20}\text{H}_{18}\text{O}_5\cdot 2\text{H}_2\text{O}$ , is obtained on hydrolysis as transparent needles. The latter is stable in a vacuum, but becomes anhydrous at 75—100°, and melts at about 150° with loss of carbon dioxide and formation of the corresponding monocarboxylic acid. *Diethyl 4-keto-2:6-diphenylcyclohexane-1:1-dicarboxylate* forms white needles, m. p. 79°. *Dimethyl  $\delta$ -keto- $\beta\zeta$ -diphenyl- $\Delta$ -hexene- $\alpha\alpha$ -dicarboxylate* (I), long, silky needles, m. p. 108°, is obtained in presence of piperidine. On oxidation with cold permanganate in acetone, it yields benzoic acid and the monomethyl ester of a tribasic acid,  $\text{C}_{13}\text{H}_{14}\text{O}_6$ , colourless prisms, m. p. 101°, which, by hydrolysis with potassium hydroxide and subsequent heating at 170—185°, yields carbon dioxide and phenylglutaric acid, m. p. 136°. (I) is converted quantitatively into (III) by adding it to a cold solution of sodium methoxide (5%) in methyl alcohol, but in presence of methyl malonate the compound (II) was obtained as long, silky needles, m. p. 109—112°. *Dimethyl  $\delta$ -keto- $\beta\zeta$ -diphenylhexane- $\alpha\alpha$ -dicarboxylate*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Me})_2$ , m. p. 57°, is obtained by the condensation of methyl malonate with phenylethyl styryl ketone in presence of sodium methoxide. Methyl cyanoacetate condenses with distyryl ketone to form a cyclohexanone derivative much more rapidly than methyl malonate. *4-Nitro-3:5-diphenylcyclohexan-1-one*, obtained by the condensation of distyryl ketone and nitromethane, forms colourless, prismatic needles, m. p. 93—94°. It forms a *sodium* derivative,

from which 4-bromo-4-nitro-3:5-diphenylcyclohexan-1-one, small prisms, m. p. 156—157°, is obtained by the action of bromine. Styryl *p*-methoxystyryl ketone and dimethyl malonate yield a cyclohexanone derivative, fine, white needles, m. p. 145—146° analogous with (III), in presence of sodium methoxide. In presence of piperidine, dimethyl  $\delta$ -keto- $\beta$ -phenyl- $\zeta$ -*p*-anisyl- $\Delta^4$ -hexene- $\alpha\alpha$ -dicarboxylate, white needles, m. p. 124°, is also obtained. Styryl  $\delta$ -phenylbutadienyl ketone yields similarly the cyclohexanone derivative,  $C_{24}H_{24}O_5$ , lustrous, transparent prisms, m. p. 156°, and the compound  $CHPh \cdot CH \cdot CH \cdot CH \cdot CO \cdot CH_2 \cdot CHPh \cdot CH(CO_2Me)_2$ , white needles, m. p. 112°, which is very readily converted into the cyclic compound. Di-*p*-methoxystyryl ketone and methyl malonate yield the cyclohexanone derivative,  $C_{24}H_{26}O_7$ , brilliant prisms, m. p. 194°, but the open-chain compound could not be isolated. *p*-Methoxystyryl  $\delta$ -phenylbutadienyl ketone and di- $\delta$ -phenylbutadienyl ketone behave similarly, with formation, respectively, of dimethyl 4-keto-2-anisyl-6-styrylcyclohexane-1:1-dicarboxylate, lustrous tables or prisms, m. p. 170°, and dimethyl 4-keto-2:6-distyrylcyclohexane-1:1-dicarboxylate, small, lustrous prisms, m. p. 112°.

F. G. W.

### Insecticides. VI. cyclopentanolone Derivatives and their Comparison with Pyrethrolone. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 377—390).—A number of simpler cyclopentanolone derivatives have been prepared by condensing ethyl glutarate or $\beta$ -methylglutarate with ethyl oxalate (Dieckmann, A., 1894, i, 324). The properties of the compounds obtained are similar in most respects to those of pyrethrolone and its derivatives (this vol., i, 523). From ethyl glutarate and ethyl oxalate, ethyl $\Delta^{2,4}$ -cyclopentadiene-3:4-diol-2:5-dicarboxylate is obtained which, by hydrolysis with 20% sulphuric acid, gives $\Delta^2$ -cyclopenten-3-ol-4-one, but with more dilute acid gives ethyl- $\Delta^2$ -cyclopenten-3-ol-4-one-2-carboxylate, m. p. 103°, b. p. 120°/1 mm. By reduction with hydrogen and palladium, the cyclopentenolone gives cyclopentan-3-ol-4-one, b. p. 77—78°/10 mm., which slowly forms a polymeride, m. p. 88—90°. Ethyl 1-methyl- $\Delta^{2,4}$ -cyclopentadiene-3:4-diol-2:5-dicarboxylate, m. p. 110° (cf. Dieckmann, A., 1899, i, 676), is hydrolysed by 10% sulphuric acid to ethyl 1-methyl- $\Delta^2$ -cyclopenten-3-ol-4-one-2-carboxylate, a pale yellow liquid, b. p. 103—107°/0.5 mm.; the acetate, a colourless oil, b. p. 95°/0.1 mm., probably has the structure

$$\begin{array}{c} \text{CH} \text{---} \text{CHMe} \\ | \\ \text{C}(\text{OAc}) \text{---} \text{C}(\text{OH}) \end{array} \geq \text{C} \cdot \text{CO}_2\text{Et}$$
 since it gives a strong reaction with ferric chloride. Reduction of the ester with hydrogen and palladium does not proceed smoothly, but some ethyl 1-methylcyclopentan-3-ol-4-one-2-carboxylate is obtained, a colourless oil, b. p. 104—105°/0.25 mm. (acetate, b. p. 104—105°/0.2 mm.), together with some 1-methylcyclopentanone. Hydrolysis of the last ester with 20% sulphuric acid gives not the expected methylcyclopentanone, but 1-methyl- $\Delta^2$ -cyclopenten-4-one, colourless liquid, b. p. 57—59°/11 mm.; semicarbazone, m. p. 223°; *p*-nitrophenylhydrazone,

m. p. 175—176°. The *ethyl ether* of the above ester is obtained by prolonged action of boiling alcoholic sulphuric acid on the ester; it forms a colourless oil, b. p. 82—83°/0.5 mm. 1-Methyl- $\Delta^2$ -cyclopenten-3-ol-4-one (or 1-methylcyclopentane-3:4-dione) is obtained by hydrolysis of the above dicarboxylate with 20% sulphuric acid; it forms yellow crystals, m. p. 58—59°, b. p. 105°/21 mm., and has an odour similar to that of cresol. With *p*-nitrophenylhydrazine, it forms an *osazone*, m. p. 180°, and also gives a *benzoate*,  $C_{13}H_{12}O_3$ , a viscous oil, b. p. 138—140°/0.2 mm., and an *acetate*,  $C_8H_{10}O_3$ , b. p. 128—130°/12 mm. The *methyl ether*,  $CH-CHMe$   
 $\begin{array}{c} | \\ C(OMe)-CO \end{array} > CH_2$ , is a colourless oil, b. p. 105—106°/15 mm. (*semicarbazone*, m. p. 192°), and the *ethyl ether* has b. p. 112—113°/10 mm. When the ethyl ether is heated at 200° with pyridine or quinoline, the ethyl group wanders from the oxygen to a carbon atom, forming a 1-methyl-2(5)-ethyl- $\Delta^2$ -cyclopenten-3-ol-4-one, a pale yellow oil, b. p. 112°/10 mm. 1-Methylcyclopentan-3-ol-4-one, obtained by reduction of the corresponding cyclopentene derivative, is a colourless oil, b. p. 86°/12 mm.; it has powerful reducing properties and by auto-oxidation forms the cyclopentenolone. With chrysanthemic acid, it forms a non-insecticidal ester. The *p*-nitrophenylhydrazine has m. p. 215—216°, and the *methyl ether* is a colourless oil, b. p. 171—172°/14 mm. 1-Methylcyclopentan-3-ol-4-one forms a *polymeride*, m. p. 85—86°, which reverts on distillation to the liquid modification. 1-Methyl-3-ethoxycyclopentan-4-one, colourless liquid, b. p. 83—85°/12 mm., is obtained by reduction (Paal-Skita) of the corresponding methylethoxycyclopentenone. The *acetate* of 1-methylcyclopentan-3-ol-4-one is a colourless oil, b. p. 109°/14 mm. (*semicarbazone*, m. p. 174°; *p*-nitrophenylhydrazine, m. p. 163°), and the *benzoate* has m. p. 55—56°.

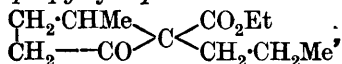
E. H. R.

**Insecticides. VIII. Preparation of Alcohols Similar to Pyrethrolone.** H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 406—441).—Experiments were made to determine whether the unsaturated side-chain of pyrethrolone (1-methyl-2-pentadienylcyclopentan-4-ol-3-one, this vol., i, 523) can be replaced by other unsaturated groups without destroying the insecticidal properties of its chrysanthemic acid ester. Methylallylcyclopentanone (IV below) forms an insecticidal ester, weaker, however, than pyrethrine.

By the action of allyl bromide on the sodium derivative of ethyl 4-acetoxy-1-methylcyclopentan-3-one-2-carboxylate, and removal of the acetyl group with cold concentrated hydrochloric acid, was obtained *ethyl 1-methyl-2-allylcyclopentan-4-ol-3-one-2-carboxylate*

(I)  $\begin{array}{c} CH_2 \cdot CHMe \\ | \\ OH \cdot CH - CO \end{array} > C < \begin{array}{c} CO_2Et \\ CH_2 \cdot CH \cdot CH_2 \end{array}$ , a viscous, colourless oil, b. p. 120°/1 mm.; *acetate*, b. p. 126°/1 mm. The ester is extraordinarily stable to acids; by the action of barium hydroxide it is converted into  $\alpha$ -hydroxy- $\delta$ -carboxy- $\gamma$ -methyl- $\Delta^5$ -octenoic acid,

$\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$  (II), the lactone of which forms a viscous mass, b. p.  $165^\circ$  in a high vacuum. The *chrysanthemumcarboxylate* of (I) is a viscous oil, b. p.  $180^\circ$  in a vacuum, and is non-insecticidal. Reduction of the acetate of (I) by the Paal-Skita method gives *ethyl 4-acetoxy-1-methyl-2-propylcyclopentan-3-one-2-carboxylate*, b. p.  $127^\circ/1$  mm., which is further reduced by aluminium amalgam in ether solution to *ethyl 1-methyl-2-propylcyclopentan-3-one-2-carboxylate*,



b. p.  $134\text{---}136^\circ/11$  mm. (*semicarbazone*, m. p.  $183^\circ$ ). Reduction of this with hydrogen iodide gives *1-methyl-2-propylcyclopentan-3-one*; *semicarbazone*, m. p.  $173\text{---}174^\circ$ . The *ethyl ether* of (I), obtained by the action of allyl bromide on the sodium derivative of *ethyl 4-ethoxy-1-methylcyclopentan-3-one-2-carboxylate*, is a colourless oil, b. p.  $96^\circ/0.1$  mm. The ether resists the action of acids, and by alkalis is converted into the *ethyl ether* of (II), b. p.  $155\text{---}160^\circ$  in a high vacuum.

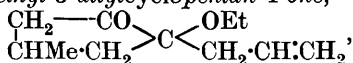
*Ethyl 1-methyl- $\Delta^4$ -cyclopenten-4-ol-3-one-2-carboxylate*, in the form of its sodium or silver salt, reacts slowly with allyl bromide, forming an *O-allyl ether*, a pale yellow oil, b. p.  $105^\circ/0.5$  mm., which when heated with pyridine isomerises into *ethyl 1-methyl-2-allyl- $\Delta^4$ -cyclopenten-4-ol-3-one-2-carboxylate*, b. p.  $120^\circ/0.9$  mm.; by acid hydrolysis this gives *1-methyl-2-propenyl- $\Delta^4$ -cyclopenten-4-ol-3-one* (III), m. p.  $110^\circ$ . The same compound is obtained by the action of allyl bromide on *ethyl 1-methyl- $\Delta^{2,4}$ -cyclopentadiene-3:4-diol-2:5-dicarboxylate*, followed by decomposition of the condensation product with acid or alkali. The compound is very sensitive to atmospheric oxidation. Its *chrysanthemumcarboxylate*, a viscous oil, b. p.  $165^\circ/1$  mm., is non-insecticidal. The presence of the propenyl group is proved from the formation of acetaldehyde by the decomposition of the ozonide; allyl derivatives give formaldehyde. Reduction of (III) with hyposulphite or electrolytically gives *1-methyl-2-propyl- $\Delta^{2(4)}$ -cyclopenten-3(4)-ol-4(3)-one*, crystals, m. p.  $46\text{---}48^\circ$ , which by further reduction gives the corresponding *cyclopentanolone*. With bromine, (III) forms a *dibromide*, white crystals, m. p.  $100\text{---}102^\circ$ . Attempts to prepare a *methylpropenylcyclopentanone* by reduction of the *acetate* (b. p.  $108^\circ/0.5$  mm.) and *methyl ether* (colourless oil, b. p.  $127\text{---}128^\circ/12$  mm.) of (III) were unsuccessful.

By the action of allyl bromide in presence of sulphuric acid on *1-methyl- $\Delta^2$ -cyclopenten-3-ol-4-one*, the *allyl ether* of the last is obtained, a mobile oil, b. p.  $76\text{---}77^\circ/0.75$  mm., which by the action of alkalis is converted into the *2-propenyl* compound, m. p.  $110^\circ$  (III, above), but when boiled alone gives *1-methyl-2-allylcyclopentanone*,

*pentanone*,  $\begin{array}{c} \text{CH}_2\cdot\text{CHMe} \\ | \\ \text{CO-C(OH)} \end{array} > \text{C} \cdot \text{CH}_2\cdot\text{CH}:\text{CH}_2$ , a pale yellow, mobile oil, b. p.  $80\text{---}82^\circ$  in a high vacuum, probably a mixture of the  $\Delta^2$ - and  $\Delta^4$ -isomerides. By reduction with zinc and acetic acid, this gives *1-methyl-2-allylcyclopentanone* (IV), an oil, b. p.  $132^\circ$

134°/14 mm., which is also probably a mixture of the two isomerides,  $\begin{array}{c} \text{CH}_2-\text{CHMe} \\ | \\ \text{CO}\cdot\text{CH}(\text{OH}) \end{array} > \text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$  and  $\begin{array}{c} \text{CH}_2-\text{CHMe} \\ | \\ \text{CH}(\text{OH})\cdot\text{CO} \end{array} > \text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ . Its *chrysanthemumcarboxylate*, b. p. 150°/1 mm., has insecticidal properties.

The sodium derivative of 1-methylcyclopentanone reacts with allyl bromide to form the *allyl ether*,  $\begin{array}{c} \text{CH}_2-\text{CO} \\ | \\ \text{CHMe}\cdot\text{CH}_2 \end{array} > \text{CH}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ , a colourless oil, b. p. 112°/12 mm. On the other hand, the ethyl ether, when treated with sodium and allyl bromide in ether solution, gives 3-ethoxy-1-methyl-3-allylcyclopentan-4-one,



a colourless oil, b. p. 110°/13 mm., which, by boiling with 20% sulphuric acid, gives 1-methyl-3-allyl- $\Delta^2$ -cyclopenten-4-one, a pale yellow oil, b. p. 112—115°/17 mm. (*semicarbazone*, crystals, decomp. 215°). When this is reduced by the Paal-Skita method, it gives 1-methyl-3-propylcyclopentan-4-one, a colourless oil, b. p. 82—83°/10 mm., having a faint odour of menthone; *semicarbazone*, m. p. 183°. This compound was synthesised by the action of propyl iodide on ethyl methylcyclopentanonecarboxylate prepared from ethyl  $\beta$ -methyladipate. Its *chrysanthemumcarboxylate*, an oil, b. p. 140—142°/0.7 mm., is not insecticidal.

Attempts to prepare methylcyclopentanone derivatives with a geranyl side-chain were unsuccessful. 1-Methyl- $\Delta^2$ -cyclopenten-3-ol-4-one geranyl ether is a pale yellow oil, b. p. 138—142°/0.75 mm.; under no conditions does the geranyl group pass from oxygen to carbon. The *benzylidene* derivative of 1-methylcyclopentanone is a viscous oil, b. p. 140°/1 mm. E. H. R.

**Insecticides. IX. Preparation of cyclopentanone Derivatives with Unsaturated Side Chains.** H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 442—448).—Continuing the search for substitutes for pyrethrolone (preceding abstract), a number of substituted cyclopentanones have been prepared, none of which, however, gave insecticidal esters with *chrysanthemumcarboxylic acid*. By boiling ethyl 1-phenyl-3:4-dihydroxycyclopentadiene-2:5-dicarboxylate with 10% sulphuric acid, 1-phenylcyclopentenolone,  $\begin{array}{c} \text{CO}-\text{CH}_2 \\ | \\ \text{C}(\text{OH})\cdot\text{CH} \end{array} > \text{CHPh}$ , was obtained, white crystals,

m. p. 103—105°, which by reduction gave the corresponding 1-phenylcyclopentanone in an impure form. Methyl 1-styryl-3:4-dihydroxycyclopentadiene-2:5-dicarboxylate, crystals, m. p. 141—142°, was obtained by condensing methyl  $\beta$ -styrylglutarate with methyl oxalate. By boiling 20% sulphuric acid, it is converted into 1-styryl- $\Delta^2$ -cyclopenten-3-ol-4-one, colourless crystals, m. p. 96—98°, which is reduced by zinc in sulphuric acid to 1-styrylcyclopentan-3-one, colourless crystals, m. p. 48—50°.

Crotonaldehyde condenses with ethyl malonate to give, not the expected propenylglutarate, but ethyl  $\beta$ -methyl- $\Delta^7$ -pentene- $\alpha\alpha\epsilon\epsilon$ -

*tetracarboxylate*, a viscous oil, b. p. 174—175°/0.5 mm.; *methyl ester*, b. p. 134°/12 mm.

Ethyl *cyclopentan-2-one-1-carboxylate* in the form of its sodium derivative condenses with allyl bromide to give *ethyl 1-allylcyclopentan-2-one-1-carboxylate*, a colourless oil, b. p. 125°/11 mm., which is converted by boiling 20% sulphuric acid into *1-allylcyclopentan-2-one*, a colourless oil, b. p. 86°/12 mm. (*p-nitrophenylhydrazone*, yellow crystals, m. p. 139°), which when heated with amyl formate gives a *3-hydroxymethylene* derivative, mobile oil, b. p. 117°/11 mm. With magnesium methyl iodide, allyl-*cyclopentanone* gives *1-methyl-2-allylcyclopentan-1-ol*, a colourless oil, b. p. 85°/13 mm. E. H. R.

**isoNitriles. VII. Interaction of Phenylcarbylamine and  $\beta$ -Naphthol.** M. PASSERINI (*Gazzetta*, 1924, **54**, 184—191).—A fuller account of work already published (this vol., i, 57). The dianil derivative of 2-hydroxy-1-naphthylglyoxal has the normal molecular weight in freezing benzene; its *benzoyl* derivative,  $C_{31}H_{22}O_2N_2$ , forms minute, pink crystals, m. p. 163—165°, and reddens rapidly in the air. 2-Hydroxy-1-naphthylglyoxal di-*phenylhydrazone*,  $OH \cdot C_{10}H_6 \cdot C(N \cdot NPh) \cdot CH \cdot N \cdot NPh$ , has m. p. 240° (decomp.). The *lactone* of 2-hydroxy-1-naphthylglyoxylic acid (*loc. cit.*), forms yellow needles, m. p. 184—185°, has an acid reaction towards indicators, and gives an intense red coloration with concentrated sulphuric acid. The *barium* salt of the corresponding acid has been prepared. T. H. P.

**3 : 3 : 5 : 6-Tetrachloro- and -Tetrabromo-1 : 2 : 4-triketocyclohexenes.** T. ZINCKE and E. WEISHAUP (*Annalen*, 1924, **437**, 86—105).—The two compounds,  $C_6H_4O_3N_2Cl_4$  and  $C_6H_4O_3N_2Br_4$ , obtained from tetrachloro-*o*-benzoquinone (Zincke, this vol., i, 163) have now been prepared by treating tetrachloropyrocatechol with fuming nitric acid containing 10% of sulphuric acid. Tetrabromopyrocatechol yields analogous compounds. The compound,  $C_6H_4O_3N_2Cl_4$ , is shown to be 3 : 3 : 5 : 6-tetrachloro-1 : 2 : 4-triketocyclohexene dihydrate,  $CO < \begin{matrix} CCl=CCl \\ CCl_2 \cdot C(OH)_2 \end{matrix} > C(OH)_2$ . It is also obtained by chlorinating (and simultaneously hydrolysing) triacetylhydroxyquinol and forms pale yellow needles, m. p. 96°. When reduced it yields 3 : 5 : 6-trichloro-1 : 2 : 4-trihydroxybenzene (Zincke and Schaum, A., 1894, i, 231) and when heated at 120—125°, or with water or dilute acid decomposes giving trichlorohydroxybenzoquinone (Zincke and Schaum, *loc. cit.*) and a compound,  $C_5O_2Cl_4$ , probably 1 : 2 : 4 : 4-tetrachloro-3 : 5-diketocyclopentene. The latter was the sole product when the triketo compound was treated with calcium hypobromite. It is a steam-volatile substance with a quinone-like odour, forming broad needles, m. p. 65°, giving an *anilide*,  $C_5O_2Cl_3 \cdot NPh$ , yellow needles, m. p. 165°, and with *o*-phenylenediamine a *eurodol*,  $C_5(OH)Cl_3 \cdot N_2C_6H_4$ , yellow needles, strongly fluorescent in alcoholic solution. Similarly, 3 : 3 : 5 : 6-tetrabromo-1 : 2 : 4-triketocyclohexene, pale yellow prisms or tables, m. p. 83—84°, was obtained (together with the compound  $C_6H_4O_3N_2Br_4$ )

by treating tetrabromopyrocatechol with the mixed acid. When reduced, it gives 3 : 5 : 6-tribromo-1 : 2 : 4-trihydroxybenzene (Thiele and Jaeger, A., 1901, i, 701), and decomposes like the chloro-compound but more readily, yielding tribromohydroxybenzoquinone, and 1 : 2 : 4 : 4-tetrabromo-3 : 5-diketocyclopentene, pale yellow prisms, m. p. 142—143°; *anilide*, yellow needles, m. p. 182°; *eurhodol*, yellow needles, darkening but not melting at 170° and giving a strongly fluorescent solution. This diketone treated with sodium hypobromite gives bromoform and dibromomaleic acid (cf. Pfeiffer and Böttler, A., 1919, i, 62); with 80% alcohol at 100° it is converted into 2 : 4 : 4-tribromo-3 : 5-diketocyclopentenol, a crystalline powder, m. p. 196° (decomp.), reconverted into the parent substance by phosphorus pentabromide; the corresponding *methoxy* (leaflets, m. p. 89—90°) and *ethoxy* (pale yellow needles, m. p. 111—112°) compounds are obtained when anhydrous alcohols are used and are hydrolysed to the hydroxy derivative by heating with dilute alcohol.

W. A. S.

**Studies in the Anthracene Series. VIII.** E. DE B. BARNETT and M. A. MATTHEWS (*J. Chem. Soc.*, 1924, 125, 1079—1083; cf. Battegay, A., 1923, i, 1103, 1104).—The anthraquinonesulphonic acids on reduction with iron and hydrochloric acid are readily converted into the corresponding anthronesulphonic acids, from which the dianthronesulphonic acids are obtained by oxidation with sodium peroxide. The following *sodium* and *aniline anthrone-* and *dianthrone-sulphonates* are described: 9-(or 10-)anthrone-1-sulphonate; -2-sulphonate; -1 : 5-disulphonate; and -1 : 8-disulphonate; dianthrone- $\beta\beta'$ -disulphonate, -1 : 5 : 1' : 5'-tetrasulphonate, and - $\alpha\alpha'\alpha'$ -tetrasulphonate. The aniline salts have no definite melting points (cf. A., 1923, i, 234). The change of colour of the anthrone-1 : 8-disulphonic acid on the addition of alkali is sufficiently sharp for use as an indicator. On reduction with aqueous sodium sulphide, the anthraquinonesulphonic acids are reduced to the corresponding anthraquinolsulphonic acids and in consequence act as catalysts in reduction reactions with sodium sulphide. The additive compounds of the anthracenemonosulphonic acids with nitric acid are too unstable to be isolated, but on treatment with pyridine are converted into the corresponding nitroanthracene-sulphonic acids. 9-(or 10-)Nitroanthracene-1-sulphonic acid, yellow needles, and 9-(or 10-)nitroanthracene-2-sulphonic acid were prepared, but no nitro compound could be obtained from anthracene-1 : 5- or -1 : 8-disulphonic acid. Anthracene-2-sulphonic acid does not give an aniline salt under the usual conditions, but the following well crystallised salts were prepared: *aniline anthracene-1-sulphonate*, *aniline anthracene-1 : 5-disulphonate*, *aniline anthracene-1 : 8-disulphonate*.

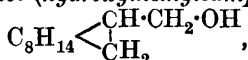
R. B.

**Trihydroxymethylantraquinones. III. Synthesis of Emodin.** R. A. JACOBSON and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, 46, 1312—1316).—3 : 5-Dimethoxy-2-(2'-hydroxy-4'-methylbenzoyl)benzoic acid was treated with bromine in glacial acetic acid with formation of the 5'-bromo derivative, thick, white needles,

m. p. 258—259°. On heating with fuming sulphuric acid and boric acid and diluting, 4-bromo-1-hydroxy-6:8-dimethoxy-3-methyl-anthraquinone, orange-red needles, m. p. 208—209°, was obtained. This yielded 1:6:8-trihydroxy-3-methylanthranol (emodin anthranol) on reduction with hydriodic acid in glacial acetic acid, from which 1:6:8-trihydroxy-3-methylanthraquinone, identical with natural emodin, was obtained on oxidation with chromic oxide in glacial acetic acid.

F. G. W.

**Camphanylcarbinol.** H. RUPE and J. BRIN (*Helv. Chim. Acta*, 1924, 7, 546—556).—Bornylenecarboxylic acid was obtained by heating borneolcarboxylic acid with acetic anhydride (cf. Bredt, A., 1909, i, 499). The *chloride* has b. p. 110°/11 mm.; *ethyl ester*, b. p. 114—115°/10 mm.; *phenyl ester*, rhombic crystals, m. p. 63—64°. By electrolytic reduction of the potassium salt, camphanecarboxylic acid was obtained; *chloride*, b. p. 110°/12 mm.; *ethyl ester*, b. p. 113°/11 mm.; *phenyl ester*, long prisms, m. p. 41°. *Camphanylcarbinol (hydroxymethylcamphane)*,



is obtained by reduction of the esters of either of the above acids with sodium and alcohol, the best yield, 65—70% of theory, being obtained from ethyl camphanecarboxylate. It has b. p. 117—118°/11 mm., m. p. 28°, is readily volatile in steam, and has a characteristic, sweet odour. It forms a crystalline compound with calcium chloride, which serves for its purification. The *formate* is a mobile liquid, b. p. 110°/11 mm.; *acetate*, b. p. 120°/11 mm.; *benzoate*, b. p. 195°/12 mm.; *p-nitrobenzoate*, long, white needles, m. p. 99—100°; *p-aminobenzoate*, glistening leaflets. The carbinol is dehydrated much less readily than camphylcarbinol (A., 1919, i, 29), but when heated with phosphoric acid is converted into

*methylenecamphane*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CH} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array}$ , a mobile oil with a strong,

unpleasant odour, b. p. 58—62°/11 mm. The constitution of this compound is proved by the formation from it of *bromomethylcamphane*, b. p. 105—108°/12 mm.,  $d_4^{20}$  1.1948,  $[\alpha]_D^{20}$  11.57°, which is also obtained by the action of hydrogen bromide and acetic acid on the carbinol. The bromo compound reacts with aniline to give

*phenylcamphanylcarbinylamine*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CH} \cdot \text{CH}_2 \cdot \text{NHPh} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array}$ , b. p. 190—193°/11 mm.; *p-tolylcamphanylcarbinylamine* forms white, silky needles, m. p. 61—62°. The bromo compound does not form a compound with magnesium, but is converted into *dicamphanylethane*, a viscous oil, b. p. 205—208°/11 mm.

E. H. R.

**The Rotation Dispersion of Camphor.** F. BÜRKI (*Helv. Chim. Acta*, 1924, 7, 537—540).—Measurements of the rotation dispersion of camphor made by Rupe (A., 1915, ii, 717) and Gumpich (*Physikal. Z.*, 1923, 24, 434) are compared by calculating Rupe's characteristic wave-length,  $\lambda_a$ , the  $\lambda_0$  of Lowry and Dickson, and Rupe's product,  $\lambda_0 \cdot \lambda_a$ . The rotation-dispersion in benzene



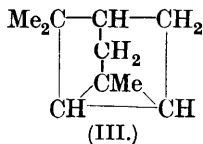
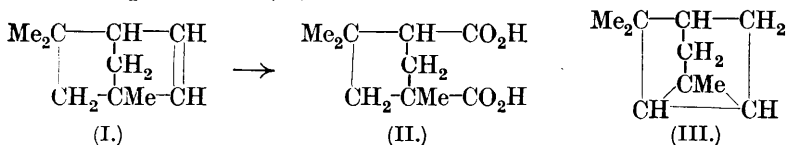
is slightly anomalous, and it is recommended to use alcohol when possible for such measurements.

E. H. R.

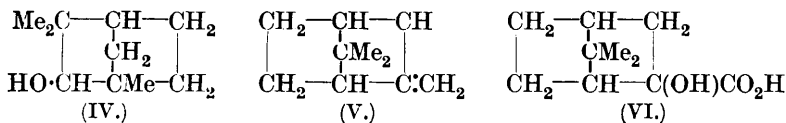
**Probable Presence of Thujone in the Essential Oil of *Artemisia Herba Alba*.** E. ALINARI (*Annali Chim. Appl.*, 1924, **14**, 109—112).—This oil,  $d_{25}^{20}$  0.9257,  $\alpha_D^{25} +3.88^\circ$ ,  $n_D^{20}$  1.4653, contains 14.4% of free, and 7.39% of combined alcohols, calculated as  $C_{10}H_{16}O$ . The presence of camphor has been demonstrated and that of thujone is probable (cf. Grimal, A., 1904, ii, 605; also B., 1924, 536).

T. H. P.

**The Xanthate Method in the Fenchone and *iso*Fenchone Series.** S. NAMETKIN (*J. pr. Chem.*, 1923, ii, **106**, 25—38).—Assuming Semmler's formulæ for fenchone and *isofenchone*, the elimination of water in the normal (1 : 2) position is only possible with *isofenchyl* alcohol, and the hydrocarbon obtained should be analogous to bornylene. This is substantiated by the fact that fenchylene (I), obtained by the decomposition of *isofenchyl* xanthate, on oxidation with potassium permanganate is converted into fenchocamphoric acid (II).



The dehydration of *isofenchyl* alcohol takes place also in the 1 : 3 position, leading to the formation of the isomeric *cyclofenchene* (III). On the other hand, fenchyl alcohol (IV) cannot eliminate the elements of water in the 1 : 2 position and, as might be expected, by dehydration gives the same *cyclofenchene*. *dl*-Fenchene (V) is also produced in the reaction, giving *dl*-hydroxyfenchenic acid (VI) by oxidation with potassium permanganate.



[With A. SELIVANOV].—*dl*-Fenchene was prepared by the dehydration of crude fenchyl alcohol with phthalic acid. The fraction, b. p. 194—199°, heated with phthalic anhydride at 170°, forms a crystalline *hydrogen phthalate* which was converted into *sodium fenchyl phthalate*, m. p. 146.5°,  $[\alpha]_D +23.23^\circ$ . On hydrolysis with alcoholic potassium hydroxide it yields pure fenchyl alcohol, b. p. 200—200.5°/750 mm., m. p. 49°,  $[\alpha]_D -10.9^\circ$ . Its steric configuration corresponds with that of borneol as shown by its stability towards the dehydrating action of phthalic acid. The stereoisomeride corresponding with *isoborneol* is probably liquid and, on account of its ready elimination of water, cannot be present in the crystalline alcohol. *cyclo*Fenchene,  $C_{10}H_{16}$ , is obtained by heating ethyl fenchylxanthate at 150—170°, finally raising the

temperature to  $230^{\circ}$ . The crude product was left with  $1\frac{1}{2}\%$  potassium permanganate solution for some time, the excess of oxidant removed, and the hydrocarbon distilled three times over sodium. It was identical with Aschan's *cyclofenchene* ( $\beta$ -pinolene); b. p.  $143-143.5^{\circ}/747.5$  mm.,  $d_4^{20}$  0.8609,  $n_D^{20}$  1.4532,  $[\alpha]_D -1.77^{\circ}$  (cf. A., 1912, i, 198). The hydration of *cyclofenchene* yields a product which on oxidation is converted into *cis*-fenchocamphoric acid and would thus seem to be *isofenchyl* alcohol, since oxidation of this alcohol has been shown to give the same product. An oily product unattacked by permanganate is also found among the products of hydration. The oxidation product obtained from the crude fenchenes by potassium permanganate contains *dl*-hydroxyfenchenic acid, m. p.  $154-155^{\circ}$ ,  $[\alpha]_D -37.42^{\circ}$  in ether, proving definitely the presence of the *dl*-fenchene in the crude fenchene.

[With A. RUSCHENTZEFF.]—Crude *isofenchyl* alcohol is obtained by hydration of *dl*-fenchene. It was purified by conversion into the xanthate from which, by the action of alcoholic ammonia, the *xanthamide* was obtained, needles, m. p.  $69-70^{\circ}$ ,  $[\alpha]_D -37.77^{\circ}$  in alcohol. Hydrolysis of the amide by alcoholic alkali gives pure *isofenchyl* alcohol, m. p.  $60.5-61^{\circ}$ ,  $[\alpha]_D -27.04^{\circ}$  in alcohol. Fenchylene is obtained by heating methyl *isofenchyl*xanthate, its amide, or the liquid *isofenchyl*xanthamide which probably contains a mixture of esters, at  $160-180^{\circ}$ . The products obtained gave the following constants: (i) from the ester, b. p.  $139-140^{\circ}/760$  mm.;  $d_4^{20}$  0.8381;  $n_D^{20}$  1.4494;  $[\alpha]_D -68.76^{\circ}$  in alcohol; (ii) from the solid amide, b. p.  $140-141^{\circ}/740$  mm.;  $d_4^{20}$  0.8397;  $n_D^{20}$  1.4502;  $[\alpha]_D -57.28^{\circ}$  in alcohol; (iii) from the liquid amide, b. p.  $140.5-141.5^{\circ}/740$  mm.;  $d_4^{20}$  0.8398;  $n_D^{20}$  1.4505;  $[\alpha]_D -50.98^{\circ}$ . Fenchylene has the lowest boiling point of all the hydrocarbons of formula  $C_{10}H_{16}$ ; it differs also from *cyclofenchene* and fenchene in its lower specific gravity and refractive index. The differences between the three preparations of fenchylene are probably due to the presence of varying amounts of a hydrocarbon of higher boiling point, specific gravity, and refractive index, but of lower specific rotatory power, probably *cyclofenchene*. Fenchylene combines readily with bromine to give an oily product which cannot be solidified. With ethyl nitrite in acetic acid solution it yields a crystalline *nitrosyl chloride*,  $C_{10}H_{16}NOCl$ , m. p.  $131^{\circ}$ . Alkaline permanganate oxidises it to *cis*-fenchocamphoric acid. F. G. P.

**Pinene. V. Preparation of  $\alpha$ - and  $\delta$ -Pinene.** L. RUZICKA and S. PONTALTI (*Helv. Chim. Acta*, 1924, 7, 489—495).—To complete the partial synthesis of *dl*- $\alpha$ -pinene, of which two stages have already been described (Ruzicka and Trebler, A., 1921, i, 36, 796), it was necessary to establish the genetic relationship between pinocamphone and pinocamphylamine. The latter was therefore prepared from pinocamphone by Wallach's method (A., 1901, i, 90) and methylated to pinocamphyltrimethylammonium iodide, m. p.  $231^{\circ}$ . The m. p. of this compound differs from that of previous preparations of Ruzicka and Trebler (m. p.  $255^{\circ}$ ), and is probably a different mixture of *cis*- and *trans*-isomerides. When

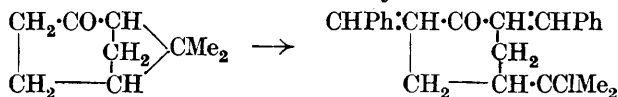
the pinocampyltrimethylammonium hydroxide was distilled in a high vacuum it gave pinocampyltrimethylamine (which when treated with methyl iodide gave the parent substance with unchanged m. p., 231°) and a hydrocarbon. The latter when oxidised gave a mixture of pinonic acid, proving the presence of  $\alpha$ -pinene, and an acid, m. p. 186—187°, identical with that obtained by Wallach (A., 1906, i, 683) by oxidation of *dl*-pinocamphone. This acid, for which the name pinocamphoric acid is proposed, must

have the formula,  $\text{CH} \begin{matrix} \nearrow \text{CH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H} \\ \searrow \text{CMe}_2 \\ \nearrow \text{CH} \cdot \text{CO}_2\text{H} \end{matrix}$ , and proves the presence

of  $\delta$ -pinene (cf. Blumann and Zeitschel, A., 1921, i, 426). The dicarboxylic acid, m. p. 192°, obtained by Gildemeister and Köhler (A., 1910, i, 180) by oxidising a hydrocarbon obtained by the decomposition of *l*-pinocampyl xanthate prepared from pinocamphone from hyssop oil, is shown to be identical with pinocamphoric acid. *l*-Pinocamphone was converted by the above reactions into a mixture of  $\alpha$ - and  $\delta$ -pinene, giving a mixture of pinonic and pinocamphoric acid (m. p. 192°) on oxidation. The dihydroverbenene of Blumann and Zeitschel (*loc. cit.*) is probably not  $\delta$ -pinene, but contains an active form of  $\alpha$ -pinene. E. H. R.

#### Terpenes and Ethereal Oils. CXXVIII. Condensation of Intracyclic Ketones with Two Mols. of Aromatic Aldehydes.

O. WALLACH (*Annalen*, 1924, 437, 187—189; cf. A., 1899, i, 532).—Dicyclic ketones having a methylene group adjacent to the carbonyl group and in which by rupture of the bridge linkings a second methylene group vicinal to the carbonyl can be formed, condense with aromatic aldehydes in the presence of hydrochloric acid, yielding chlorodibenzylidene compounds. Thus nopinone and benzaldehyde yield 3:5-dibenzylidene- $\alpha$ -chloroisopropylcyclohexan-4-one, yellow needles, m. p. 148—149°, the bridge ring being first ruptured by addition of hydrogen chloride, followed by condensation with two molecules of aldehyde:



In the presence of alkali, nopinone and benzaldehyde yield the monobenzylidene derivative, m. p. 106° (cf. A., 1901, i, 89), which with benzaldehyde and hydrochloric acid in alcoholic solution yields the dibenzylidene derivative. Similarly, verbanone yields a chlorodibenzylidene derivative,  $\text{C}_{24}\text{H}_{25}\text{OCl}$ , m. p. 143°, and sabina ketone a chlorodibenzylidene derivative,  $\text{C}_{23}\text{H}_{25}\text{OCl}$ , m. p. 157°, and with anisaldehyde a condensation product, m. p. 198°. R. B.

**Terpenes and Ethereal Oils. CXXIX. Review of the Boiling Points of Stereoisomeric Modifications of Alicyclic Compounds.** O. WALLACH (*Annalen*, 1924, 437, 190—194; cf. A., 1893, i, 274; 1898, i, 485; 1913, i, 482; 1915, i, 423).—The boiling points of *l*- and *d*-menthone as given by various authors fluctuate between 204° and 210°. A careful redetermination under exactly

comparable conditions gives the b. p. 210—210.25° for *l*-menthone and 210.5° for *dl*-menthone. Attempts to determine the boiling points of the different menthonoximes gave no satisfactory results, and it is doubtful whether stereoisomeric compounds can be distinguished from one another by their boiling points. The semi carbazone (m. p. 209°) from trimethylcyclopentanone (A., 1915, i, 499) was separated by crystallisation into two fractions, m. p. 178° and 214°, which on decomposition with oxalic acid yield ketones, b. p. 162—168°, and 167—171°, giving oximes, m. p. 78° and 110°, respectively. The original trimethylcyclopentanone (b. p. 164—167°, oxime, m. p. 105°) is evidently a mixture, but it was not possible to decide from these results whether the isomerism was purely physical, or chemical through the formation of the two theoretically possible isomerides, 1:1:2-trimethylcyclopentan-4-one and 1:1:4-trimethylcyclopentan-2-one. R. B.

**Essential Oils from *Leptospermum Liversidgei*.** A. R. PENFOLD (*J. Roy. Soc. New South Wales*, 1922, **56**, 82—87).—There appear to be two, and probably three, distinct forms of this shrub, yielding, respectively, 0.25—0.3% of oil with 35—50% of citral (no citronellal; cf. Baker and Smith, *ibid.*, 1905, **39**, 124), about 0.55% of oil containing 70—80% of citronellal (no citral), and about 0.6—0.8% of oil containing about 70—80% of citral (no citronellal?).

W. T. K. B.

**A New Stearopten occurring in some Essential Oils of the *Myrtaceæ*.** A. R. PENFOLD and F. R. MORRISON (*J. Roy. Soc. New South Wales*, 1922, **56**, 87—89).—The essential oils of *Bæckeia crenulata* and *Darwinia grandiflora* contain 5.5% and 2%, respectively, of a solid crystallising from alcohol in primrose-yellow needles or monoclinic prisms, m. p. 103—104°. Its solution in alcohol is optically inactive. The compound appears to have the formula  $C_{13}H_{18}O_4$ , and to contain two methoxy groups; it is considered to be a phenol ether.

W. T. K. B.

**Miscibility Test for Eucalyptus Oils.** C. E. FAWSITT and C. H. FISCHER (*J. Roy. Soc. New South Wales*, 1922, **56**, 109—114).—The determination of the critical solution temperature by mixing the oil in definite proportions with a suitable liquid (*e.g.*, aqueous alcohol) giving two layers at the ordinary temperature, heating until only one layer is formed, and then allowing to cool until a cloudiness develops, affords a more sensitive test than the method in which the volume of aqueous alcohol required for complete solution of one volume of the oil is determined. [Cf. B., 1924, 536.]

W. T. K. B.

**Australian *Melaleucas* and their Essential Oils.** VI. R. T. BAKER and H. G. SMITH (*J. Roy. Soc. New South Wales*, 1922, **56**, 115—124).—The oil from *Melaleuca ericifolia* (yield 0.84%) differs from oil of cajuput, by having a lower sp. gr. ( $d^{15}$  0.8938), by the terpenes being strongly dextrorotatory, by containing *d*-terpineol in some quantity, by containing considerably less cineol, and by the principal oxygenated constituent being terpineol and not

cinol. It has  $[\alpha]_D +13.3^\circ$ ,  $n_D^{20}$  1.4705, and saponification value 6.96. The oil obtained from young growths of *M. Deanei* (yield 0.7%) consists mainly of *d*-pinene, with only a small amount of oxygenated substances. The crude oil has  $d^{15}$  0.8888,  $[\alpha]_D +22.7^\circ$ ,  $n_D^{22}$  1.4646, and saponification value 5.7. W. T. K. B.

**Essential Oil of *Backhousia myrtifolia* [Grey or "Scrub" Myrtle].** I. A. R. PENFOLD (*J. Roy. Soc. New South Wales*, 1922, 56, 125—129).—When the leaves and terminal branchlets of this tree are distilled with steam a brownish-yellow oil of pleasing odour and  $d^{15}$  1.026—1.057 is obtained in an average yield of 0.42%, this being greatest in spring. The oil contains 75—80% of the rare phenol ether elemicin, together with pinene, a paraffin (m. p. 62—63°), a sesquiterpene, b. p. 120—138°/10 mm., an alcohol, b. p. 95—109°/10 mm.,  $d^{15}$  0.9018, rotation  $+7.6^\circ$ ,  $n_D^{20}$  1.4770, and a phenol (0.24—0.5%). W. T. K. B.

**Oak Moss Oil.** H. WALBAUM and A. ROSENTHAL (*Ber.*, 1924, 57, [B], 770—773).—The odoriferous substance obtained by extraction or steam distillation of oak moss has been identified as orcinol monomethyl ether. The oil also contains ethyl  $\beta$ -orcinolcarboxylate (methyl 2:4-dihydroxy-3:6-dimethylbenzoate), m. p. 142°. By extracting the lichen with alcohol, ethyl everninate (6-hydroxy-4-methoxy-2-methylbenzoate), m. p. 76°, was isolated, but it is probable that the free acid occurs in the lichen and is esterified by the alcohol. Everninic acid may be the parent substance of the monomethyl orcinol. R. B.

**Refractive Index of Caoutchouc.** D. F. TWISS (*Nature*, 1924, 113, 822).—Caoutchouc has  $n_D^{15}$  1.525. A. A. E.

**The African Poison, Acocantherine.** J. MOIR (*J. S. Afr. Chem. Inst.*, 1924, 7, 28—33).—Acocantherine, prepared from *Acokanthera venenata*, dissolves in concentrated sulphuric acid yielding an orange-yellow solution showing an absorption band at  $\lambda$  476; after some time the colour darkens, a green fluorescence develops, and a band appears at  $\lambda$  495. When hydrolysed with 2% sulphuric acid it yields rhamnose and acocanthic acid lactone; the latter gives a fluorescent orange-coloured solution in concentrated sulphuric acid with a band at  $\lambda$  470, and a yellow solution in sodium hydroxide solution with a band at  $\lambda$  440. Acocantherine therefore resembles ouabaine, and there is but little difference between the properties of acocanthic acid and those of the synthetic substance *benzoumbelliferone* (2:4-dihydroxydiphenyl-2'-carboxylic acid lactone). W. P. S.

**Insecticides. X. Synthesis of Pyrethrines.** H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 448—458).—Both active constituents of insect powder (this vol., i, 700) have been synthesised from their acid and alcoholic components, but the synthesis is incomplete, as synthetic chrysanthemumic acid has not yet been resolved and pyrethrolone has not been completely synthesised (cf. i, 522). Pyrethrine I, from chrysanthemumcarb-

oxylic chloride and pyrethrolone in presence of pyridine, is a colourless, viscous oil, b. p. 145—150°/0.125 mm.,  $[\alpha]_D^{25} -16.2^\circ$ ; the semicarbazone is crystalline, but melts indefinitely between 80° and 90°. Pyrethrine II, obtained similarly from the chloride of methyl hydrogen chrysanthemumdicarboxylate, is a colourless, odourless, viscous oil, b. p. 195°/0.167 mm.; its semicarbazone is amorphous. A large number of esters of pyrethrolone with organic acids and of chrysanthemumcarboxylic acids with alcohols of many types were prepared, but none of these had insecticidal properties at all comparable with those of the pyrethrines. E. H. R.

**Furoyl Peroxide.** H. GELISSEN and J. D. VAN ROON (*Rec. trav. chim.*, 1924, **43**, 359—366).—*Furoyl peroxide*,  $(C_4H_3O \cdot CO)_2O_2$ , white crystals, m. p. 86°, which turn yellow in the air, is prepared by the action of cold alkaline hydrogen peroxide on pyromucyl chloride. It is less stable than benzoyl peroxide, is hydrolysed by water, and liberates iodine from potassium iodide solution. It is also more sensitive to shock than benzoyl peroxide, and explodes without smoke. Diphenyl can be obtained by warming benzoyl peroxide in benzene solution, but difuryl is not analogously formed from furoyl peroxide. E. H. R.

**Trimethylene Trisulphides.** O. HINSBERG (*Ber.*, 1924, **57**, [B], 836—838; cf. A., 1914, i, 185, 797; 1923, i, 1056).—The sulfoxide obtained by the action of hydrogen peroxide on trimethylene trisulphide  $(CH_2S)_3$ , is smoothly oxidised by permanganate in faintly acid solution to yield trimethylene trisulphone,  $(CH_2SO_2)_3$  (cf. Fromm and Schultis, A., 1923, i, 580). The sulfoxide must therefore be the trimeric form,  $(CH_2SO)_3$ . Since hydriodic acid converts it into the trisulphide of m. p. 247°, and since it is re-formed from the latter by oxidation with hydrogen peroxide, this trisulphide must be trimeric, and stereoisomeric with that of m. p. 216°. Possibly the crude trisulphide forms a third stereoisomeride which changes into the 216° form on crystallisation. F. A. M.

**Synthesis of Cyclic Polysulphides.** I. SIR P. C. RAY (*J. Chem. Soc.*, 1924, **125**, 1141—1144).—When dithioethylene glycol (2 mols.) and benzylidene chloride (1 mol.) are boiled together gently during 30 hours, the chief products are *benzylidenediethylene tetrasulphide*,  $CHPh \begin{smallmatrix} \text{S} \cdot C_2H_4 \cdot S \\ \text{S} \cdot C_2H_4 \cdot S \end{smallmatrix}$ , and *trisulphide*,  $CHPh \begin{smallmatrix} \text{S} \cdot C_2H_4 \\ \text{S} \cdot C_2H_4 \end{smallmatrix} S$ , both of which are oily liquids; diethylene di- and tri-sulphides are also formed as by-products. According to the duration of heating, benzylidenediethylene trisulphide reacts with boiling methyl iodide to form *methiodides* approximating in composition to  $C_4H_8S_2 \cdot 2MeI$  and  $C_4H_8S \cdot 3MeI$ ; with ethyl iodide it forms an *ethiodide*,  $2C_{11}H_{14}S_2 \cdot EtI$ , together with diethylene di- and tri-sulphides.

With mercuric chloride and platinic chloride, benzylidenediethylene tri- and tetra-sulphides form additive compounds; in the

substances formed from platinic chloride, the valency of platinum may vary (cf. T., 1923, **123**, 133).

Oxidation of benzylidenediethylene trisulphide with nitric acid yields benzoic acid, ethanedisulphonic acid, and sulphuric acid.

C. J. S.

**Strychnine and Brucine.** R. CIUSA and G. SCAGLIARINI (*Gazzetta*, 1924, **54**, 202—203).—The authors reply to Oliveri-Mandalà and Comella (A., 1923, i, 1223) on certain points concerning the structure of *isostrychnine*.

T. H. P.

[**Partial**] **Synthesis of 2-*n*-Butylpyrrolidine.** E. E. BLAISE and A. CORNILLON (*Compt. rend.*, 1924, **178**, 1186—1188; cf. Blaise and Houillon, A., 1906, i, 692, also following abstract).—Magnesium *n*-butyl iodide converts ethyl cyanoacetate into *ethyl n-valerylacetate*, b. p. 112°/18 mm., converted by semicarbazide and phenylhydrazine into the *carbamylpyrazolone*, m. p. 165°, and *butylphenylpyrazolone*, m. p. 79°, respectively. The potassium derivative of the valeryl ester reacts with  $\beta$ -iodoethylphthalimide to give a compound which when hydrolysed with hydrobromic acid affords 2-*n*-butylpyrrolidine, b. p. 68·5°/19 mm. [*chloroplatinate*, m. p. 182—183° (decomp.)]. The hydrochloride reacts with potassium cyanate, yielding the *carbamide*,  $C_9H_{16}ON_2 \cdot H_2O$ , m. p. 104—105°. Hydrogenation of the base has not yet been effected. H. J. E.

**Synthesis of 2-*n*-Butylpyrrolidine.** E. E. BLAISE and A. CORNILLON (*Compt. rend.*, 1924, **178**, 1617—1619).—2 : 5-Dimethylpyrroline, obtained by reducing the product of the interaction of ammonia and acetylacetone, forms a chloroaurate, m. p. 77° [Knorr and Rabe (A., 1902, i, 54) gave 68—69°], and a phenylcarbamide, m. p. 130°. When reduced in an atmosphere of hydrogen and in presence of platinum chloride previously reduced by means of gum arabic, it yields 2 : 5-dimethylpyrrolidine as a colourless liquid, b. p. 106·5°; the chloroaurate has m. p. 85° [Fenner and Tafel (A., 1900, i, 111) gave 96—100°] and the phenylcarbamide, m. p. 142°. 2-*n*-Butylpyrrolidine, similarly prepared from 2-*n*-butylpyrroline, agrees exactly with the compound previously obtained by Blaise and Houillon (A., 1906, i, 692), so that Hess' compound (A., 1920, i, 85) must have another constitution. It is suggested that the use of hydriodic acid as a reducing agent should be avoided in all synthetic processes used for the determination of constitution.

T. H. P.

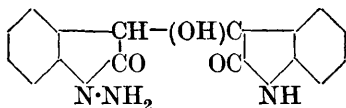
**Nitropyrrole and Pyrrole-aldehydes.** A. ANGELI (*Ber.*, 1924, **57**, [B], 834—836).—A criticism of recent work by Fischer, Zerweck, and Smeykal (A., 1922, i, 758; this vol., i, 201); their statement that alkylated pyrroles can be nitrated smoothly is not strictly accurate, as they worked with carboxylic esters of pyrrole-ketones and -aldehydes, dicarboxylic esters, etc. Angeli had already shown that pyrrole, but not methyl pyrrol ketone, is rapidly oxidised by permanganate. Fischer and Zerweck overlooked Angeli's synthesis of pyrrole-aldehydes using formic ester

and sodium alkoxide, which favours a hydroxymethylene structure for these substances (cf. A., 1915, i, 454; and Fischer, A., 1913, i, 1225). Pyrrole-aldehyde and its di-ortho substituted derivatives do not respond to Baudisch's reagent (A., 1921, ii, 337), whereas 1-methylpyrrole-aldehyde does.

F. A. M.

**1-Amino-oxindole.** P. W. NEBER and H. KEPPLER (*Ber.*, 1924, 57, [B], 778—787).—1-Amino-oxindole (A., 1922, i, 546) on treatment with 1 or 2 mols. of benzaldehyde yielded 1-amino-3-benzylideneoxindole (pale yellow crystals, m. p. 116°) or 1-benzylideneamino-3-benzylideneoxindole (yellow needles, m. p. 161°), respectively. The monobenzylidene compound with amyl nitrite and hydrochloric acid gave 3-benzylideneoxindole, m. p. 172° (cf. Wahl and Bagard, A., 1909, i, 735). With the three nitrobenzaldehydes the products were the 1-nitrobenzylideneamino-oxindoles, which were conveniently prepared from the corresponding nitrobenzylidenephénylhydrazine-*o*-acetic acids. N'[*o*-Nitrobenzylidene]-phenylhydrazine-*o*-acetic acid forms orange needles, m. p. 158°; the *meta* compound forms orange leaflets, m. p. 166°, the *para* compound scarlet needles, m. p. 175°; boiling glacial acetic acid converts the acids into the corresponding 1-nitrobenzylideneamino-oxindoles, which form yellow needles, *ortho*, m. p. 168—170°; *meta*, m. p. 160°; *para*, m. p. 220—227°. These are stable to mineral acids and insoluble in alkalis. The *o*-nitrobenzylidene compound on treatment with amyl nitrite and hydrochloric acid affords  $\beta$ -isatoxime.

1-Amino-oxindole condensed with isatin in hot acetic acid to form N-aminoisindigotin, yellow needles, m. p. 205—207°; this gave the indophenin reaction. 1-Acetamido-oxindole also condensed with isatin to form N-acetamidoisindigotin (a bright red, microcrystalline powder, m. p. 303—306° [indef.]), which dissolved easily in dilute alkali, from which it was reprecipitated by acids. A solution of N-aminoisindigotin in aqueous potassium hydroxide on acidification gave a substance,  $C_{16}H_{13}O_3N_3$ , golden-yellow leaflets, m. p. 234—236°, which was insoluble in sodium carbonate but soluble in warm dilute alkali. On condensing 1-amino-oxindole with isatin in absolute alcohol in presence of piperidine a substance (annexed formula), was obtained as ivory-coloured leaflets, m. p. (decomp.) 208° upwards. On heating with alcoholic potassium hydroxide and acidifying, the yellow isomeride,



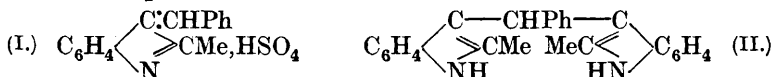
$C_{16}H_{13}O_3N_3$ , m. p. 234—236°, was obtained. N-Aminoindirubin was obtained by condensing 1-amino-oxindole and isatin- $\alpha$ -anil in alcoholic solution and formed almost black needles, m. p. (indef.) 253—256° (with previous sublimation). N-Acetamidoindirubin was obtained similarly from 1-acetamido-oxindole and isatin- $\alpha$ -anil as reddish-violet needles, m. p. about 299—302° (with previous sublimation). 1-Acetamido-oxindole forms colourless needles (+ $H_2O$ ), m. p. 186—187°. 1-Benzoylamido-oxindole forms faintly coloured leaflets, m. p. 189°. Both the acetyl and benzoyl com-



pounds are soluble in dilute alkalis. Treatment of 1-acetamido-oxindole in acetic acid with amyl nitrite and hydrochloric acid gave bright green needles of *N*-acetamido- $\beta$ -isatoxime (annexed formula), m. p. 245—246° (decomp.); this, when boiled with sulphuric acid (1:3), afforded indazole-3-carboxylic acid. Condensation of 1-acetamido-oxindole with *p*-nitrosodimethylaniline gave *N*-acetamido-isatin- $\beta$ -*p*-dimethylamino-anil as a dark brown powder, m. p. 214° (with previous sublimation) (red sodium salt, soluble), which with dilute mineral acids gave indazolecarboxylic acid. 1-Acetamido-oxindole was converted by dimethyl sulphate into 1-acetylmethylamino-oxindole, colourless leaflets, m. p. 146°; treatment with amyl nitrite and hydrochloric acid gave *N*-acetylmethylamino- $\beta$ -isatoxime, greenish-yellow needles, m. p. 192—194° (methyl ether, yellowish-brown leaflets, m. p. 205—207°; also obtained directly by methylation of *N*-acetamido- $\beta$ -isatoxime). On boiling the oxime with dilute sulphuric acid, 2-methylindazole-3-carboxylic acid was obtained as colourless leaflets, m. p. 215° (decomp.). Complete methylation of 1-amino-oxindole afforded 1-dimethylamino-oxindole as colourless leaflets, m. p. 81°; this condensed with nitrosobenzene in presence of piperidine to give *N*-dimethylaminoisatin-3-anil, orange needles, m. p. 125°, which when hydrolysed gave *N*-dimethylaminoisatin, dark red needles, m. p. 239°. 1-Dimethylamino-oxindole on treatment with amyl nitrite in hydrochloric-acetic acid solution afforded *N*-dimethylamino- $\beta$ -isatoxime, yellow needles, m. p. 166—167°.

F. A. M.

**The Humin formed by Acid Hydrolysis of Proteins. VIII. Condensation of Indole Derivatives with Aldehydes.** G. O. BURR and R. A. GORTNER (*J. Amer. Chem. Soc.*, 1924, **46**, 1224—1246; cf. Freund and Lebach, A., 1905, i, 663).—2-Methylindole condenses with benzaldehyde in presence of concentrated sulphuric acid to form *phenyl-2-methylindolidenemethane hydrogen sulphate* (I), orange needles, darkening above 100°, m. p. 172—173° with re-solidification at 175°. The free base was amorphous. On boiling with water, the sulphate is converted into phenyldi-2-methylindylmethane (II) (Fischer's "benzylidene dimethyl ketole") and benzaldehyde, the reaction being reversed in presence of concentrated sulphuric acid.



*p*-Dimethylaminophenyl-2-methylindolidenemethane hydrochloride, similarly obtained using hydrogen chloride as condensing agent, forms a hard, golden mass, m. p. 150—160°, purple-red in solution. The base has m. p. about 100°, dependent on the rate of heating. Its alcoholic solution is colourless at  $p_H$  7.58, brilliant red at  $p_H$  6.48. It yields a humin-like material on treatment with alcoholic hydrogen chloride, and both substances form ferrocyanides of the com-

position  $(\text{Base})_4\text{H}_4\text{Fe}(\text{CN})_6\cdot 2\text{H}_2\text{O}$ . The violet humin-like base similarly obtained from *o*-hydroxyphenyl-2-methylindolidenemethane has m. p.  $305^\circ$ . *Anisyl-2-methylindolidenemethane hydrochloride*, golden, irregular plates, m. p.  $181^\circ$  (darkening at  $155^\circ$ ); *cinnamyl-2-methylindolidenemethane hydrochloride*, golden needles, blackening at  $160^\circ$ , sintering at  $180^\circ$ , m. p.  $195\text{--}205^\circ$ ; *o*-tolyl-2-methylindolidenemethane hydrochloride, yellow prisms, m. p.  $178^\circ$  (darkening at  $165^\circ$ ); *p*-hydroxyphenyl-2-methylindolidenemethane hydrochloride, orange-red plates and wedges, m. p.  $189^\circ$ ; *m*-nitrophenyl-2-methylindolidenemethane, a brown powder, exploding at a high temperature; and 2:4:6-trinitrophenyl-2-methylindolidenemethane, minute, orange needles, m. p.  $152^\circ$ , are described. 2-Phenylindole condenses with benzaldehyde (excess) in presence of sulphuric acid, to form Fischer's "benzylidene-Pr<sub>2</sub>-phenylindol." Using excess of sulphuric acid, *phenyl-2-phenylindolidenemethane* is formed as an orange powder, m. p.  $182\text{--}184^\circ$ , hydrolysed by boiling water to *benzylidenedi-2-phenylindole*. *p*-Hydroxyphenyl-2-phenylindolidenemethane hydrochloride, red prisms, m. p. indef.; *cinnamyl-2-phenylindolidenemethane*, a brown powder, m. p.  $146\text{--}148^\circ$ ; *o*-hydroxyphenyl-2-phenylindolidenemethane hydrochloride, minute needles, sintering at  $165^\circ$ , but having no m. p.; *o*-chlorophenyl-2-phenylindolidenemethane hydrochloride, an orange powder, m. p.  $212\text{--}214^\circ$ ; *anisyl-2-phenylindolidenemethane*, a red powder, m. p. indef.; *p*-dimethylaminophenyl-2-phenylindolidenemethane, a purple powder, m. p.  $155^\circ$ ; *o*-tolyl-2-phenylindolidenemethane, a brownish-yellow powder; *m*-nitrophenyl-2-phenylindolidenemethane, a yellow powder; and 2:4:6-trinitrophenyl-2-phenylindolidenemethane, an unstable, orange powder, are described. 2:3-Diphenylindole gave no condensation products analogous with the above, benzaldehyde etc. giving a grey, powdery substance, m. p.  $123^\circ$ . 2-Phenyl-3-methylindole yielded, similarly, a grey substance, m. p.  $221\text{--}223^\circ$ . Tryptophan condenses with salicylaldehyde with formation of a grey, powdery substance,  $\text{C}_{12}\text{H}_{24}\text{O}_5\text{N}_2\text{Cl}$ , excess of the aldehyde giving a humin. Humin-like products, derived from the condensation of 1 mol. of the indole with 2 mols. of aldehyde, were obtained by boiling the indoles, or the primary condensation products analogous to (I) and (II) above, with excess of the appropriate aldehyde in 20% hydrochloric acid. Yields were generally quantitative except with trinitrobenzaldehyde; humins were not obtainable from 2:3-diphenylindole. The solubilities of the humin hydrochlorides in acids, alkalis, and organic solvents, the solubility of the bases in ether, and their fusibility are tabulated. The artificial humins are precipitated from chloroacetic acid solution by water, but fibrin humins require the addition of hydrochloric acid to bring about coagulation. Humins of constant composition cannot be obtained from proteins. The humin from *o*-tolualdehyde and 2-methylindole was the most readily purified, whilst 2-phenylindole and benzaldehyde gave the only oxygen-free humin. The mol. weights of two fibrin humins, determined cryoscopically in chloroacetic acid, were found to be 439 and 760—780, respectively. Mol.-weight determinations of the indole humins in aniline were

unsuccessful. In phenol, the values obtained indicated that humin formation from 1 mol. of indole and 2 mols. of aldehyde is accompanied by polymerisation of the simple end-product. In benzene, further association was found in the one case examined. The mol. weights of hydrolytic humins and those derived from aromatic aldehydes were of the same order, whilst those derived from formaldehyde and indoles were much higher. 2-Methylindole remains unchanged on boiling with 20% hydrochloric acid. Phenyl-2-methylindolidenemethane hydrogen sulphate loses 1 mol. of water at 140—150°, with formation of a sulphonic acid. It yields amorphous, reddish-violet products on boiling with acids or on exposing its solutions to the light of a tungsten lamp. Some of these products condense more readily with benzaldehyde than does the original substance, indicating that humin formation from the indolidenemethane intermediates is preceded by molecular rearrangement. The humins obtained from 2-methylindole and benzaldehyde, 2:4:6-trinitrobenzaldehyde, and *o*-tolualdehyde, respectively, were stable to alkaline permanganate or alkali fusion, but were completely oxidised (to benzoic acid) by boiling chromic-acetic acid. The *o*-tolualdehyde humin formed a black, amorphous dibromide,  $C_{26}H_{21}NBr_2$ , the humin being regenerated by the action of sodium in alcohol. An unstable hydrochloride, but no picrate, was obtained.

F. G. W.

### Isatin. Condensation of Isatin with Phenylhydroxylamine.

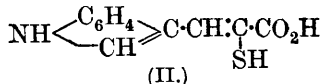
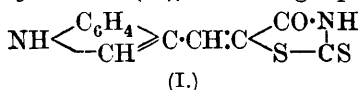
H. RUPE and E. STÖCKLIN (*Helv. Chim. Acta*, 1924, 7, 557—566).—Isatin reacts readily with phenylhydroxylamine to form *isatin-phenylhydroxylamine*,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown N \end{smallmatrix} > C \cdot NPh \cdot OH$ , large, red needles, m. p. 216° (decomp.), which is decomposed by alkalis into isatinic acid and phenylhydroxylamine. The same compound is obtained from isatin chloride and phenylhydroxylamine. With methyl sulphate in presence of alkali it gives *O-methylisatin-β-phenylhydroxylamine*, long, orange prisms, m. p. 152° (decomp.). On one occasion an *isomeride*, probably the *N*-methyl derivative, brown crystals, m. p. 181° (decomp.), was obtained, which, unlike the *O*-ether, is readily hydrolysed by alkali. The *O-acetyl* derivative of isatinphenylhydroxylamine, long needles, m. p. 179° (decomp.), and the *O-benzoyl* derivative, orange needles, m. p. 196°, are stable in presence of alkali. By the action of thionyl chloride on isatinphenylhydroxylamine, *isatin-N-chloroanilide*,  $C_6H_4ON \cdot NPh \cdot Cl$ , is obtained, small, brownish-red tablets, m. p. 182°. Isatinphenylhydroxylamine reacts with phenylhydrazine and semicarbazide to form isatinphenylhydrazone and isatinsemicarbazone. 7-Methylisatin-β-phenylhydroxylamine forms dark red crystals, m. p. 222—225° (decomp.).

By condensing 5-nitroisatin with phenylhydroxylamine, or by nitrating isatinphenylhydroxylamine with nitric acid (*d* 1.35), 5-nitroisatinphenylhydroxylamine is obtained, glistening bronze leaflets, m. p. 227° (decomp.). Its *O-methyl* ether forms orange, felted needles, m. p. 213°, and its *benzoyl* derivative, orange needles,

m. p. 203°. The nitro compound is readily soluble in alkalis, even in ammonia, with a deep red colour, and probably has the pseudo-acid structure,  $\text{NO}_2\text{H}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CO} \\ \text{N} \end{smallmatrix}\text{C:NPh}\cdot\text{O}$ .

A new nitro derivative of isatin, 6-nitroisatin, obtained by nitrating isatin in concentrated sulphuric acid, forms reddish-yellow needles, m. p. 244°. 6-Nitroisatin- $\beta$ -phenylhydroxylamine forms long needles, m. p. 224–227°, much redder than the 5-nitro derivative. E. H. R.

**Use of Rhodanine in Organic Syntheses. IV. Indole- and Furyl-pyruvic Acids.** C. GRÄNACHER, M. GERÖ, and V. SCHELING (*Helv. Chim. Acta*, 1924, 7, 575–578; cf. A., 1923, i, 706, 713).—3-Indolealdehyde condenses with rhodanine in acetic acid or acetic anhydride to form 3-indolylidenerhodanine (I), glistening brown leaflets, decomposing above 200°. This substance is converted by hot potassium hydroxide solution into  $\alpha$ -thiol- $\beta$ -3-indoleacrylic acid (II), an orange powder, decomp. 190°. When the



ammonium salt of this acid is warmed in solution with lead powder, it is converted into  $\beta$ -3-indolepyruvic acid,  $\text{C}_8\text{H}_6\text{N}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ .

$\beta$ -2-Furylpyruvic acid has been obtained by hydrolysing  $\alpha$ -oximino- $\beta$ -2-furylpyruvic acid (A., 1922, i, 850) with sulphurous acid. It forms unstable, pale yellow needles, m. p. 131°. E. H. R.

**Use of Rhodanine in Organic Syntheses. V. Indole-2-carboxylic acid.** C. GRÄNACHER, A. MAHAL, and M. GERÖ (*Helv. Chim. Acta*, 1924, 7, 579–586).—A new synthesis of indole-2-carboxylic acid is described. *o*-Nitrobenzylidenerhodanine (Bondzynski, A., 1887, 1108) is reduced in aqueous solution with ferrous hydroxide, and the solution of *o*-aminobenzylidenerhodanine, after making strongly alkaline with sodium hydroxide, is filtered and boiled, whereby  $\alpha$ -thiol-*o*-aminocinnamic acid is formed. Ammonium chloride is added in small portions, whereupon a vigorous reaction ensues, and the resulting indole-2-carboxylic acid is precipitated by acidification. Ethyl indole-2-carboxylate (m. p. 124–125°) condenses with benzaldehyde to form ethyl phenyl-3 : 3'-di-indylmethane-2 : 2'-dicarboxylate,  $\text{CHPh}(\text{C}_8\text{H}_5\text{N}\cdot\text{CO}_2\text{Et})_2$ , white needles, m. p. 239°; the corresponding acid crystallises in needles containing 1 mol. of alcohol, m. p. 243–244° (decomp.); potassium salt,  $\text{C}_{25}\text{H}_{16}\text{O}_4\text{N}_2\text{K}_2\cdot\text{H}_2\text{O}$ . Similarly, *p*-anisaldehyde condenses to give ethyl *p*-methoxyphenyl-3 : 3'-di-indylmethane-2 : 2'-dicarboxylate, white crystals, m. p. 222° (decomp.); the corresponding acid has m. p. 267° (decomp.), and turns red on exposure to air. Formaldehyde condenses with ethyl indole-2-carboxylate to give, in poor yield, ethyl 3 : 3'-di-indylmethane-2 : 2'-dicarboxylate, a yellow, crystalline powder, m. p. 260° (decomp.); the acid forms pale yellow needles containing 1 mol of alcohol, m. p. 265°. E. H. R.

**Formation of 3-Halogencarbazoles from Carbazole-3-diazonium Halides.** S. H. TUCKER (*J. Chem. Soc.*, 1924, **125**, 1144—1148).—Carbazole-3-diazonium chloride has been obtained (cf. T., 1922, **122**, 2711) anhydrous and as di- and tri-hydrates. When treated, in acetone solution, with copper-bronze it yields a yellow product which, when acetylated, yields 3-chloro-*N*-acetylcarbazole, and this on hydrolysis gives 3-chlorocarbazole. *Carbazole-3-diazonium bromide*,  $C_{12}H_8N_3Br \cdot 2H_2O$ , yellow crystals, m. p. 110° (decomp.), was prepared from 3-aminocarbazole, and also from carbazole-3-diazonium chloride and potassium bromide; by treatment, in methyl ethyl ketone, with copper-bronze and acetylating and hydrolysing the resulting product there is formed 3-bromocarbazole. 3-Acetoxy-*N*-acetylcarbazole is obtained when carbazole-3-diazonium bromide is boiled with acetic anhydride and a little concentrated sulphuric acid.

*Carbazole-3-diazonium iodide*,  $C_{12}H_8N_3I \cdot H_2O$ , is precipitated as a canary-yellow, crystalline substance on mixing aqueous solutions of carbazole-3-diazonium chloride and potassium iodide. It decomposes spontaneously in organic solvents to form 3-iodocarbazole, colourless, nacreous plates, m. p. 192—194° (*N*-acetyl derivative, needles, m. p. 145—147°). C. J. S.

**Condensation of Acetaldehyde with Ammonia in Presence of Alumina.** A. E. TSCHITSCHIBABIN, P. A. MOSCHKIN, and L. S. TJASCHELOWA (*J. pr. Chem.*, 1924, [ii], **107**, 132—137).—The product obtained by passing acetaldehyde and ammonia over alumina at 300° resembled closely that from acetylene and ammonia (this vol., i, 313). The crude condensate contained neutral compounds (20—25%), secondary bases, and tertiary bases (42½% of the raw condensate or about 60% of the theoretical yield). Further examination was confined to the last mixture; it was fractionally distilled and then separated into its components by fractional precipitation of their picrates (cf. *loc. cit.*).  $\alpha$ -Picoline,  $\gamma$ -picoline, and 2-methyl-5-ethylpyridine ("aldehyde-collidine") were present in nearly equal amounts, together with smaller quantities of  $\beta$ -collidine and the two other bases already described (*loc. cit.*). There were no indications that pyridine was formed. W. A. S.

**Products formed when Paraldehyde and Aldehyde-ammonia are heated together.** A. E. TSCHITSCHIBABIN and M. P. OPARINA (*J. pr. Chem.*, 1924, [ii], **107**, 138—144).—For comparison with the results obtained in other experiments (cf. foregoing abstracts) this condensation (Dürkopf and Schlaugk, A., 1888, 1314, etc.) has been reinvestigated. A mixture of paraldehyde (3 mols.) and aldehyde-ammonia (1 mol.), heated in a sealed tube for 4 hours at 220°, gives an oily product, one-third of which is insoluble in acid. The remainder, separated into its components by fractional distillation and precipitation with picric acid, consists (above 80%) of 2-methyl-5-ethylpyridine; about 11% is  $\alpha$ -picoline, whilst  $\gamma$ -picoline and  $\beta$ -collidine are also present in small amount. There is also a little of the collidine (the picrate is now stated to have m. p. 139° and the chloroplatinate m. p. 190°) found in the

product of interaction of acetaldehyde and ammonia in presence of alumina. The trimethylpyridine of Knudsen and others (A., 1895, i, 562) and lutidine were not detected. W. A. S.

**Condensation of Propionaldehyde with Ammonia.** A. E. TSCHITSCHIBABIN and M. P. OPARINA (*J. pr. Chem.*, 1924, [ii], **107**, 145—154).—By passing propionaldehyde and ammonia over alumina at 310—320°, a product was obtained which consisted of neutral substances (about 50%), secondary bases (about 15%), and tertiary bases, the yield of which therefore was about 40% of the theoretical, in agreement with that obtained by other methods (cf. Dürkopf and others, A., 1890, 1002, etc.). The mixture of tertiary bases contained some tarry material of high b. p., but otherwise consisted almost entirely of the following three compounds: 3:5-dimethyl-2-ethylpyridine (picrate, yellow leaflets, m. p. 156—157°, cf. Dürkopf, *loc. cit.*), about 60%; 3:5-dimethyl-4-ethylpyridine (b. p. 219—220°/748 mm.,  $d_4^{26.7}$  0.9516,  $n_D^{26.7}$  1.5064; picrate, prisms, m. p. 155—156°), about 23%; this substance was isolated by Dürkopf (*loc. cit.*), who supposed it to be a tetramethylpyridine; the authors have now oxidised it to 4-ethylpyridine-3:5-dicarboxylic acid, m. p. 261° (decomp.), and converted the latter into 4-ethylpyridine (cf. Tschitschibabin, A., 1906, i, 451). The remaining 17—18% of the mixture is 3:5-dimethylpyridine. W. A. S.

**Synthesis of Pyridine from Aldehydes and Ammonia.** A. E. TSCHITSCHIBABIN and M. P. OPARINA (*J. pr. Chem.*, 1924, [ii], **107**, 154—158).—A more detailed account of work already noted (this vol., i, 312). W. A. S.

**2-Amino-4-methylpyridine and certain Derivatives.** O. SEIDE (*Ber.*, 1924, **57**, [B], 791—794; cf. Tschitschibabin and Zeide, A., 1915, i, 590; Zeide, A., 1923, i, 600).—2-Amino-4-methylpyridine, lustrous leaflets, m. p. 98°, is prepared by the action of sodamide on 4-methylpyridine dissolved in boiling xylene; the hydrochloride, m. p. 176—177°, nitrate, m. p. 139°, picrate, m. p. 227° (decomp.), and chloroplatinate, m. p. 208°, are described. 2-Acetylamino-4-methylpyridine, colourless prisms, m. p. 102—103°, yields a picrate, yellow needles. Benzoylation of 2-amino-4-methylpyridine gives a mixture of the dibenzoyl derivative, colourless needles, m. p. 182—183°, and monobenzoyl compound, colourless prisms, m. p. 114°. Diazotisation of 2-amino-4-methylpyridine in very concentrated hydrochloric acid solution yields mainly 2-chloro-4-methylpyridine, a colourless liquid, b. p. 194—195°,  $d_4^{20}$  1.1459,  $n_D^{20}$  1.5293 [chloroplatinate, orange-coloured prisms (+H<sub>2</sub>O) which blacken at 219° but do not melt below 290°]; 2-hydroxy-4-methylpyridine, rhombs, m. p. 130° (monohydrate, m. p. 65°), is produced in minor amount, but is more conveniently prepared by diazotisation of the amine dissolved in dilute hydrochloric acid. 4-Amino-2-methylpyridine dissolved in concentrated sulphuric acid is converted by nitric acid (d 1.4) at 0° into 2-nitroamino-4-methylpyridine, pale yellow prisms, m. p. 182° (decomp.), which is transformed by prolonged contact with sulphuric acid at the

atmospheric temperature into a mixture of (?) 3-nitro-2-amino-4-methylpyridine, yellow needles, m. p. 136°, and (?) 5-nitro-2-amino-4-methylpyridine, yellow prisms, m. p. 220°. H. W.

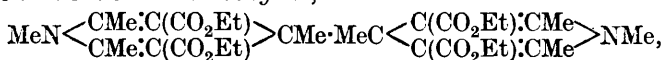
**Constitution of Roth's 2-Stilbazolealkine and Synthesis of 2-Stilbazoleisoalkine.** C. RÄTH (*Ber.*, 1924, 57, [B], 840—842).—Pyridine-2-aldehyde (cf. Lénart, A., 1914, i, 574) is converted by magnesium benzyl bromide into 2- $\alpha$ -hydroxy- $\beta$ -phenylethylpyridine, colourless cubes, m. p. 104° (the hydrochloride, leaflets, m. p. 152°, and the non-crystalline picrate are described). It is not identical with the compound described by Roth (A., 1901, i, 165), which must therefore be 2- $\beta$ -hydroxy- $\beta$ -phenylethylpyridine. H. W.

**Dihydroquinoline Bases.** G. HELLER (*Ber.*, 1924, 57, [B], 764; cf. Râth, this vol., i, 555).—The compound considered by Doebner (A., 1898, i, 384) to be 2-methyldihydroquinoline should be deleted from the literature (cf. Heller and Sourlis, A., 1908, i, 914; Heller, A., 1911, i, 747). H. W.

**Quinoline Dyestuffs.** E. ROSENHAUER [with A. SCHMIDT and W. SCHLEIFENBAUM] (*J. pr. Chem.*, 1924, [ii], 107, 232—240).—2-Methylene-1-methyl-1:2-dihydroquinoline (“quinaldineiso-base”) combines with bromine to form a perbromide-like compound, C<sub>11</sub>H<sub>11</sub>NBr<sub>3</sub> (yellow crystals, decomp. 152°), which decomposes when dissolved in acetone, giving bromoacetone and 2-bromomethylquinoline methobromide, pale yellow prisms, decomp. 205°. Either substance interacts with phenylhydrazine, giving 2-benzeneazomethylene-1-methyldihydroquinoline hydrobromide, violet needles, decomp. 250°; the corresponding base forms bronzy, dark red needles, m. p. 140—141°. Similar compounds were obtained with *p*-bromophenylhydrazine (base: red needles, m. p. [indef.] 162°; hydrobromide: needles, decomp. 259°) and *p*-nitrophenylhydrazine (base: bluish-green needles, decomp. 186°; hydrobromide: red needles, decomp. 248°).  $\alpha$ -Bromomethylquinoline methobromide and *p*-aminodimethylaniline interact to give the methobromide (green prisms, decomp. 198°) corresponding with  $\alpha$ -*p*-dimethylaminophenyliminomethylenequinoline ethiodide (Kaufmann and Valette, A., 1912, i, 655). The extension of these experiments to lepidine and  $\alpha$ -picoline is announced. W. A. S.

**1:1'-Dialkyltetrahydrodipyridyls.** O. MUMM, O. RÖDER, and H. LUDWIG (*Ber.*, 1924, 57, [B], 865—880).—In continuation of previous work (Mumm and Beth, A., 1921, i, 686), the preparation is described of a 4:4'-disubstituted dipyridyl; it is bimolecular in freshly-prepared solution in freezing benzene, but gradually dissociates when preserved. It is intensely active chemically. Since, however, solutions which contain the unimolecular form are not intensely coloured, this activity is not ascribed to fission into radicals, but to the powerful “divided” partial valencies of the nitrogen and 2-carbon atoms.

*Ethyl 1:2:4:6:1':2':4':6'-octamethyltetrahydro-4:4'-dipyridyl-3:5:3':5'-tetracarboxylate*,



pale yellow, lustrous needles, m. p. 80—82°, is prepared in 90—100% yield by the action of sodium amalgam on an aqueous solution of ethyl 2:4:6-trimethylpyridine-3:5-dicarboxylate methosulphate (cf. Mumm and Hingst, this vol., i, 83) in an atmosphere of carbon dioxide. When heated above its m. p. in an atmosphere of hydrogen, it is transformed into equivalent amounts of ethyl 1:2:4:6-tetramethyldihydropyridine-3:5-dicarboxylate and ethyl trimethylmethylenedihydropyridine-3:5-dicarboxylate, m. p. 72—73° (cf. Mumm and Hingst, *loc. cit.*); a similar “disproportionation” is observed under the influence of dilute hydrochloric acid. The dipyridyl compound (1 mol.) reacts with iodine (2 atoms) in alcoholic solution in the absence of air to give ethyl 2:4:6-trimethylpyridine-3:5-dicarboxylate methiodide. As intermediate or by-products, the *periodides*,  $\text{C}_{14}\text{H}_{19}\text{O}_4\text{N}, \text{MeI}, \text{I}_2$ , m. p. 102—103°, and  $\text{C}_{14}\text{H}_{19}\text{O}_4\text{N}, \text{MeI}, \text{I}$ , m. p. 114°, are observed. These substances can also be prepared from ethyl 2:4:6-trimethylpyridine-3:5-dicarboxylate and iodine in alcoholic solution; they are bimolecular. The dipyridyl compound when dissolved in benzene absorbs oxygen very rapidly, giving ethyl trimethylmethylenedihydropyridine-3:5-dicarboxylate, mixed with small amounts of ethyl 1:2:4:6-tetramethyldihydropyridine-3:5-dicarboxylate. It is readily hydrogenated in alcoholic solution in the presence of colloidal palladium to the unsymmetrical ethyl 1:2:4:6-tetramethyldihydropyridine-3:5-dicarboxylate, b. p. 145—152°/0.3 mm. (cf. Mumm and Hingst, *loc. cit.*). The latter compound is most sharply differentiated from its isomeride, m. p. 85°, by its behaviour towards hydrogen in the presence of spongy platinum and glacial acetic acid, whereby it is converted solely into ethyl 1:2:4:6-tetramethyltetrahydropyridine-3:5-dicarboxylate (*picrate*, yellow rhombohedra, m. p. 130—131°); the solid isomeride is more slowly hydrogenated, but is ultimately transformed into ethyl 1:2:4:6-tetramethylhexahydropyridine-3:5-dicarboxylate, a pale yellow liquid, b. p. 162—164°/11 mm. (*picrate*, m. p. 153°; *hydrochloride*, m. p. 66°; *hydrobromide*, m. p. 48°; *additive* compound with mercuric chloride, m. p. 147°). The tetrahydro ester is more conveniently prepared by the catalytic hydrogenation of ethyl 2:4:6-trimethylpyridine-3:5-dicarboxylate methosulphate, whereby the hexahydro derivative is also produced in small amount (cf. Neuhaus, *Diss.* Kiel, 1923). H. W.

**isoIndigotin.** C. W. HANSEN (*Ann. Chim.*, 1924, [x], 1, 94—134). —*iso*Indogenides, formed by condensation of *o*- and *p*-chloroaldehydes and an *o*-sulphonated aldehyde with oxindole, were prepared (cf. Wahl and Bagard, A., 1909, i, 735; Stollé, A., 1914, i, 992; Martinet and Dornier, A., 1921, i, 516). The chloro derivatives have been described independently by Neber and Röcker (A., 1923, i, 945); *sodium benzylideneoxindole-2-sulphonate* forms pale yellow crystals.



*iso*Indogenides exhibit slight tinctorial properties. The leuco-compound obtained by reduction of indine (Wahl and Hansen, A., 1923, i, 607) yields from concentrated alkaline solution a *tetra-benzoyl* derivative, m. p. 209°, which indicates that under the conditions specified the leuco-compound exists wholly or in part as

$$\text{C}_6\text{H}_4 < \begin{array}{c} \text{---C---} \\ \text{NH} \end{array} > \text{C} \cdot \text{OH} \quad \text{OH} \cdot \text{C} < \begin{array}{c} \text{---C---} \\ \text{NH} \end{array} > \text{C}_6\text{H}_4$$
 Reduction of indine by means of zinc and acetic acid in presence of sodium acetate affords *diacetyl-leucoisindigotin*, colourless crystals, m. p. 220°, isomeric with the diacetyl-leucoindigo described by Liebermann (A., 1888, 492). Disulphoisatide may be converted directly into indine by the action of ammonia in its alcoholic solution.

The paper contains a more detailed account of work already published on disulphoisatide, isatin, etc. (Wahl and Hansen, this vol., i, 322; cf. Dornier and Martinet, A., 1923, i, 852).

H. J. E.

**Constitution of Salipyryne.** S. BODFORSS and A. GUTHE (*Ber.*, 1924, 57, [B], 842—846).—Although salipyryne is usually represented as antipyryne salicylate, it may possibly be an additive compound, e.g.,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \dots \text{H} \dots \text{C}_{11}\text{H}_{12}\text{ON}_2$ . Antipyryne is a very weak base ( $k=2.8 \times 10^{-13}$ ), its salts in dilute solution being considerably hydrolysed. Aqueous or alcoholic solutions of salipyryne show only the reactions of its components. The alteration of *E.M.F.* produced by the addition of salipyryne to a cell containing a suspension of silver salicylate in saturated salicylic acid against a standard calomel electrode has been determined in comparison with the effect produced by the addition of acids and bases, and from the results it is concluded that undissociated salipyryne consists of an additive complex corresponding with the above formula. The conductivity of solutions of antipyryne hydrochloride has been studied and additive compounds of antipyryne with the following phenols have been obtained: vanillin, *p*-cresol, nitroresorcinol, protocatechualdehyde, and *p*-hydroxybenzaldehyde. R. B.

**Thallous Picrolonate.** M. GIUA (*Gazzetta*, 1924, 54, 204—206).—Almost pure thallous carbonate is obtainable in good yield by passing dried air through 95% or absolute ethyl, propyl, *isobutyl*, or *isoamyl* alcohol containing in suspension thallium in powder or thin strips.

*Thallous picrolonate*,  $\text{C}_{10}\text{H}_7\text{O}_5\text{N}_4\text{Tl}$ , separates when a dilute acetic acid solution of picrolonic acid is added to a similar solution of the carbonate, and forms pale yellow needles, exploding above 300°.

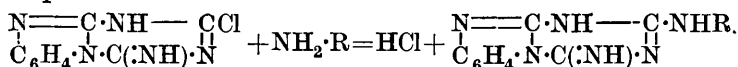
T. H. P.

**Quinazolines. XXXV. Stereoisomeric Styryl Derivatives of some 4-Quinazolone Alkiodides, and their Bearing upon the Problem of Photosensitising Dyes.** M. T. BOGERT and H. CLARK (*J. Amer. Chem. Soc.*, 1924, 46, 1294—1301).—Quaternary alkyl salts could not be obtained from 2:4-dimethyl-, 2-styryl-4-methyl-, and 2-phenyl-4-methyl-quinazolines; 2:4-dimethyl-quinazoline could not be condensed with aromatic aldehydes. The

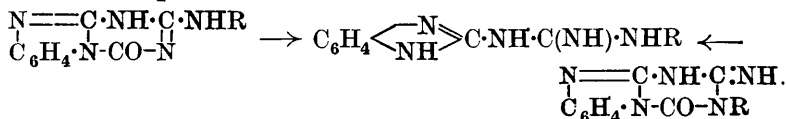
condensation of substituted 4-quinazolone alkiodides with *p*-dimethylaminobenzaldehyde yielded 2-*p*-dimethylaminostyryl-4-quinazolone alkiodides, the stereoisomeride obtained being dependent on whether piperidine or acetic anhydride was used as condensing agent, or, using the latter, on the conditions of experiment. The stable (purple) isomerides had higher m. p. than the (red) labile isomerides. The latter were converted into the stable forms by acetic anhydride at 120°, but the reverse change could not be effected. Both isomerides yielded the same monobromo-dibromides. The products have no value as dyes or photosensitisers. The following compounds are described. 2-*p*-Dimethylaminostyryl-4-quinazolone methiodide, reddish-purple needles, m. p. 265.7° (decomp.) with previous sublimation or darkening, or bright red needles, m. p. 214°; 2-*p*-dimethylaminostyryl-3-methyl-4-quinazolone methiodide, similar, m. p. 263.5° (decomp.) after subliming and darkening, or m. p. 216° (decomp.); tribromo derivative, orange needles, m. p. 178°; 2-*p*-dimethylaminostyryl-3-methyl-4-quinazolone ethiodide, similar, m. p. 264.7° (decomp.) after subliming and darkening, or m. p. 205.5°; 2-*p*-dimethylaminostyryl-3-ethyl-4-quinazolone methiodide, similar, m. p. 255° (decomp.) after subliming and darkening, or bright red needles with blue lustre, m. p. 212°; tribromo derivative, yellowish-orange needles, m. p. 152°.

F. G. W.

**Action of Cyanogen Halides on Phenylhydrazine. VIII. Exo-alkyl Derivatives of Melamine.** G. PELLIZZARI (*Gazzetta*, 1924, 54, 177—184).—*o*-Phenyleneammethyl chloride (cf. A., 1922, i, 585) reacts readily with primary amines to form melaminic bases having the alkyl group united to a nitrogen atom which does not form part of the nucleus :

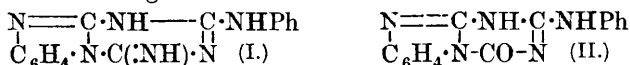


Such *exo*-alkylphenylenemelamines are isomeric with those obtained from the same amines and dicyanophenyleneguanidine (A., 1921, i, 620). Phenyleneammethyl chloride reacts also with secondary amines; with methylaniline, *e.g.*, it gives phenyl-*exo*-phenylenemethylmelamine (a white, crystalline powder, not melting at 300°), which is formed also by direct addition of methylaniline to dicyanophenyleneguanidine. Phenyleneammethyl chloride acts also on ammonia, giving a compound identical with that formed by direct addition of ammonia to phenyleneguanidine. When heated with hydrochloric acid, the *exo*-alkylphenylenemelamines behave like their isomerides, giving the corresponding ammelines. Treatment of the *exo*-ammelines thus formed with hot potassium hydroxide solution affords a single substituted diguanide, even from a pair of isomeric compounds :



This result confirms the scheme given for the addition of hydrogen chloride to  $\alpha\beta$ -dicyano-*o*-phenyleneguanidine (A., 1922, i, 585), since, if the chlorine atom were fixed in the other possible position, the subsequent reactions would yield different melamine, ammeline, and diguanide.

*Phenyl-exo-phenylenemelamine* (I) is basic and forms minute needles not melting at 300°.



*Phenyl-exo-phenyleneammeline* (II), forms a white powder with high m. p. (decomp.).

*Phenyl-exo-phenylenemethylammeline*,  $\text{C}_{16}\text{H}_{13}\text{ON}_5$ , forms a white, microcrystalline powder, exhibits both acid and basic properties, and forms a hydrochloride (+H<sub>2</sub>O). *o*-Phenyleneguanylphenylmethylguanidine,  $\text{C}_6\text{H}_4\langle\text{NH}\rangle\text{C}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NMePh}$ , forms colourless, lustrous, flat needles, m. p. 163°.

T. H. P.

**Thiazoles. IV. The Synthesis of Benzthiazoles from *o*-Nitrochlorobenzene.** M. T. BOGERT and F. D. SNELL (*J. Amer. Chem. Soc.*, 1924, 46, 1308—1311).—*o*-Aminothiophenol is obtained as the zinc salt by reducing *o*-nitrophenyl disulphide with zinc dust in glacial acetic acid. A suspension of the zinc salt in aqueous ammonium hydroxide is oxidised by a current of air to *o*-aminophenyl disulphide. 2-Phenylbenzthiazole is obtained by boiling the zinc salt of *o*-aminothiophenol with benzoyl chloride, or *o*-benzoylaminophenyl disulphide (m. p. 142·6°) with tin and dilute hydrochloric acid (etc.). 2-*p*-Nitrophenylbenzthiazole, similarly obtained, forms nearly colourless needles, m. p. 231°, and when reduced gives the corresponding amino derivative, which is also obtained by the reduction of 2-*p*-nitrobenzoylaminophenyl disulphide, pale yellow prisms, m. p. 217° (decomp.). F. G. W.

**Azoxy-esters.** A. PIERONI and G. GIANNINI (*Gazzetta*, 1924, 54, 162—177).—The authors have prepared various members of a new class of compounds of the formula  $\text{R}\cdot\text{N}_2\text{O}\cdot\text{CO}_2\text{Et}$ , in which R represents an aromatic residue, by treating the corresponding azo-esters with peracetic acid for a period of some months (cf. Angeli, A., 1917, i, 228, 417).

By treating ethyl chlorocarbonate with the phenylhydrazine in pyridine solution (cf. Busch and Heinrichs, A., 1900, i, 314) almost quantitative yields may be obtained of ethyl phenylhydrazine-carboxylate (cf. Widman, A., 1895, i, 603) and of its *p*-chloro- and *p*-bromo-derivatives. Oxidation of these hydrazine compounds by means of potassium permanganate in acetic acid solution yields the corresponding azo-esters as deep red liquids of high density, which increases with the atomic weight of the substituent halogen. In presence of alkali, these azo-esters react with aldehydes thus:  $\text{NR}\cdot\text{N}\cdot\text{CO}_2\text{Et} + 2\text{KOH} = \text{Et}\cdot\text{OH} + \text{K}_2\text{CO}_3 + \text{NR}\cdot\text{NH} + \text{NR}\cdot\text{NH} + \text{R}\cdot\text{CHO} = \text{R}\cdot\text{NH}\cdot\text{NH}\cdot\text{COR}$ , these reactions being strictly analogous to those occurring with the azocarbonamides (cf. Angeli, A. 1917,

i, 228) and with the azoxy-esters (*vide infra*), from which normal diazotates are thus formed.

Treatment of the azo-esters in alcoholic solution with alcoholic potassium hydroxide results in the immediate separation of the potassium salts of the azocarboxylic acids, previously obtained from the azocarbonamides only by more or less complicated treatment (cf. Widman, *loc. cit.*; Thiele, A., 1896, i, 94). The corresponding silver and lead salts, prepared from the potassium salts by double decomposition, immediately decompose with copious liberation of nitrogen.

The azoxy-esters are dense, pale yellow, oily liquids, which in the light become brown, probably owing to the occurrence of a transformation similar to that taking place with azoxybenzene,  $\text{O:NPh}\cdot\text{NPh} \rightarrow \text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N:NPh}$ . Since the azoxy-esters are indifferent to the halogens, the constitution  $\text{O:NR}\cdot\text{N}\cdot\text{CO}_2\text{Et}$  must be attributed to them. Just as was found with phenylazocarbonamide, the other isomeride is not formed under the conditions of oxidation employed, probably owing to the influence of the negative carbonyl group attached to the nitrogen atom.

When treated with alkali, the azoxy-esters undergo decomposition analogous to that shown by the azo derivatives, giving a normal diazotate,  $\text{O:NR}\cdot\text{NH}$  (cf. Angeli, *loc. cit.*), which is unstable and decomposes, with formation of ammonia and a nitro derivative:  $\text{O:NPh}\cdot\text{NH} + \text{H}_2\text{O} = \text{NH}_3 + \text{Ph}\cdot\text{NO}_2$ .

When the oxidation of the azo-esters by peracetic acid is carried out at  $50-60^\circ$ , the azoxy-esters formed are accompanied by (1) the corresponding azoxybenzenes, which are probably due to the reaction  $\text{O:NR}\cdot\text{N}\cdot\text{CO}_2\text{Et} + \text{NR}\cdot\text{N}\cdot\text{CO}_2\text{Et} \rightarrow \text{O:NR}\cdot\text{NR}$ , but may result from the oxidation of the azobenzenes formed as intermediate products; (2) chloro- or bromo-benzoic acid, the origin of which is as yet uncertain.

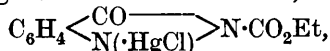
By a procedure analogous to that followed for the preparation of the hydrazo-esters, attempts have been made to obtain from the acid  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$  the hydrazo-ester,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , but the resulting compound contains a mol. of water less than the latter and is regarded as ethyl *o*-hydrazinobenzoylcarboxylate,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix}\rangle\text{N}\cdot\text{CO}_2\text{Et}$ . *Ethyl phenylhydrazinocarboxylate*,



forms white crystals, m. p.  $85^\circ$ ; *ethyl p*-chlorophenylhydrazinocarboxylate, white needles, m. p.  $92-93^\circ$ , and *ethyl p*-bromophenylhydrazinocarboxylate, white needles, m. p.  $110-111^\circ$ ; all these esters colour slightly in the air and light.

*Ethyl benzeneazocarboxylate*,  $\text{NPh}\cdot\text{N}\cdot\text{CO}_2\text{Et}$ , gives the iodoform reaction in methyl-alcoholic solution. *Ethyl p*-chloro- and *p*-bromobenzeneazocarboxylates show the same reaction. The three corresponding potassium salts form golden-yellow leaflets. *Ethyl benzeneazoxycarboxylate*,  $\text{O:NPh}\cdot\text{N}\cdot\text{CO}_2\text{Et}$ , was obtained as a slightly impure, straw-yellow oil and gives the iodoform reaction in methyl-alcoholic solution. *Ethyl p*-chloro- and *p*-bromobenzeneazoxycarboxylates were not obtained sufficiently pure for analysis.

*Ethyl o-hydrazinobenzoylcarboxylate* has m. p. 194°. The silver derivative,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \text{N} \text{Ag} \end{smallmatrix} N \cdot CO_2Et$ , and the corresponding mercurous compound form colloidal solutions and gradually decompose when separated as hydrogels. The mercurichloride,



forms a microcrystalline, white precipitate. *Potassium o-hydrazinobenzoylcarboxylate*, which was not obtained pure, instantly reduces ammoniacal silver nitrate solution.

T. H. P.

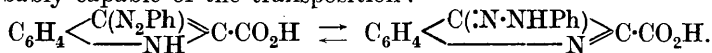
**Azoxyamides and Pyrroles.** A. PIERONI (*Gazzetta*, 1924, **54**, 157—161).—Like phenyldiazonium chloride (cf. Fischer and Hepp, A., 1886, 1041; Plancher and Soncini, A., 1903, i, 449), azoxyamides react with pyrrole and a number of its derivatives, yielding azo compounds. This reaction is effected best by *p*-bromo- and *p*-chloro-phenylazoxycarbonamides, which in an alkaline medium react in the usual way:



coupling with the pyrrole then following. A similar reaction takes place between phenylazoxycarbonamides and indole, the azo group entering in the 3-position of the pyrrole nucleus.

2 : 2'-*Bis-p-bromobenzeneazopyrrole*,  $C_{16}H_{11}N_5Br_2$ , forms deep red crystals with copper reflection, m. p. 208°. *p-Bromobenzeneazopropylpyrrole*,  $C_{12}H_{10}ON_3Br$ , crystallises in yellow laminæ, m. p. 168°. 2 : 5-*Dimethyl-3-benzeneazopyrrole* forms an orange-yellow, crystalline powder, m. p. 134°; 2 : 4-*dimethyl-3-p-bromobenzeneazopyrrole* has m. p. 152°. 3-*p-Bromobenzeneazaindole* crystallises in golden-yellow scales, m. p. 170°, and 3-*benzeneazaindole* in yellow crystals, m. p. 135°.

3-*Benzeneazaindole-2-carboxylic acid*,  $C_{15}H_{11}O_2N_3$ , obtained from sodium indole-2-carboxylate and benzeneazocarbonamide in methyl-alcoholic solution containing potassium methoxide, forms deep red, lustrous needles, m. p. 216° (decomp.). Its yellow solution in dilute alkali gives a precipitate of the red form on addition of mineral acid; its acetic acid solution is also red; it is therefore probably capable of the transposition:



The product obtained under similar conditions from indole-3-carboxylic acid loses carbon dioxide, forming 3-benzeneazaindole (*vide supra*); if, with the same acid, *p*-bromophenylazoxycarbonamide is used, 3-*p*-bromobenzeneazaindole, m. p. 170°, is obtained.

2-*Methyl-3-p-chlorobenzeneazaindole*,  $C_{15}H_{12}N_3Cl$ , forms yellow needles, m. p. 168°.

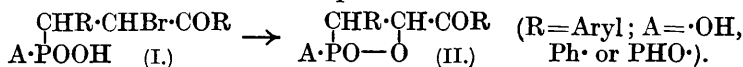
T. H. P.

**Reduction of Nitronaphthalenes.** II.  $\beta$ -*Nitronaphthalene*. W. M. CUMMING and G. S. FERRIER (*J. Chem. Soc.*, 1924, **125**, 1108—1111; cf. T., 1923, **123**, 2466).—The reduction of 2-nitronaphthalene with zinc dust and alcoholic ammonium chloride yields 2 : 2'-azoxynaphthalene, m. p. 164° (cf. Meisenheimer and Witte, A., 1904, i, 193), and 2 : 2'-azonaphthalene. Further reduction

undoubtedly occurs, giving hydrazonaphthalene; this at once undergoes atmospheric oxidation to 2 : 2'-azonaphthalene, or in absence of air, benzidine transformation to 2 : 2'-diamino-1 : 1'-dinaphthyl. 2 : 2'-Azonaphthalene is stable in air, but on oxidation with perhydrol in acetic acid yields 2 : 2'-azoxynaphthalene. Exposure to light in alcoholic solution converts 2 : 2'-azoxynaphthalene into a red *isomeride*, m. p. 162°, which, from a comparison of its absorption spectrum with that of 2-naphthaleneazo-2-naphthol, is considered to be a hydroxyazo compound (cf. Baudisch and Fürst, A., 1913, ii, 39).  
R. B.

**Metallic Compounds of Dibenzoylhydrazide.** A. BENRATH (*J. pr. Chem.*, 1924, [ii], 107, 211—224; cf. A., 1904, i, 935).—The solubility of dibenzoylhydrazide in water is 4.7 mg. per 100 c.c. at 17°. That of the monosodium derivative is 0.346 g./100 c.c. This salt is hydrolysed to the extent of 14% in aqueous solution and dibenzoylhydrazide is precipitated. The hydrolysis, therefore, is independent of the dilution; addition of sodium hydroxide lessens the hydrolysis but also decreases the solubility. Neutral salts, e.g., sodium chloride, nitrate, or sulphate, likewise depress the solubility. The same behaviour is shown by the potassium salt; its solubility is 0.447 g./100 c.c. and it is hydrolysed 13.1%. The *lithium* salt, yellow crystals, has solubility 0.08 g./100 c.c. and 15.4% is hydrolysed. The *rubidium*, *cæsium*, *magnesium*, *calcium*, *barium*, *silver*, *thallium*, *copper*, *cobalt*, *nickel*, *zinc*, *cadmium*, and *manganese* salts are described, all being obtained by precipitation or double decomposition in an appropriate solvent. A third *lead* compound,  $C_{14}H_{10}O_2N_2Pb$ , a yellow powder, and two *mercury* derivatives,  $[C_{14}H_{10}O_2N_2]_2Hg$  and  $C_{14}H_{10}O_2N_2Hg \cdot HgCl_2$ , are also described. Dibenzoylhydrazide combines with metallic sodium in boiling toluene solution to a *disodium* compound, presumably  $CPh(ONa):N:N:CPh(ONa)$ , a yellow substance.  
W. A. S.

**Mechanism of the Decomposition of  $\beta$ -Bromophosphinic Acids in Alkaline Solution.** J. B. CONANT and E. L. JACKSON (*J. Amer. Chem. Soc.*, 1924, 46, 1003—1018; cf. A., 1923, i, 69).—Certain  $\beta$ -bromophosphinic acids of the type (I) are quantitatively decomposed in aqueous alkaline solution. It was thought that an inner ester analogous to a  $\beta$ -lactone (a  $\beta$ -“phostone”) (II) might be formed as an intermediate product:



Attempts to prepare such  $\beta$ -phostones were unsuccessful.  $\beta$ -p-Chlorobenzoyl- $\alpha$ -phenylethylphosphinic acid, colourless crystals with 1 mol. of water, m. p. 112—114°, was prepared by the action of phosphorus trichloride on p-chlorophenyl styryl ketone in glacial acetic acid. The  $\beta$ -bromo derivative, m. p. 204°, obtained by bromination in chloroform solution, was difficult to obtain pure. The *phenyl* ester,  $C_6H_4Cl \cdot CO \cdot CH_2 \cdot CHPh \cdot PO(OPh)_2$ , obtained by the action of phenol and thionyl chloride on the acid, formed crystals, m. p. 109°. Partial hydrolysis of the latter yielded the *phenyl*

hydrogen ester, crystals, m. p. 180°. The  $\beta$ -bromo derivative of the phenyl ester had m. p. 127—129°. The  $\beta$ -bromo derivative of the phenyl hydrogen ester forms two *isomerides*, one, difficultly soluble in 5% sodium hydrogen carbonate, m. p. 195—196°, the other readily soluble, m. p. 150—151°. Both isomerides were decomposed by cold dilute sodium hydroxide with formation of *p*-chlorophenyl styryl ketone, showing them to be stereoisomerides. They were soluble in aqueous sodium carbonate without decomposition. It was not found possible by warming to eliminate the bromine atom (with  $\beta$ -phostone formation) without also splitting off the phosphinic group. Experiments carried out in "buffer" solutions of various alkalinities showed that the rate of decomposition was a function of the hydroxyl-ion concentration. This together with other evidence excludes  $\beta$ -phostone formation as an intermediate step in the decomposition of  $\beta$ -bromophosphinic acids. To obtain the corresponding methyl esters as crystallisable products with satisfactory yields, it was necessary to use a Carius tube. Methyl hydrogen  $\beta$ -*p*-chlorobenzoyl- $\alpha$ -phenylethylphosphinate, m. p. 152—153°, is obtained in 65—74% of the theoretical yield. It is accompanied by methyl  $\beta$ -*p*-chlorobenzoyl- $\alpha$ -phenylethylphosphinate, m. p. 123—124°. They are separated by means of sodium carbonate solution, in which only the former is soluble. The  $\beta$ -bromo derivative of the monomethyl ester is difficult to obtain pure (yield 25% of theory, m. p. 163—164°). It dissolves readily in sodium hydroxide with loss of the bromine atom. Its rate of decomposition was studied. The chief decomposition product was a monomethyl ester of either an unsaturated or a hydroxy-phosphinic acid. It is suggested that the first step in the decomposition of the  $\beta$ -bromophosphinic acids is the interaction of the organic molecule and the hydroxyl ion to form an unstable ionised hydroxyl compound. The further decomposition may take place in various ways corresponding with the several products obtained by the action of alkalis on different types of bromophosphinic acids. A. C.

**Complex Boric Acid Compounds and the Optically Active Boron Atom.** J. BÖSEKEN and J. MEULENHOEF (*Proc. K. Akad. Wetensch.*, 1924, 27, 174—177).—The ammonium, aniline, *p*-chloroaniline, dimethylaniline, and pyridine salts of the dipyrocatechol-boric acid compound (cf. A., 1923, i, 557; ii, 406) have the composition  $[B(O_2C_6H_4)_2]M$  or  $[B(O_2C_6H_4)_2]H, NH_2R$ , and form anhydrous crystals; the ammonium salt appears to volatilise unchanged. The free acid has the composition  $[B(O_2C_6H_4)_2]H$ . The aniline and pyridine salts of the dipyrogallol-boric acid compound have also been prepared, and likewise the potassium, ammonium, and aniline salts of the di-(3-nitropyrocatechol) and the di-(4-nitropyrocatechol) compounds, these having the constitution  $[B(O_2C_6H_3(NO_2)_2)_2]R$  and forming anhydrous crystals.

The salicylic acid-boric acid compound forms anhydrous aniline, ammonium, potassium, sodium, and silver salts,  $[B(O_2COC_6H_4)_2]R$ , whilst the pyridine salt contains 1 mol., and the zinc, copper, cobalt, manganese, nickel, magnesium, and calcium salts 10 mols.

of water of crystallisation. The asymmetry of the anion is shown by the fact that the strychnine salt is separable into dextro- and lævo-rotatory components.

T. H. P.

**Stable Partial-valency Compounds of Triphenylboron, a Contribution to the Problem of the Valency of Boron.** E. KRAUSE (*Ber.*, 1924, 57, [B], 813—818).—Triphenylboron (cf. Krause and Nitsche, A., 1922, i, 694) unites readily with ammonia and with aromatic amines to form well-crystallised additive compounds stable to atmospheric oxygen; they contain 1 mol. of base, the boron having therefore the co-ordination number 4. The stability of the compounds is attributed in large part to steric effects, and also to a species of salt formation due to the acidifying effect of the phenyl groups. The following compounds, all of which form colourless crystals, were prepared by adding the requisite amine to triphenylboron in ethereal solution and have the general formula,  $\text{Ph}_3\text{B}_2\text{R}$  (R=base): R= $\text{NH}_3$ , m. p. above  $212^\circ$  (decomp.); R= $\text{NH}_2\text{Me}$ , m. p.  $208\text{--}209^\circ$  (decomp.  $210\text{--}211^\circ$ ); R= $\text{NH}_2\text{Et}$ , m. p.  $166\text{--}168^\circ$ , decomp. above  $200^\circ$ ; R= $\text{NH}_2\text{Pr}^a$ , m. p.  $101\text{--}102^\circ$ , decomp. above  $180^\circ$ ; R= $\text{NHMe}_2$ , m. p.  $186\text{--}187^\circ$ , decomp.  $187\text{--}200^\circ$ ; R= $\text{NMe}_3$ , m. p.  $135\text{--}137^\circ$ ; R= $\text{NH}_2\text{Ph}$ , m. p.  $138\text{--}140^\circ$  (decomp.). Additive products were obtained (not crystalline) with *ethyl-* and *diethyl-aniline*. R=*pyridine*, decomp. above  $214^\circ$ ; R=*quinoline*, m. p.  $160\text{--}170^\circ$  (decomp.); R=*quinaldine*, m. p.  $110\text{--}112^\circ$  (decomp.); R=*piperidine*, m. p.  $213\text{--}214^\circ$ , decomp. above  $216^\circ$ ; R=*phenylhydrazine*,  $\text{Ph}_3\text{B}_2\text{Ph}\cdot\text{NH}\cdot\text{NH}_2$ , m. p.  $138\text{--}140^\circ$ ; it is not stable in air indefinitely. Diphenylamine does not combine with triphenylboron.

F. A. M.

**Factors affecting the Stability of Mercurials and the Mercurisation of Substituted Phenylammonium Salts.** M. S. KHARASCH and L. CHALKLEY, jun. (*J. Amer. Chem. Soc.*, 1924, 46, 1211—1223).—Certain mercuri-organic compounds form a suitable means for testing the hypothesis that the comparative non-labilisation of a chlorine atom, *ortho* or *para* to one or two negative groups (as compared with a similarly situated bromine or iodine atom), may be due to intramolecular oxidation-reduction between the chlorine and carbon atoms, since the grouping  $-\text{HgX}$  undoubtedly remains positive, and any intramolecular oxidation-reduction is accompanied by the immediate separation of metallic mercury. 3-Dimethylamino-6-acetoxymercuriphenol, from mercuric acetate and *m*-dimethylaminophenol, in alcoholic solution, forms dirty yellow crystals decomposing with liberation of metallic mercury on storing for 10—14 days. It melts at  $100\text{--}110^\circ$  (decomp., with formation of a pink dye). On methylation it affords 3-dimethylamino-6-acetoxymercurianisole hydrochloride, faintly pink, leaf-like crystals, m. p.  $140\text{--}150^\circ$ , decomp. at  $190^\circ$ , to give a pink, fluorescent dye. On boiling a glacial acetic acid solution of mercuric acetate and *m*-dimethylaminophenol, metallic mercury is precipitated, and a mercury-free, pink dye is formed, the base of which,  $\text{C}_{18}\text{H}_{22}\text{O}_2\text{N}_2$ , is precipitated by ammonia.



3-Dimethylamino-6-acetoxymercuriphenyl acetate, similarly prepared from *m*-dimethylaminophenyl acetate, forms colourless crystals, m. p. 110°, which blacken on storing. 4:6-Diacetoxymercuriresorcinoldimethyl ether, similarly prepared, forms white, feathery crystals, m. p. 218—220°. Mercuri-bis-*m*-hydroxyphenyltrimethylammonium acetate (annexed formula), obtained by the

action of mercuric acetate on *m*-hydroxyphenyltrimethylammonium hydroxide, forms a hygroscopic, white powder, m. p. 116—117° (decomp.). On treatment with mercuric chloride in 60% alcohol, it affords *m*-hydroxychloromercuriphenyltrimethylammonium anhydride,  $\text{ClHg}\cdot\text{C}_6\text{H}_3(\text{NMe}_3\text{O})$ , as a white solid, m. p. 130—150° (decomp.).

4-Hydroxy-3:5-diacetoxymercuriphenyltrimethylammonium acetate forms colourless needles, m. p. 155—160° (decomp.), which are stable when dry. 4-Hydroxy-3-chloromercuriphenyltrimethylammonium acetate is obtained from the mother-liquors of the last compound by treatment with sodium chloride, as small, slightly brown needles, m. p. 155—160° (decomp.).

2-Hydroxy-3:5-dichloromercuriphenyltrimethylammonium anhydride (annexed formula), obtained by treating the product of the reaction between *o*-hydroxyphenyltrimethylammonium hydroxide and mercuric acetate with sodium chloride, forms a white, amorphous solid, m. p. 215—220° (decomp.), after turning violet at 200—210°.

*m*-Aminophenyltrimethylammonium chloride hydrochloride,  $\text{C}_6\text{H}_4(\text{NMe}_3\text{Cl})\cdot\text{NH}_2\cdot\text{HCl}$ , obtained by heating *m*-nitroaniline hydrobromide with methyl alcohol under pressure at 90—100° and reducing the product, forms pale yellow needles, m. p. 190—200° (decomp.). On treatment with silver hydroxide, it yields the base without decomposition, and this reacts with mercuric acetate with formation of 3-amino-4:6-dichloromercuriphenyltrimethylammonium acetate, colourless crystals, m. p. 200° (decomp.). The times required for blackening to commence when the above compounds are treated with hydrogen sulphide in pyridine or pyridine-water solution are given, and the bearing of these results on the two-stage mercurisation hypothesis of Kharasch and Jacobsohn (A., 1922, i, 189) is discussed.

F. G. W.

**Hydroferrocyanides and Hydroferricyanides of the Organic Bases.** III. W. M. CUMMING (*J. Chem. Soc.*, 1924, 125, 1106—1108).—The hydroferrocyanides obtained from a number of organic bases by precipitation in alcoholic solution are described (cf. T., 1922, 121, 1287; 1923, 123, 2457).

Hydroferricyanides have also been produced in acid and neutral alcoholic solutions. Even at  $-20^\circ$ , the salts of primary bases oxidise very rapidly. Most secondary bases only give pure salts at low temperatures, whereas tertiary bases yield well-defined salts at the ordinary temperature. The formation of a hydroferricyanide is hindered by the presence of an acidic substituent in the nucleus, except in the case of *p*-bromo- and *p*-nitroso-dimethyl-

aniline; such substituents in a primary amine appear to prevent oxidation. The hydroferricyanides form well-defined crystals which are more highly coloured and more stable than the corresponding hydroferrocyanides previously described (T., 1922, **121**, 1288). The constitution of the salts depends on the acidity of the solution, except in the case of methylaniline. C. J. S.

**Halogenated Proteins. II. Bromopeptone.** A. J. J. VANDEVELDE (*Rec. trav. chim.*, 1924, **43**, 326—328).—Witte's peptone reacts with bromine in carbon tetrachloride solution, forming *bromopeptone A*, a hygroscopic, yellow powder having an irritating odour and containing 37.55% of bromine. When treated with hot alkali hydroxide solution, it loses bromine corresponding with 33.29% of its weight. At 100°, bromopeptone A undergoes partial decomposition, forming the hygroscopic *bromopeptone C*, containing 30.83% of bromine, and losing 25.61% when warmed with potassium hydroxide solution. Bromopeptone A can be separated into its constituents in the same way as the original peptone; the quantity of albumoses is found to have diminished and the amino acids increased. The precipitates obtained from a solution of the bromopeptone with zinc sulphate or with phosphotungstic acid contain very little bromine (cf. this vol., i, 678).

E. H. R.

**Nitration of Proteins. I. and II.** F. LIEBEN (*Biochem. Z.*, 1924, **145**, 535—554; 555—559).—I. From a quantitative study of the course of nitration of silk-fibrin, casein, and blood-fibrin with concentrations of nitric acid varying from 5 to 60%, it is concluded that in each case the process consists in the formation of the mononitro derivatives of the tyrosine residues, and if tryptophan is also present, as in casein and blood-fibrin, this amino-acid also gives rise to a mononitro derivative. Nitrofibroin and nitrocasein are reduced to colourless products by hydrogen and sodium hyposulphite in the presence of sodium carbonate. The amino nitrogen of the reduced products determined by Van Slyke's method is the same as that of the nitroproteins (a new amino-protein is therefore not formed on reduction), and slightly greater than that of the original protein, an increase which is ascribed to degradation during nitration.

II. The quantitative course of the nitration of serum-albumin, serum-globulin, lactalbumin, edestin, gliadin, and keratin is in agreement with the supposition (cf. I.) that the mononitro derivatives of the tyrosine and tryptophan present in these proteins are formed. J. P.

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## Biochemistry.

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**Blood as a Physico-chemical System. II.** L. J. HENDERSON, A. V. BOCK, H. FIELD, and J. L. STODDARD (*J. Biol. Chem.*, 1924, 59, 379—431).—A complete description of the changes known to occur in blood during the respiratory cycle and of the physico-chemical system which determines them is given. It has been shown (cf. A., 1921, i, 473) that all external changes in oxygen or carbon dioxide tension are invariably accompanied in blood, not only by changes in free and combined oxygen and carbonic acid concentrations, but also by changes in hydrogen-ion concentration and in the distribution of chlorides between cells and plasma. This study of the physico-chemical system was incomplete, since the movement of water between cells and plasma was left out of account. This factor is now further investigated and it appears that the theory concerning water and chloride distribution as a function of buffer actions of proteins, of alkali reserve, and of osmotic pressure (A., 1909, ii, 157) is valid. All the known phenomena of the respiratory cycle in blood have been described with a good approach to accuracy with the following seven variables: free oxygen, total oxygen, free  $\text{CO}_2$ , total  $\text{CO}_2$ ,  $p_{\text{H}}$  of the serum, the volume of the corpuscles, and the ratio of the concentrations of anions within and without the cell. D. R. N.

**Oxygen and Carbon Dioxide Dissociation Curves of Human Blood.** A. V. BOCK, H. FIELD, and G. S. ADAIR (*J. Biol. Chem.*, 1924, 59, 353—378).—The oxygen dissociation curves for the blood of normal subjects at carbon dioxide tensions varying between 3 and 80 mm. do not conform to Hill's formula (*J. Physiol.*, 1910, 40, 4). Carbon dioxide dissociation curves on fully reduced and fully oxygenated blood as well as the true plasma curves have also been studied. Both corpuscles and plasma transport carbon dioxide, the former carrying 40% of the total and the latter 60%. D. R. N.

**Chemistry of Hæmoglobin. II. Equilibrium between Oxygen and Hæmoglobin.** R. M. FERRY (*J. Biol. Chem.*, 1924, 59, 295—327).—The equilibrium between oxygen and hæmoglobin has been examined by a method based on a study by purely physical means of the gas phase in equilibrium with hæmoglobin and susceptible of considerable accuracy. A measured volume of hæmoglobin is brought into equilibrium with varying quantities of oxygen in an apparatus having a known volume, so arranged that a portion of the gas phase can be removed and measured without altering the equilibrium in the liquid phase and thus not only the amount of oxygen in the entire gas phase, but also its tension can be calculated through the application of gas laws. The difference between the quantity of oxygen introduced and that in the gas phase corresponds with the amount in combination with hæmoglobin. D. R. N.

**Variations in the Acid-Base Balance of the Blood in Disease.** V. C. MYERS and L. E. BOOHER (*J. Biol. Chem.*, 1924, 59, 699—712).—A series of determinations of the  $p_H$  and the carbon dioxide content of the venous blood plasma of normal and diseased individuals was made. It was found that in pathological condition the  $p_H$  may be within normal limits whilst the carbon dioxide content is abnormal, and *vice versa*, so that the determination of one of these quantities alone is an insufficient index of the state of the acid-base balance. C. R. H.

**Effect of Ether added *in vitro* on the Distribution of Carbon Dioxide and Chloride between Cells and Serum.** J. H. AUSTIN and H. C. GRAM (*J. Biol. Chem.*, 1924, 59, 535—541).—Observations on the carbon dioxide and chloride content, the hydrogen-ion concentration, and the relative volume of cells and serum in blood equilibrated at a known tension of carbon dioxide, reveal no change in any of these quantities whether or no ether in anæsthetic concentration is present in the blood. C. R. H.

**Changes in the Stability and Potential of Cell Suspensions.**  
**II. Potential of Erythrocytes.** A. H. EGGERTH (*J. Gen. Physiol.*, 1924, 6, 587—596).—When erythrocytes from human or sheep blood are washed with physiological salt solution and then suspended in solutions of  $p_H$  5.2 or more acid, they become progressively more electropositive. This change is coincident with hæmolysis, and is, in fact, due to the escape of hæmoglobin from the cells, as in shown by the effect of adding hæmoglobin to a fresh suspension of cells. The isoelectric point of erythrocytes in the absence of salts or in the presence of salts with univalent ions is at  $p_H$  4.7; in the presence of salts with bivalent anions it becomes more acid. C. R. H.

**Agglutination of Red Blood Cells.** J. H. NORTHROP and J. FREUND (*J. Gen. Physiol.*, 1924, 6, 603—613).—The agglutination of unsensitised sheep erythrocytes by electrolytes usually occurs when the potential difference between cells and solution is reduced below 6 millivolts; in the case of sensitised cells, the corresponding critical potential difference is about 12 millivolts. It therefore appears that agglutination by immune serum is due to an increase in the critical potential difference and not to a lowering of the actual potential of the cells. C. R. H.

**Coloration of so-called "Oxydasic" Granulations of Cells Obtained by Synthesis with Indophenol and Hydroxybenzidine.** A. C. HOLLANDE (*Compt. rend.*, 1924, 178, 1215—1217).—Human leucocytes which take up colouring matters derived from indophenol and hydroxybenzidine do so as a result of that type of dyeing which involves precipitation of the colour. The portions which become coloured are the granulations and also the liquid substances which are formed from or give rise to them. They are not dyed by phenylene-blue or toluylene-blue, and there appears to be no relation between existence of oxydase or per-oxydase and power of colour-absorption. H. J. E.

**Urea Content of Red Blood Cells.** Z. ASZÓDI (*Biochem. Z.*, 1924, **146**, 343—348).—In the blood of normal individuals the urea is uniformly distributed between corpuscles and plasma, whilst in cases of kidney affections the plasma may contain rather more urea than the corpuscles (cf. Falta and Richter-Quittner, *ibid.*, **100**, 148; Andresen, *ibid.*, **116**, 266). J. P.

**Cause of the Rapid Disappearance of Catalase in Blood Solutions.** O. STEPPUHN and A. TIMOFEJEWA (*Biochem. Z.*, 1924, **146**, 108—114).—From measurements of the "protease number" (Bach and Zubkova, A., 1922, i, 392) of dilute blood solutions in the presence of trypsin, it is concluded that the latter has no effect on the protease, as measured by the catalase activity, and that no evidence is forthcoming in support of the view that blood catalase is destroyed by proteases (cf. Wäntig and Steche, *Z. physiol. Chem.*, 1914, **93**, 228). The disappearance of catalase is associated with the presence of erythrocytes, and does not occur in serum. It is not affected by the presence of sodium oleate. In physiological salt solution, the catalase activity first falls rapidly, then rises to normal values. J. P.

**Behaviour of the Lipoids of the Blood Immediately after Fat Ingestion in Normal and Diabetic Cases with and without the Administration of Insulin.** H. U. HARTMANN (*Biochem. Z.*, 1924, **146**, 307—317).—The lipoids of the blood are not affected by the ingestion of dextrose. One hour after the administration of 50 g. of butter and 20 g. of oatmeal to normal and diabetic subjects, a rise in the blood lipoids occurs, but these return to a normal level after 4 hours. The individual components of the lipid fraction show irregular variations. In one case of diabetes (no acidosis), the blood lipoids were permanently above normal, chiefly due to an increase in neutral fat and cholesterol ester. In three out of four cases of diabetes, insulin slightly depressed the total lipoids of the blood, but no specific effect on any one component was observed. A previous injection of insulin has no effect on the increase of lipoids following the ingestion of butter and oatmeal, and the blood-sugar curve is independent of the lipid curve. J. P.

**Fatty Acids of Blood Plasma. II. Distribution of Unsaturated Acids.** W. R. BLOOR (*J. Biol. Chem.*, 1924, **59**, 543—556).—A fractionation of the total lipoids of blood plasma indicates that the greater part of the unsaturated fatty acids are present in the form of cholesterol esters; the iodine values of the acids from these esters show that they must include acids of a higher degree of unsaturation than oleic. C. R. H.

**Detection of Higher Multiple Unsaturated Free Fatty Acids in Blood.** A. VON SZENT-GYÖRGYI.—(See ii, 508.)

**Quantitative Determination of the Free Fatty Acids of Blood.** A. VON SZENT-GYÖRGYI and T. TOMINAGA.—(See ii, 508.)

**Uric Acid Content of the Serum and Spinal Fluid in Children.** E. LESNÉ, HASARD, and LANGLE (*Compt. rend. Soc. Biol.*, 1923, **89**, 891—893; from *Chem. Zentr.*, 1924, i, 681).—In the blood-serum of children aged between 3 months and 12 years, the mean uric acid content was found to be 0.0035% as against 0.0049% in the case of the blood-serum of adults. The mean uric acid content of the spinal fluid of children was 0.0018%. In tubercular meningitis no appreciable increase in the uric acid content of the spinal fluid was observed. With meningococcal meningitis, on the other hand, there was a marked increase to 0.0038% of uric acid. G. W. R.

**Nuclein Metabolism. II. Isolation of a Nucleotide from Human Blood.** H. JACKSON (*J. Biol. Chem.*, 1924, **59**, 529—534).—The precipitate obtained by treating a protein-free filtrate from blood with lead acetate in the presence of acetic acid yielded a substance which gave the reaction for pentoses and from which, after hydrolysis with dilute sulphuric acid, adenine was isolated as the picrate. C. R. H.

**Diffusibility of the Calcium of Blood-serum through Collodion Membranes. Effect of Sodium Chloride and Changes in Hydrogen-ion Concentration.** R. F. LOEB [with S. STEINBERGER] (*J. Gen. Physiol.*, 1924, **6**, 453—456).—Only 55—75% of the calcium present in serum is dialysable through collodion membranes against distilled water at  $p_H$  7.4, but the whole of the calcium is dialysable against 0.8% sodium chloride solution of  $p_H$  7.4, or against hydrochloric acid of  $p_H$  2.5. W. O. K.

**Action of Bicarbonate and Secondary Phosphate on the Dissociation of Calcium.** H. BEHRENDT.—(See ii, 456.)

**Accurate Determination of Calcium in Whole Blood.** A. C. ALPORT.—(See ii, 500.)

**Micro-determination of Methyl Alcohol in Blood.** N. V. BILDSTEN.—(See ii, 506.)

**Coagulation of Blood.** J. AMAR (*Compt. rend.*, 1924, **178**, 1628—1630; cf. this vol., ii, 144).—Further experiments show the bearing on the coagulation of blood of those physico-chemical factors which determine the coagulation of colloids by depressing the surface tension of the medium. Coagulation of blood is due to the disturbance of the equilibrium of its components resulting from a fall in the surface tension. This may be due to the action of a solid partition which is moistened by water, and to the standing of the blood, this causing separation of the components of the emulsion in the order of their densities, so that the solubilising salts of the supernatant liquor leave the corpuscles free to precipitate. Addition of salts, alcohols, or poisons capable of coagulating the proteins hastens the formation of the clot. Coagulation exhibits also an enzymic aspect, the diminution in the surface

tension liberating the fibrin-coagulating enzyme of the leucocytes; that this is the case is shown by the observation that the production of filaments begins round the white corpuscles.

The view that sodium salts have anti-coagulating properties only because they precipitate the calcium salts is inaccurate, sodium carbonate, chloride, and phosphate being true anti-coagulants. Further, excess of calcium chloride exerts a toxic action on the leucocytes, shrivelling and coagulating their protoplasm and preventing the discharge of the fibrin enzyme and hence the coagulation of the blood; such effect is the opposite of that usually attributed to calcium chloride.

T. H. P.

**Lipolytic Theory of Immune Hæmolysis.** R. BRINKMAN and A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1924, **146**, 212—216).—Immune hæmolysis of blood by the addition of amboceptor and complement is not associated with liberation of higher fatty acids. After complete complement-fixation, the lipolytic activity of the serum is undiminished, and it is concluded that complement is not identical with blood lipase (cf. Olsen and Goette, *ibid.*, 1920, **112**, 188). Normal erythrocytes after reversal of hypotonic hæmolysis (*J. Physiol.*, 1923, **58**, 204) show immune hæmolysis, but reversal is not possible after the latter process. Amboceptor and complement are active in blood hæmolysed by hypotonic saline.

J. P.

**Formation of Porphyrin from Sulphur-Hæmoglobin.** P. LIST (*Z. physiol. Chem.*, 1924, **135**, 95—107; cf. Schumm, A., 1923, i, 631).—The author has prepared porphyrins from blood treated with hydrogen sulphide (sulphur-hæmoglobin) by the action of hydrochloric acid. Weak acids, such as phosphoric and acetic acids, are also able to produce colouring matters of the porphyrin type. The products closely resemble the better known porphyrins in absorption spectra, but differ from them in being readily soluble in chloroform.

E. M. C.

**Determination of Hydrogen Ions in the Gastric Contents.** J. F. McCLENDON (*J. Biol. Chem.*, 1924, **59**, 437—442).—A fairly accurate and rapid method is described for the determination of the  $p_H$  of the gastric juice based on the colorimetric determination of the percentage dissociation of quinaldine-red.

D. R. N.

**Polarimetric Observations on Solutions of Glucose after Contact with Intestinal Mucosa.** H. V. HUME and W. DENIS (*J. Biol. Chem.*, 1924, **59**, 457—464).—In order to prove the transitory formation of  $\gamma$ -glucose in glucose solutions after contact with intestinal mucosa, experimental technique other than that involving the use of the polarimeter will have to be employed (cf. A., 1920, i, 508, 648). Although this method gives unmistakable evidence of the existence of mutarotation, it could scarcely be ascribed to the formation of  $\gamma$ -glucose, as in some experiments an increase and in others a decrease in the rotation are observed.

D. R. N.

**Inorganic Substances in Carbohydrate Metabolism.** G. A. HARROP and E. M. BENEDICT (*J. Biol. Chem.*, 1924, **59**, 683—697).—During a period of active assimilation of carbohydrate there is a lessened excretion of phosphate; coincidently with this, there is a reduction of the concentration of inorganic phosphate in the blood-serum and an increase in its concentration in the muscle-tissue. These results are in favour of the view that inorganic phosphate is a necessary intermediate in the storage of carbohydrate as glycogen. C. R. H.

**Formation and Origin of Acetaldehyde in the Intermediate Cellular Metabolism of Warm-blooded Animals.** C. NEUBERG and A. GOTTSCHALK (*Biochem. Z.*, 1924, **146**, 164—184).—The presence of acetaldehyde—originating from glycogen—in the surviving cells of guinea pig liver pulp can be demonstrated by the use of calcium hydrogen sulphite, and the acetaldehyde may be determined quantitatively by alkalimetric titration using hydroxylamine sulphate (Sieber, *Chem.-Ztg.*, 1921, **45**, 349). The amount of acetaldehyde formed is increased by the addition of sugars and other related substances, and is greatly increased if insulin be added simultaneously. The activity in forming acetaldehyde diminishes in the following order: glycogen, *dl*-glyceraldehyde, zymophosphate, hexose monophosphate, dihydroxyacetone, glycollaldehyde, *d*-fructose, *d*-glucose, whilst from the following compounds the yields of aldehyde also diminished in the order: ethyl alcohol, alanine, *d*-mannitol, *dl*-glyceric acid, glycerol, and glycerophosphoric acid. J. P.

**Separation and Identification of Acetaldehyde Formed in the Intermediary Metabolism of Surviving Cells of Warm-blooded Animals.** C. NEUBERG and A. GOTTSCHALK (*Biochem. Z.*, 1924, **146**, 185—187).—The identity of the acetaldehyde obtained as the calcium sulphite compound in investigating the metabolism of surviving cells of the liver (cf. preceding abstract) is established by the isolation and analysis of the crystalline *p*-nitrophenylhydrazone (m. p. 128°). J. P.

**Some Oxidation Processes of Normal and Cancer Tissue.** A. FLEISCH (*Biochem. J.*, 1924, **18**, 294—311).—Glutathione has the same effect with thermostable sarcoma residue as with thermostable muscle residue. Unwashed sarcoma tissue reduces methylene-blue more slowly than muscle. The total amount of oxygen taken up is greater for sarcoma tissue, although it shows a lower initial velocity of oxygen uptake than muscle. Hydrogen cyanide inhibits the oxygen uptake, but not the methylene-blue reduction of unwashed tissue in both cases. Citric acid accelerates the methylene-blue reduction of washed muscle, but not of washed sarcoma. Cyanide has no influence. Muscle as well as sarcoma oxidises citric acid in the Barcroft apparatus. This oxidation is not sensitive to hydrogen cyanide. The most favourable reaction for it is  $p_H$  6.0. Glutamic acid is oxidised by washed muscle and



sarcoma in presence of methylene-blue; lactic acid, on the other hand, is less actively oxidised by sarcoma than by muscle. Fumaric, maleic, and malic acids are not oxidised in this way by either tissue. Succinic acid is oxidised freely whether in the presence of methylene-blue or oxygen, and muscle is the more active of the two in this respect. The quantity of oxygen used corresponds with 1 atom of oxygen for 1 mol. of succinic acid. Whilst hydrogen cyanide has no effect on the methylene-blue reduction, the oxygen uptake by succinic acid is inhibited by it. The oxidation of succinic acid with oxygen can in the case of muscle be restored if methylene-blue is added to the system. This indirect oxidation of succinic acid induced by the methylene-blue occurs to a much less extent in the case of sarcoma. There is evidence that a "hydrogen transport factor" exists which is of importance for the transport of hydrogen to methylene-blue. The factor is distinct from "succinoxidase," and can be washed out. Its concentration is much smaller in sarcoma than in muscle-tissue. The mechanism of the aërobic oxidation of succinic acid is discussed.

S. S. Z.

**Biological Oxidation. I. Absorption of Oxygen by the System Linoleic Acid-SH Group.** A. VON SZENT-GYÖRGYI.—(See this vol., i, 708.)

**Biological Oxidation. II. Mechanism and Significance of SH-Catalysis.** A. VON SZENT-GYÖRGYI.—(See this vol., i, 708.)

**Effect of Exercise in Diabetes. I.** H. E. HIMWICH, R. O. LOEBEL, and D. P. BARR (*J. Biol. Chem.*, 1924, **59**, 265—293).—Following short periods of vigorous exercise in the diabetic, there are changes in acid-base equilibrium somewhat greater than in normal individuals doing a comparable amount of work, as is apparent from a reduction of CO<sub>2</sub> capacity, CO<sub>2</sub> tension, and alkalinity of arterial blood. There is a marked increase of lactic acid and the reduction of CO<sub>2</sub> capacity can be quantitatively accounted for by this increase. After exercise for short periods, no significant change in the concentration of acetone compounds could be observed. The accumulation of lactic acid in the blood of diabetics after exercise indicates that the conversion of carbohydrate into lactic acid is employed as the chemical mechanism of muscular contraction.

D. R. N.

**Mechanism of the Action of Insulin. The Carbohydrate Balance in Avitaminosis.** A. BICKEL and J. A. COLLAZO (*Deuts. med. Woch.*, 1923, **49**, 1408—1410; from *Chem. Zentr.*, 1924, i, 685).—The liver and muscles of pigeons suffering from avitaminosis are practically free from glycogen and the blood-sugar is above normal. Insulin decreases the blood-sugar content and with repeated injections and subsequent administration of sugar recovery takes place. The liver and muscle contain glycogen 6 hours after injection of insulin, whilst the content of fats and amino-acids in the blood falls. The effect of a single injection

of insulin disappears after 24 hours. Insulin appears to facilitate the storage of glycogen. G. W. R.

**Changes in the Ionic Content of the Blood after Administration of Insulin.** H. STAUB, F. GÜNTHER, and R. FRÖHLICH (*Klin. Woch.*, 1923, **2**, 2337—2338; from *Chem. Zentr.*, 1924, **i**, 685).—After administration of large doses of insulin to normal dogs and to dogs suffering from diabetic coma, decrease of acidosis, increase of  $p_H$ , and increase of the content of sodium, potassium, calcium, and magnesium occur. A marked decrease in inorganic phosphorus in the blood is noted. G. W. R.

**Cholesterol Synthesis in the Animal Body.** H. BEUMER and F. LEHMANN (*Z. ges. Exp. Med.*, 1923, **37**, 274—280; from *Chem. Zentr.*, 1924, **i**, 684).—Newly-born dogs fed for 4 weeks on a diet poor in cholesterol, showed an increase in cholesterol in 4 weeks amounting to 20 times the amount of cholesterol administered in the food. The formation of cholesterol therefore probably takes place exclusively from constituents not found in the ether extract of the food substances. G. W. R.

**Nitrogen Metabolism in Avitaminosis.** J. A. COLLAZO (*Biochem. Z.*, 1924, **145**, 436—441).—In dogs, the urinary purine nitrogen, uric acid, allantoin, ammonia, and amino-acids increase slightly with progressive avitaminosis, but shortly before death they may fall. The variations in uric acid and allantoin are sometimes parallel, sometimes divergent. Urea shows a continuous diminution in avitaminosis, whilst the urinary phosphates are normal in the initial stages, but increase with decreasing body-weight during the late stages. The residual nitrogen of the blood may remain normal for some time, but has a slight tendency to increase. Blood urea behaves in a similar way, whilst the amino-acids of the blood show a slow increase, which becomes more marked in advanced avitaminosis. The increase in the residual nitrogen of the blood is conditioned more by the amino-acids than by urea. It is concluded that in avitaminosis nitrogen metabolism is not disturbed so quickly as carbohydrate and fat metabolism. J. P.

**Amino-acids in Nutrition. VIII. Proline.** B. SURE (*J. Biol. Chem.*, 1924, **59**, 577—586).—Rats show a marked increase in the gain in weight per gram of protein intake on the addition of proline to a diet composed of edestin together with cystine and lysine. This effect was not obtained with an equivalent amount of pyrrolidonecarboxylic acid. It is concluded that proline is essential for growth. C. R. H.

**Synthesis of Amino-acids in the Animal Organism. III. Cystine.** J. A. MULDOON, G. J. SHIPLE, and C. P. SHERWIN (*J. Biol. Chem.*, 1924, **59**, 675—681).—The fact that bromobenzene is detoxicated in the animal body by conjugation with cysteine, to form *p*-bromophenylmercapturic acid, was utilised to test the

ability of the dog to synthesise cystine. It was found that only when cystine was fed was there a synthesis of *p*-bromophenylmercapturic acid; neither the cystine of the tissues of the animal itself nor sulphur in other forms in the diet could be utilised for this purpose.

C. R. H.

**Cystine Deficiency and Vitamin Content of the Lentil, (*Lens esculenta*).** D. B. JONES and J. C. MURPHY (*J. Biol. Chem.*, 1924, 59, 243—253).—The proteins of the lentil, like those of beans, are inadequate for nutritive purposes because of their deficiency in cystine and are further characterised by a form of indigestibility which can be corrected by cooking, although the effect of cooking is much less marked in the case of the lentil than in that of other legumes. The vitamin-A and vitamin-B contents of lentils appear to be much higher than in most other seeds.

D. R. N.

**Metabolism of Sulphur. VII. Oxidation of Sulphur Compounds Related to Cystine in the Animal Organism. VIII. Behaviour of Thiophenol and Thiocresol in the Animal Organism.** R. M. HILL and H. B. LEWIS (*J. Biol. Chem.*, 1924, 59, 557—567, 569—575).—VII.—After administration of the sodium salts of thiolactic and thioglycollic acid to rabbits, either subcutaneously or orally, practically all the sulphur is eliminated in the urine in the first day, 50—70% of it being in the form of inorganic sulphate. Under similar conditions, the sulphur of thiodiglycollic acid is excreted in the unoxidised form.

VIII.—Thiophenol and *p*-thiocresol when administered to rabbits are absorbed only to a small extent; the sulphur is excreted entirely in the unoxidised form.

The authors suggest that in order that a sulphur compound may be susceptible of oxidation in the animal body, the sulphur must be present in an aliphatic mercapto group, or must be able to be transformed into such a condition.

C. R. H.

**Experiments upon Vitamin-A.** H. C. SHERMAN and M. M. KRAMER (*J. Amer. Chem. Soc.*, 1924, 46, 1055—1063).—Young rats (4 weeks) placed on a diet devoid of vitamin-A, but adequate in all other respects for healthy nutrition, showed very different growths and survival periods, depending on the food eaten previous to the experimental period. It is suggested that the stores of vitamin-A in the bodies of the animals experimented on seriously vitiate the value of much of the earlier work on this subject. Vitamin-A was shown to be stored at later ages, and the length of time adult animals can survive on a diet devoid of it, but otherwise adequate, also depends on the amount of this vitamin stored in the body and is an indication of the relative amounts contained in earlier diets.

A. C.

**Experimental Rickets in Rats on a Purified Synthetic Diet Deficient in Phosphorus and Fat-soluble Organic Factor.** H. GOLDBLATT (*Biochem. J.*, 1924, 18, 414—418).—The addition to a purified synthetic diet low in phosphorus and the fat-soluble organic factor of calcium carbonate in such an amount that the

proportion of calcium to phosphorus was raised from 1:0.88 to 1:0.20 had the effect of changing the diet from a non-rickets-producing to a rickets-producing one. S. S. Z.

**Remarks on Papers of W. R. Hess and K. Rohr, "The Action of Thermal Treatment of Dry Yeast, etc., and Avian Beriberi," and of Roelli, "The Activation of *in vitro* Respiration by Muscle Juice, etc."** E. ABDERHALDEN (*Z. physiol. Chem.*, 1924, **134**, 97—99; cf. *Z. physiol. Chem.*, 1923, **192**, 268, 284).—Polemical. W. O. K.

**Necessary Conditions for Testing with the Reagent for Vitamin-C.** (Answer to H. D. Kay and S. S. Zilva.) N. BEZSONOFF (*Biochem. J.*, 1924, **18**, 384—386).—Polemical. S. S. Z.

**Supposed Influence of Irradiated Air on Growth.** T. A. WEBSTER and L. HILL (*Biochem. J.*, 1924, **18**, 340—346).—The authors cannot confirm Hume and Smith's results regarding the growth-promoting effects of irradiated air (cf. A., 1923, i, 728). S. S. Z.

**Influence of Cell Salts on Intermediate Metabolism.** K. TADENUMA (*Biochem. Z.*, 1924, **145**, 481—491).—Dogs kept on a diet containing only sodium chloride as salt component, but otherwise adequate, show a diminution in body-weight, an increase in the residual nitrogen of the blood, and in general an increase in the blood-sugar compared with similarly fed animals receiving an artificial cell salt mixture. The neutral fat of the blood has a slight tendency to increase. In dogs kept on an insufficient diet, substitution of sodium chloride for the salt mixture accentuates the disturbances in metabolism. In general, it is concluded that dogs receiving a diet of adequate calorie value but insufficient in salts exhibit symptoms similar to those of avitaminosis. J. P.

**Presence of Silicon in Tissues.** L. ISAACS.—(See ii, 499.)

**Importance of Zinc in the Feeding of Animals.** G. BERTRAND and B. BENZON (*Ann. Inst. Pasteur*, 1924, **38**, 405—419).—A more detailed account of work already published (A., 1922, i, 893).

**Part Played by Iron and Fat in the Recovery of Rats from Chronic Experimental Anæmia.** J. M. D. SCOTT (*Biochem. J.*, 1924, **18**, 347—350).—Rats were cured from subchronic anæmia by the administration of ferrous chloride when fed on diet of bread and whole milk. When the whole milk was replaced by skimmed milk and palm kernel oil the iron salt had no curative action. S. S. Z.

**Method for Estimating the Retention of Calcium and Phosphorus in Young Growing Rats.** M. A. BOAS (*Biochem. J.*, 1924, **18**, 425—432).—A method for estimating the retention of calcium and phosphorus in young growing rats for periods of 3 to 7 weeks is described. Rats on normal diet showed a retention which declined week by week, and smooth curves plotted from the figures obtained were similar in shape to the curve of normal growth. S. S. Z.

**Mechanism of Vital Staining with Basic Dyes.** M. McCUTCHEON and B. LUCKE (*J. Gen. Physiol.*, 1924, **6**, 501—507).—The degree of staining obtained with basic dyes in living cells was compared in solutions containing ammonium hydroxide, sodium hydroxide, carbon dioxide, and hydrochloric acid. A greater degree of staining was obtained in a solution of sodium hydroxide than in one of ammonium hydroxide of the same  $p_H$ , which means that with constant extracellular reaction staining is hindered by intracellular alkalinity. With constant intracellular reaction, it is found that staining is favoured by increased extracellular alkalinity.  
C. R. H.

**Basic Peptones from the Mucous Membrane of the Stomach.** K. FELIX (*Z. physiol. Chem.*, 1924, **135**, 175—179).—The mucous membrane of the stomach of pigs gives on extraction with cold water peptones of a strongly basic character. These contain considerable quantities of the hexone bases, arginine, histidine, and lysine. They give the biuret reaction and generally the diazo-reaction and are very hygroscopic.  
E. M. C.

**Animal Urease.** O. STEPPUHN and X. UTKIN-LJUBOVZOV (*Biochem. Z.*, 1924, **146**, 115—121).—The livers of the dog and horse contain a small amount of urease, which is better detected in acid extracts than in the expressed juice from the organ. It is probably derived from vegetable sources. It is not mobilised during acidosis for the purpose of neutralising acidity, and it is concluded that it is devoid of physiological significance.  
J. P.

**Autolysis. II.** P. RONA and E. MISLOWITZER (*Biochem. Z.*, 1924, **146**, 1—25).—The autolysis of guinea pig liver pulp at the optimum  $p_H$  3.6 is inhibited by sodium chloride, bromide, sulphate, citrate, and tartrate in 0.2M concentration, whilst sodium acetate is inactive. At  $p_H$  5—6.0, the action of these salts is reversed and autolysis is increased. The cations sodium, potassium, and calcium at  $p_H$  3.6, in concentrations of from 1.0 to 0.5N, inhibit, and in concentrations between 0.25 and 0.1N increase autolysis. Within the former range of concentrations, sodium has a more marked inhibitory effect than potassium, whilst in the latter range potassium increases autolysis more than sodium. Calcium, in concentrations between 1.0 and 0.1N, has a greater increasing and a lesser inhibiting action than potassium. In 0.05N solution, the order of activity in increasing autolysis is  $Na > K > Ca$ . At  $p_H$  5.0, a reversal of action, similar to that of the anions, is also observed in the case of the cations. Lithium and rubidium increase autolysis to a less extent than does sodium.  
J. P.

**Autolysis. III. Autolysis of Phosphorus-poisoned Liver.** P. RONA, E. MISLOWITZER, and S. SEIDENBERG (*Biochem. Z.*, 1924, **146**, 26—35).—The autolysis of a phosphorus-poisoned guinea pig liver is greater than that of the normal liver. This is ascribed to the gradual increase in the hydrogen-ion concentration, since if the pulp be buffered at the optimum  $p_H$  3.6 or at higher  $p_H$ , the extent of autolysis observed is normal. In the buffer-poisoned liver, the

autolysis products have amino-nitrogen values from 70 to 100% higher than the normal. J. P.

**Chemistry of Gaucher's Disease.** E. EPSTEIN (*Biochem. Z.*, 1924, **145**, 398—414).—A histo-chemical and qualitative investigation of the "Gaucher substance" found in the cell vacuoles of the spleen from cases of Gaucher's disease. It is concluded that this substance is not homogeneous, and its formation is associated with a diminution in the nitrogen and an increase in the carbohydrate of the spleen. The ethereal extract of the affected spleen does not differ qualitatively or quantitatively from that of the normal organ, whilst the alcoholic extract, when precipitated with mercuric chloride, yields a colourless, micro-crystalline, phosphorus-free substance, m. p.  $176^{\circ}$ , capable of swelling in water, with the physical and chemical properties of a sphingogalactoside. The presence of such a substance is not demonstrable in the normal spleen. J. P.

**Creatine and Creatinine in Muscle Extracts.** F. S. HAMMETT (*J. Biol. Chem.*, 1924, **59**, 347—351).—Creatine is formed from creatinine in muscle tissue or its extracts on incubation or autolysis. The rate of this transformation is practically the same in extracts of brain- and muscle-tissues, when the two extracts are obtained from tissues from the same animals using Tyrode's solution as the extraction agent and phosphate mixture as buffer during simultaneous aseptic incubation at  $37-38^{\circ}$ . This rate is twice as great as that in buffered Tyrode's solution. It is further shown that in the brain, as in the muscle, there are no enzymes which produce creatine or which destroy creatinine or creatine. It is concluded that creatinine formation occurs in brain as well as in muscle, thus supporting Folin's view that creatinine formation is a function of the total normal tissue metabolism. D. R. N.

**Succinic Acid in Muscle.** I. D. M. MOYLE (*Biochem. J.*, 1924, **18**, 351—364).—Fresh ox muscle yields a small quantity of succinic acid. This yield is increased when the muscle of the ox, dog, sheep, rabbit, and possibly frog is incubated anaërobically in a phosphate buffer solution of  $p_H$  7.0—8.4. A bigger yield of the acid is also obtained if glutamic or aspartic acid is added. The addition of sugar does not alter the yield, whilst the addition of certain pancreatic preparations markedly decreases it. In the red muscle of the rabbit a greater yield is obtained than in the white. A method for the determination of succinic acid is described. It is based on the volumetric determination of the silver in the silver succinate precipitate of the muscle extract after the removal of all other interfering constituents. S. S. Z.

**Distribution and Variation of Carnosine in Cat Muscle.** G. HUNTER (*Biochem. J.*, 1924, **18**, 408—411).—The carnosine content of various muscles in a number of cats has been ascertained. In the same animal, carnosine is a variable constituent of white muscle, but is approximately constant in red. S. S. Z.

**Testing for Incipient Putrefaction [of Foodstuffs].** J. TILLMANS and R. OTTO (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 25—37).—The flesh of fish decomposes differently from that of mammals. Incipient decomposition of fish can be detected by determining the ammonia and amino-acid nitrogen, although this method fails to indicate the incipient decomposition of meat. Fish containing more than 0.03% of ammonia or more than 0.1% of amino-acid nitrogen, as determined by methods the details of which are given, may be considered to be in a state of incipient decomposition. Other methods of detecting incipient decomposition of fish, depending on the content of amino-acids and polypeptides, on oxygen absorption, and on the reduction of potassium nitrate and of methylene-blue, are described. The identification and determination of peptones, carbonic acid, indole, soluble nitrogen, and substances combining with iodine lead to uncertain or negative results and no new method of indicating the incipient decomposition of fish could be founded on these substances as criteria.

H. C. R.

**Proteolytic Enzymes in the Thymus.** G. WIDMARK (*Z. physiol. Chem.*, 1924, **135**, 122—128).—The soluble products of autolysis of acidified calf thymus contain enzymes showing optimum activity at  $p_H$  5.6 and 7.6, respectively, comparable to those obtained by Hedin (*A.*, 1923, i, 507) from milk, lymphatic glands, and kidney and by Zachrisson (*Upsala Läkaref förhandl.*, 1923, **28**, 333) from the liver. The insoluble products give a sodium chloride extract containing an enzyme with an optimum at about  $p_H$  8.0.

E. M. C.

**Reduction of Sodium Nitrate and Potassium Chlorate during the Putrefaction of Viscera.** C. GHIGLIOTTO (*Ann. Falsif.*, 1924, **17**, 93—95).—Sodium nitrate and potassium chlorate are reduced rapidly during the putrefaction of animal organs.

W. P. S.

**Reduction of Aromatic Nitro Groups by the Tissue of Guinea Pigs after Treatment with Proteins and during Anaphylactic Shock. IX. The Effect of Proteins.** H. LÖHR (*Z. ges. exp. Med.*, 1923, **37**, 442—453; from *Chem. Zentr.*, 1924, i, 682).—The ability of isolated cells to reduce nitro groups, *e.g.*, in *m*-dinitrobenzene, can be increased by preliminary administration of milk and serum. The greatest activation was produced in the kidneys, followed by the muscles and the brain. The liver was practically unaffected. Peptone injection decreased reducing power. The same effect was also shown by peptone on muscle cells *in vitro* and also during anaphylactic shock.

G. W. R.

**Carotin. The Principal Cause of the Red and Yellow Colours in *Perillus bioculatus* (Fab.) and its Biological Origin from the Lymph of *Leptinotarsa decemlineata* (Say).** L. S. PALMER and H. H. KNIGHT (*J. Biol. Chem.*, 1924, **59**, 443—449).—The yellow and red colours of the hypodermis of the stink-bug, *Perillus bioculatus* (Fab.), are due largely to carotin, which is

derived from the food, chiefly the lymph of the potato-beetle, *Leptinotarsa decemlineata* (Say). The lymph of the potato-beetle is coloured exclusively by carotin, amounting to 0.0136% in the fresh lymph, which is about the same concentration as that found in fresh green leaves. Experiments showing that the amount of carotin deposited in the hypodermis of insects can be permanently modified by environment without removing the source of pigment require substantiation before they may be accepted as illustrating the inheritance of acquired characters. D. R. N.

**Anthocyanin and Flavone-like Pigments as Cause of Red Colorations in the Hemipterous Families, Aphididae, Coreidae, Lygaeidae, Miridae, and Reduviidae.** L. S. PALMER and H. H. KNIGHT (*J. Biol. Chem.*, 1924, **59**, 451—455).—Red pigment in both phytophagous and predaceous families of Hemiptera is not limited to one type of substance, as water-soluble pigments appear to be more common than carotin. The aphid, *Tritogenaphis rudbeckia*, owes its vermilion colour chiefly to an anthocyanin-like pigment, although small quantities of carotin are also present. The red colour of the red and black patterned phytophagous box-elder plant-bug and other bugs is due to a flavone-like pigment. From these results it is difficult to understand how environment can cause a permanent modification of an insect colour pattern involving an animal pigment which is derived from the food and is subject to fundamental physiological processes of the protoplasm without first causing a permanent modification of the processes to which the derived pigment is subject. The view that the red pigment in insects can thus be modified and the modification become inheritable is weakened in the light of these findings that the pigment is likely to be a carotinoid, anthocyanin, or flavone derived from food. D. R. N.

**Composition of Herring Roe. VI. Monoamino-acids of Ichthulin.** K. IGUCHI (*Z. physiol. Chem.*, 1924, **135**, 188—197; cf. Steudel and Takahashi, A., 1923, i, 729, 1257).—A fractionation of the monoamino-acids of ichthulin, the protein from herring eggs, has completed the data necessary for showing the fundamental identity of the protein in the ripe eggs and in the empty egg casing. E. M. C.

**Gases of the Air-bladder of *Porichthys notatus*.** C. W. GREENE (*J. Biol. Chem.*, 1924, **59**, 615—621).—The oxygen content of the gas from the air-bladder of this fish ranges from 30% to 88.2%; the carbon dioxide from 0 to 2.4%; the nitrogen from 4.8% to 70%. The gas obtained after the bladder has refilled is not markedly different from the first sample. C. R. H.

**Echinococcal Anaphylaxis.** J. H. BOTTERI (*Z. ges. exp. Med.*, 1923, **37**, 175—183; from *Chem. Zentr.*, 1924, i, 682).—In echinococcal infections the hydatid fluid contains albuminoid and lipid substances. The proteins, separated by salting out with sodium chloride and redissolved, give the anaphylactic reaction with the diseased animals. The reaction is still given after removal of



coagulable proteins from the solution. Hydatid fluids, from oxen, giving no sulphosalicylic acid or biuret reaction and giving only a positive "ninhydrin" reaction, are found to be biologically active. The intensity of the reaction is correlated with protein content. Of the proteins isolated, euglobulins give the strongest reaction, followed by the pseudoglobulins. The albumins are scarcely reactive. Lipoids and products of protein hydrolysis do not produce anaphylaxis. The positive intracutaneous reaction given by hydatid fluid appears to be associated either with the presence of small amounts of protein which can be detected serologically but not chemically, or with the presence of differently constituted substances having anaphylactic properties.

G. W. R.

**Acetaldehyde Content of the Urine in Normal and Pathological Conditions.** W. STEPP and I. ROTHMAN-MANHEIM (*Biochem. Z.*, 1924, **146**, 349—360).—In normal urines the amount of acetaldehyde excreted (2—4 mg. in 24 hours) is not influenced by withholding carbohydrates from the dietary nor by starvation, from which it is concluded that the formation and excretion of the aldehyde is not related to that of acetone. In cases of nephritis, nephrosis, uræmia, in liver affections, and in various other pathological conditions, no significant variations in acetaldehyde excretion were observed, whilst in cases of diabetes insipidus this was markedly increased (16—27 mg. per diem). Excretion of acetaldehyde is not of constant occurrence in diabetes, being most marked in, whilst showing no parallelism to, advanced glycosuria with associated ketonuria, but falling off in acidosis and in coma. As in normal cases, the excretion of acetaldehyde is not influenced by dietetic conditions.

J. P.

**Excretion of Amino-acids by Infants during Starvation and on a Protein-rich Diet. Formol Titration in Small Quantities of Urine.** F. VON BEMUTH and F. GOEBEL (*Biochem. Z.*, 1924, **146**, 336—342).—In a newly-born child with a closure of the œsophagus and therefore unable to feed, abnormally high amino-nitrogen values were found in blood and urine. This is ascribed to an impairment of de-aminising powers induced by starvation. From feeding experiments in normal infants, the high amino-nitrogen excretion is ascribed to the high permeability of the kidney to amino-acids, a condition dependent to a certain extent on diet. Improvements in the Sørensen method of formol titration are described which render the process more readily applicable to small quantities of urine.

J. P.

**Are Guanidines Present in the Urines of Parathyroidectomised Dogs?** I. GREENWALD (*J. Biol. Chem.*, 1924, **59**, 329—337).—The author's experiments did not afford conclusive evidence of an increased formation or decreased destruction of guanidines after parathyroidectomy, nor did they prove the absence of guanidines from the urines of parathyroidectomised dogs. There are only two well authenticated metabolic changes after parathyroidectomy,

viz., lowered calcium content of serum or plasma, and diminished excretion of phosphorus in the urine. D. R. N.

**Proteinogenous Amines. XVI. Excretion of Iminazoles in the Urine.** K. K. KOESSLER and M. T. HANKE (*J. Biol. Chem.*, 1924, 59, 803—834).—If urine be treated with lead acetate and sodium hydroxide, all the iminazole compounds are left in the filtrate. A series of determinations by the colorimetric method shows that the normal daily excretion of these compounds is between 120 and 220 mg. In cases of nephritis with nitrogen retention, the daily excretion is definitely lower than in the normal person on the same diet. C. R. H.

**Urinary Hydrogen-ion Concentration in Normal Man during Fasting.** LE NOIR and A. M. DE FOSSEY (*Compt. rend.*, 1924, 178, 1632—1633).—During fasting, the value of  $p_H$  for human urine normally undergoes only very slight variation, but falls slightly if the subject indulges in prolonged muscular effort. T. H. P.

**Relation of the Alkaline-earth Metals to the Acidity of Urine.** L. LESCEUR and L. MOQUET (*Compt. rend. Soc. Biol.*, 1923, 89, 1036—1038; from *Chem. Zentr.*, 1924, i, 682).—Acidity in urine may be correlated with high specific gravity and high content of alkaline-earth and other salts. The elimination of magnesium in urine increases with the acidity. Calcium shows a less close relationship. G. W. R.

**Colloids in the Urine and the Blood.** J. WOHLGEMUTH and T. KOGA (*Biochem. Z.*, 1924, 146, 36—51).—The property of frothing shown by urine is ascribed to the presence of a positively charged colloid, since the property is lost by shaking the urine with kaolin but not with aluminium oxide. Starvation increases the amount of this colloid in the urine. If the urine be dialysed, the foam-forming colloid loses its positive charge and becomes amphoteric, a result which is ascribed to the removal of the cations which are responsible for the charge. The colloid is not affected by boiling or by low temperature ( $-12^\circ$ ), nor is its presence related to the surface tension of the urine. It contains nitrogen, and its particles have a size of  $1\ \mu$ . Nephritic and icteric urines contain more of the colloid than normal urines. A similar foam-forming colloid is present in blood-sera, notably in nephritic sera, but it has a negative charge. Aqueous suspensions of blood-corpuscles foam but slightly on shaking, but on acidification with acetic acid this property is much increased. It is not influenced by kaolin or alumina. J. P.

**Effect of Metallic Salts on the Bactericidal Action of Blood-plasma.** L. E. WALBUM (*Compt. rend. Soc. Biol.*, 1923, 89, 1007—1010; from *Chem. Zentr.*, 1924, i, 681).—On addition of one drop of a 24-hour bouillon culture of *Bacillus coli* to fresh citrate plasma containing different metallic chlorides, the first effect with incubation at  $37^\circ$  was a diminution in bacterial numbers, followed

eventually by an increase so that after 2 hours bacterial numbers were greater than originally. Considering the effect in the first period, it was found that with salts of calcium, magnesium, silver, ferric salts, and chromic salts the bactericidal effect increased with decreasing atomic weight. The reverse held for the platinum group, and for cobalt, nickel, and manganese. Intravenous injection of manganous chloride increased the bactericidal action of the blood in the case of a goat. G. W. R.

**Poisoning from Barium Sulphate in an X-Ray Examination.**

E. DINSLAGE and F. BARTSCHAT (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 7—9).—A case of fatal barium poisoning due to the presence of barium carbonate in a sample of barium sulphate administered previous to an X-ray examination is described. H. C. R.

**Action of Thorium-X on the Maturation of Eggs, the Germination of Seeds, and the Growth of Plants.** AVERSENQ, DELAS, JALOUSTRE, and MAURIN (*Compt. rend.*, 1924, **178**, 1491—1492).—Experiments with eggs of *Ascaris lumbricoides* show that small doses of thorium-X increase the rate of maturation whilst larger doses much retard it. Similar effects are observed on the germination of seeds of *Raphanus*, and the growth of *Lemna polyrrhiza*. A. B. H.

**Uranium Diuresis.** R. HEILIG (*Z. ges. exp. Med.*, 1923, **37**, 163—174; from *Chem. Zentr.*, 1924, i, 684).—Subcutaneous injection of 3—15 mg. of uranium nitrate produced intense diuresis in dogs without, apart from a short period, increasing the output of sodium chloride. In the initial stages, loss of water from the blood took place accompanied by increase in hæmoglobin, erythrocytes, and residual nitrogen. In the later stages of diuresis, these effects disappeared. The effect of uranium nitrate appears to be principally on the kidneys, but extra-renal factors may also be involved. G. W. R.

**Drug Resistance of Trypanosomes.** C. VOEGTLIN, H. A. DYER, and D. W. MILLER (*J. Pharm. exp. Ther.*, 1924, **23**, 55—86).—A strain of trypanosomes resistant to arsenic may be produced by inoculating an animal which has previously been treated with an arsenical drug of a type which is slowly excreted; this resistance can be reduced by passing the strain through another host. Only arsenic in a compound of the type  $R\cdot As\cdot O$  is toxic to trypanosomes *in vitro*, and the toxicity of this type of arsenic compound is completely inhibited by the presence of a substance containing the sulphhydryl group. It is suggested that the toxic action of the arsenic compound depends on a condensation of the latter with the glutathione of the organisms and a consequent derangement of their cell respiration. The variations in arsenic resistance of different strains are thus explained as being due to the different amounts of glutathione which may be present in the organisms in excess of their normal physiological requirements. C. R. H.

**Comparative Studies on Narcosis with Chloroform and Dichloroethylene. Effect on Protein Balance of Rats.** R. W. RIGLER and R. RINGEL (*Z. ges. exp. Med.*, 1923, **37**, 429—441; from *Chem. Zentr.*, 1924, i, 686).—Chloroform produces a marked decrease of respiration frequency, an effect which is not observed with *cis*-dichloroethylene. There is a pronounced rise in the curve for urine nitrogen where chloroform is administered. Both *cis*- and *trans*-dichloroethylene are without serious effect on the nitrogen balance. G. W. R.

**Properties of the Constituents of Witte's Peptone.** J. J. ABEL and E. M. K. GEILING (*J. Pharm. exp. Ther.*, 1924, **23**, 1—27).—By half-saturation and subsequent complete saturation with ammonium sulphate of a solution of Witte's peptone, there were obtained two albumose fractions. From the filtrate a further fraction soluble in acid alcohol was obtained. The albumose fractions were only slightly toxic, but the alcohol-soluble fraction behaved physiologically like histamine. Further, this fraction gave the Pauly reaction. The authors consider that the toxic substance is histamine, but that its origin is not bacterial. C. R. H.

**Active Principles of Peptone.** A. J. CLARK (*J. Pharm. exp. Ther.*, 1924, **23**, 45—54).—Peptones contain a substance, soluble in alcohol, having a physiological action resembling that of extracts of the posterior lobe of the pituitary; there is sometimes also found a second alcohol-soluble substance with sympathomimetic properties. No evidence could be found of the presence of histamine. The author considers that the lethal action of peptone injected intravenously is due to the alcohol-insoluble portion, although this portion is without action on isolated organs.

C. R. H.

**New Synthetic Nitrophenol Glucosides and the Disinfectant Action and Toxicity of the Nitrophenols.** E. GLASER and W. WULWEK (*Biochem. Z.*, 1924, **145**, 514—534).—*o*-Nitrophenol tetra-acetyl glucoside,  $C_6H_4O_2N \cdot O \cdot C_6H_4O_5(Ac)_4$ , long, colourless needles, m. p. 158—159°,  $[\alpha]_D^{18} +36.14^\circ$ , is obtained by the action of an aqueous alkaline solution of nitrophenol on tetra-acetyl-bromoglucose in acetone, and on hydrolysis with ammonia in methyl alcohol it yields  $\beta$ -*o*-nitrophenol glucoside,  $C_6H_4O_2N \cdot O \cdot C_6H_{11}O_5 \cdot H_2O$ , colourless, hygroscopic crystals, m. p. 130—131°, having  $[\alpha]_D^{18} -82.72^\circ$ . *m*-Nitrophenol tetra-acetyl glucoside, m. p. 136—137°,  $[\alpha]_D^{18} -18.26^\circ$ ,  $\beta$ -*m*-nitrophenol glucoside (+1H<sub>2</sub>O), m. p. 167—168°,  $[\alpha]_D^{22} -84.89^\circ$ , *p*-nitrophenol tetra-acetyl glucoside, m. p. 174—175°,  $[\alpha]_D^{18} -27.17^\circ$ , and  $\beta$ -*p*-nitrophenol glucoside (+1H<sub>2</sub>O), m. p. 164—165°,  $[\alpha]_D^{22} -99^\circ$ , are obtained in analogous manners. The three glucosides are hydrolysed by emulsin. The nitrophenols are intermediate in bactericidal power between phenol and the cresols, the meta compound being the most active, whilst the corresponding glucosides formed from them are devoid of disinfectant properties. The para compound is the most toxic of the three nitrophenols,

whilst the derived glucosides have but a slight toxicity. This is correlated with the detoxication of phenols by conjugation with glucuronic acid in the animal organism. J. P.

**Quantitative Protozoöcidal Comparison of some Opium Alkaloids.** C. E. BILLS and D. I. MACHT (*J. Pharm. Exp. Ther.*, 1924, **23**, 261—268).—Adopting unity as representing the toxicity of morphine to *Paramoecium* at  $p_H$  5.7, the degree of toxicity of various opium alkaloids is as follows: morphine 1, codeine 1, dionine 2, heroine 7, thebaine 30, pantopium (the total alkaloids of opium) 30, papaverine 30, peronine (benzylmorphine) 100. With increasing  $p_H$  (6.6—7.7), morphine becomes less toxic, whilst codeine, heroine, and thebaine become much more toxic. Some evidence exists in favour of the view that *Paramoecia* become more resistant to given opium alkaloids after being subjected to non-lethal doses of the same alkaloid. J. P.

**Behaviour of Bacteria towards the Alkaloids.** H. H. GREEN and I. LONSTEIN (*J. S. Afr. Chem. Inst.*, 1924, **7**, 6—8).—The authors have isolated a non-spore-forming aërobie from nicotine sheep-dips; the organism does not liquefy gelatin, does not form acid or gas from dextrose, lactose, sucrose, or glycerol, is non-chromogenic, and non-diastatic. It destroys nicotine rapidly when the latter is the sole source of food supply as regards nitrogen and carbon, but if grown in media containing ammonium salts or simple nitrogenous compounds the organism loses its power of destroying nicotine. The organism tolerates morphine and atropine in concentrations up to 2%, but its growth is inhibited by strychnine, brucine, and quinine. Numerous putrefying organisms will grow in media containing 0.2% of nicotine, morphine, or atropine but not in those containing strychnine, brucine, or quinine. W. P. S.

**Diastases. The Two Enzyme Theory.** K. HIZUME (*Biochem. Z.*, 1924, **146**, 52—71).—The liquefying action of human salivary diastase is increased in the same way as the saccharifying power by potassium and sodium chlorides and bromides, whilst iodides and fluorides are devoid of action. Diluted blood-serum has a similar activating effect. Dialysis lowers the liquefying power of saliva on starch, and this is entirely regenerated by the addition of chlorides and bromides. Nitrates act in a similar way on dialysed and undialysed saliva, nitrites are less active, whilst sulphates have no action on undialysed, but regenerate the activity of dialysed saliva. Alkalis and acids exert the same influence on the liquefying properties as on the saccharifying action of salivary diastase. The liquefying and saccharifying powers of malt diastase are not affected by salts. Maltose and dextrose protect salivary diastase from inactivation by heat, whilst sucrose and lævulose are much less active in this respect. Chlorides, bromides, and diluted serum also protect the enzyme against heat-inactivation, whilst iodides and nitrates have no such action. Malt diastase is more easily inactivated by heat in the presence of chlorides and bromides than in their absence (cf. A., 1923, i, 1254). J. P.

**Purification of Malt Diastase by Electro-dialysis and Electro-osmosis. II.** R. FRICKE (*Ber.*, 1924, 57, [B], 765—768).—Improved methods are described for the preparation of the membranes and anode and for the regulation of the acidity of the solutions in the purification of malt diastase by electro-dialysis (cf. Fricke and Kaja, this vol., i, 469). The activity of the ultimate products is not thereby increased, but the heavy incidental losses of material are avoided. Increased attention to the acidity of the solutions in the electro-osmotic experiments has resulted in improved activity in the malt diastase, which, however, is very unstable in solution.

H. W.

**Influence of the New Sulphur-containing Amino-acid (Mueller) on the Activity of Pancreatic Amylase.** M. L. CALDWELL (*J. Biol. Chem.*, 1924, 59, 661—665).—The new amino-acid (cf. A., 1923, i, 869; this vol., i, 438) exerts a favourable influence on the amylolytic action of pancreatic amylase which is similar to that previously observed with naturally occurring  $\alpha$ -amino-acids.

C. R. H.

**Liver Amylase.** O. HOLMBERGH (*Z. physiol. Chem.*, 1924, 134, 68—96).—The value of  $Sf = K \times (\text{g. maltose formed from starch}) / (\text{g. preparation used})$ ,  $K$  being the unimolecular reaction constant, differs for samples from various lobes of a pig's liver, the mean value being 0.0038. In all cases, it is very much less than the value obtained for a piece of pancreas. The addition of liver substance to a pancreas extract results in an activity lower than the sum of the activities of the two components. It appears that the liver contains a substance which inhibits pancreatic amylase. The activity of liver amylase is highest at  $p_H$  6.9, and in presence of 0.008—0.5*N*-sodium chloride or potassium chloride, or 0.008—0.04*N*-calcium chloride. Sodium iodide decreases the production of maltose, but increases that of dextrose. Various methods of extracting liver amylase have been investigated. Dialysis at first increases the activity of the preparation,  $Sf$  increasing more than 500%, but further dialysis results in a decrease of activity. The action of liver amylase on starch is inhibited by maltose, but this inhibition disappears if the maltose is removed by maltase. If yeast is treated with toluene containing ethyl acetate so as to destroy the maltase, it no longer retains its power of increasing the activity of amylase.

W. O. K.

**Invertase. IV.** H. VON EULER and K. JOSEPHSON (*Ber.*, 1924, 57, [B], 859—865; cf. A., 1923, i, 721; this vol., i, 466).—Elementary analyses of purified invertase (*If* 225—245) gave results which are closely similar to those of the proteins, the slight discrepancies being probably attributable to the presence of carbohydrates in invertase. Colorimetric determinations indicate the presence of tryptophan 5.5% and histidine <6%>2% in invertase; tyrosine is absent. As judged from the sulphur content, cystine is present to the extent of 2%.

H. W.

**Uniformity in Invertase Action. III. Stability of the Enzyme.** J. M. NELSON and R. W. E. KERR (*J. Biol. Chem.*, 1924, **59**, 495—527).—Invertase preparations could be made abnormal by treatment with dialysed iron, accompanied by an increase in the activity per unit of dry weight. Abnormal invertase prepared in this way is unstable at  $p_H$  about 4.5 and 25°. It can be re-stabilised by the addition of inactivated normal invertase preparation. This re-stabilisation may be effected in varying degree according to the concentration of the added inactivated normal invertase preparation, and is reversible with dilution. Normal invertase preparation which is rendered unstable by dilution is re-stabilised by the addition of gelatin, egg-albumin, or inactivated normal invertase preparation. At  $p_H$  2.2 and 25°, abnormal invertase is less stable than normal invertase, and the addition of inactivated normal invertase preparation causes an increase in the stability of the former and a decrease in that of the latter. The rate of inactivation of invertase solutions at  $p_H$  2.2 and 25° is higher in the more concentrated solutions and falls off in the latter part of the inactivation. The inactivation of concentrated invertase solutions brought about in this manner is partly reversible with dilution and changing the  $p_H$  from 2.2 to about 4.5, although the reversibility is not observed with less concentrated solutions. At  $p_H$  4.8 and 60—65°, both the normal and the abnormal invertase preparations possess the same stability. D. R. N.

**Characteristics of Invertase Action.** J. M. NELSON and G. BLOOMFIELD (*J. Amer. Chem. Soc.*, 1924, **46**, 1025—1043).—Arising out of the observation that different invertase preparations at different temperatures gave a maximum velocity of inversion at nearly the same sucrose concentrations (Nelson and Vosburgh, A., 1917, ii, 252), the influence of the temperature and of the hydrogen-ion concentration on the relation between the sucrose concentration and the rate of hydrolysis has been studied. The sucrose concentration at which the hydrolysis reaches its maximum velocity is independent of the temperature and hydrogen-ion concentration. Further, the limits of hydrogen-ion concentration within which the hydrolysis with invertase follows a normal course extend from  $p_H$  2.75—3.3 (depending on the temperature) in the acid region to  $p_H$  8.4 in the more alkaline region. Between 25° and 35°, the hydrogen-ion concentration at which invertase first shows inactivation decreases regularly. The zone of the optimum action of invertase at 25°, 30°, 35° lies between the hydrogen-ion concentrations  $p_H$  4.5 and 5.0, which are narrower limits than previously determined. The relation between the activity ( $n$ ) and the hydrogen-ion concentration approximately satisfies the equation for the dissociation residue curve,  $\rho = [H^+]/([H^+] + k)$ , where  $\rho$  is the fraction of the compound not dissociated and  $k$  is the dissociation constant, as claimed by Michaelis and Davidsohn (A., 1911, i, 1052). The temperature does not affect this relation. The temperature coefficient of the hydrolysis of sucrose in the presence of invertase increases with decreasing acidity,

hence the hydrolysis is inherently different from that by acid, where the same coefficient is independent of the hydrogen-ion concentration. The hydrolysis of sucrose is thus shown to involve two distinct stages, one of which is characterised by the sucrose concentration at which the hydrolysis reaches its maximum velocity and is independent of the temperature and acidity, whilst in the other it changes with each of these. A. C.

**Calculation of the Activity- $p_H$  Curve of Invertase.** H. VON EULER, K. JOSEPHSON, and K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **134**, 39—49).—Assuming that the adsorption compound between invertase and sucrose dissociates as a weak acid between  $p_H$  5 and  $p_H$  8 and that the undissociated compound only is active, the variation of the rate of inversion with the  $p_H$  can be calculated. The experimental results agree well with theory. If, as has been shown to be probable by Willstätter and Kuhn (cf. A., 1923, i, 401), raffinase is identical with invertase, and this enzyme has an affinity constant for raffinose of only about 1/15 of that for invertase, then it may be shown by calculation that the variation with  $p_H$  of the rates of fermentation of the two sugars should be very similar, as is found experimentally. W. O. K.

**Affinity of Invertase for Different Sugars.** II. K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **134**, 50—67).—Invertase suffers no loss of activity when it is kept for 30 minutes at  $p_H$  2.63. There is thus no destruction of invertase due to acid alone. The depressing effect of acid on the activity of invertase which appears when the inversion is carried out in a medium more acid than  $p_H$  4.5 (the optimum  $p_H$ ) is shown to be largely accounted for by the change in the affinity constant  $K_M$  of the enzyme for the substrate occasioned by the low  $p_H$ . A small discrepancy between the theoretical and experimental results is probably caused by the basic dissociation of the enzyme-substrate compound. Inversion is inhibited by dextrose and lævulose less at  $p_H$  2.75 than at  $p_H$  4.5. In the case of dextrose, the inhibition is maximum at  $p_H$  4.5, whilst in the case of lævulose, inhibition continues to increase with the  $p_H$ . W. O. K.

**Hydrolysis of the Endosperm of *Phytelphas macrocarpa* by its own Enzymes.** F. J. PATON, D. R. NANJİ, and A. R. LING (*Biochem. J.*, 1924, **18**, 451—454).—Vegetable ivory shavings contain an enzyme which hydrolyses the mannan present in them to mannose and a trisaccharide which is presumably mannotriose. The hydrolysis was greatest at about  $p_H$  4.2. When the enzyme is allowed to act for a long period, namely, 10 days, mannose alone is produced. It is probable, therefore, that the trisaccharide is an intermediate product. S. S. Z.

**Synthesising Action of  $\alpha$ -*D*-Mannosidase in Presence of Ordinary Glycol and Glycerol.** H. HÉRISSEY and J. CHEYMOL (*Compt. rend.*, 1924, **178**, 1372—1374).—Combination of mannose with glycol or glycerol is effected by the action of the  $\alpha$ -*D*-mannosidase contained in germinated lucerne seeds (cf. this vol., i, 234).

T. H. P.  
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**Enzymic Hydrolysis of Hexose-monophosphoric Acid by Extracts of the Femur.** Y. TAKAHASHI (*Biochem. Z.*, 1924, **146**, 161—163).—The hexose-monophosphate prepared by Neuberg (A., 1918, i, 423) by partial hydrolysis of hexose-diphosphate, is hydrolysed by aqueous extracts of the femur with the liberation of phosphoric acid (cf. Robison, A., 1922, i, 730). J. P.

**Dried Yeast.** H. SOBOTKA (*Z. physiol. Chem.*, 1924, **134**, 1—21).—The rate of fermentation of dextrose by yeast dried by various methods has been measured by determining the rate of production of carbon dioxide. With such dried yeasts there usually occurs a more or less marked period of induction. Increase of the concentration of the yeast decreases this period. If the yeast is first of all incubated with sugar solution the incubation period disappears. After being ground up in a mortar, dried yeast ferments sugar more slowly. Determination of the sugar at intervals during the fermentation by dried yeast shows that a certain disappearance of the carbohydrate takes place, amounting to from 20—50% of the sugar used, which cannot be accounted for by the carbon dioxide produced. W. O. K.

**Mechanism of Alcoholic Fermentation. III.** A. LEBEDEV (*Z. physiol. Chem.*, 1924, **134**, 160; cf. this vol., i, 464).—The liquid obtained after fermentation of sugar in presence of phosphate, on treatment with lead acetate and hydrogen sulphide, yielded no osazone but a white precipitate of either hydrazone or hydrazide. W. O. K.

**Adenine Hexoside from Yeast.** P. A. LEVENE (*J. Biol. Chem.*, 1924, **59**, 465—472).—The sugar constituent in adenine hexoside from yeast (A., 1912, i, 320) appears to possess certain peculiarities and differs from other known hexoses. It is not oxidised by bromine water and hence is ketonic, although apparently it is not a common  $\beta$ -ketohexose (A., 1915, ii, 494). The mutarotation of the phenylosazone of the new sugar closely resembles that of *d*-gulosazone, the initial rotation being practically 0° and the equilibrium slightly to the right. The m. p. of the new osazone is 165° (corr.), which is nearly the same as that of gulosazone, although the decomposition points are 208° and 180°, respectively. It further differs from gulosazone in being less soluble in alcohol and in water. These differences are more marked in the two *p*-bromophenylosazones. Taking dextrose as a standard of reduction, 1 g. of the hexoside should yield 0.6 g. of the sugar, whereas the maximum yield obtained from the hexoside was only 0.18 g. Further, on the basis of the rotation of the osazones, the sugar should belong to *d*-series, but *d*-sorbose rotates to the left, whereas the new sugar is dextrorotatory. Thus the new sugar does not seem to be identical with any one of the known  $\beta$ -ketohexoses.

D. R. N.

**Effect of Nitrogenous Nutrition on the Activity of Brewer's Yeast.** I. BAY (*Compt. rend. Soc. Biol.*, 1923, **89**, 1044—1045; from *Chem. Zentr.*, 1924, i, 680).—Fermentation with brewer's

yeast is most active and produces the maximum amount of ethyl alcohol and acid at 15° in a bouillon containing 0.1% of ammonium hydrogen carbonate.

G. W. R.

**Variability of Lactic Acid Fermentation.** A. LUMIÈRE (*Ann. Inst. Pasteur*, 1924, **38**, 344—357; cf. this vol., i, 353).—The author replies to criticisms of his previous work on the subject, and brings forward further experimental evidence in support of his contention that, provided his technique is rigidly followed, lactic acid fermentation is a perfectly regular process, both in normal media and in the presence of small concentrations of antiseptics, and, in the latter case, regardless of whether or not the bacteria used are acclimatised to the antiseptic.

C. R. H.

**Fermentation of the Unsaturated Dicarboxylic Acids. I. Fumaric Acid.** J. H. QUASTEL (*Biochem. J.*, 1924, **18**, 365—380).—Succinic and fumaric acids are fermented by *Bacillus pyocyaneus*, with the production of lower fatty acids. In the case of fumaric acid, acetic acid is chiefly formed. This fermentation is accelerated by aëration, and proceeds more rapidly in the case of fumaric acid than in that of succinic acid. A 1% solution of ammonium fumarate is entirely utilised in 30 hours. The fermented fumarate medium gives colour tests with nitroprusside and with guaiacol due to the formation of pyruvic acid. The colour tests can be utilised as a test for differentiating *B. pyocyaneus* and *B. fluorescens* liq. from other bacteria capable of growing on a fumarate medium and which do not give these colour reactions. From the quantities of oxygen utilised and carbon dioxide formed during the fermentation of a known amount of fumaric acid a scheme representing the intermediate stages of fermentation in which oxalacetic acid figures is advanced; 90% of fumaric acid can be accounted for in the fermentation.

S. S. Z.

**Optimum and Limiting Concentrations of Hydrogen Ions for Bacterial Cultures. Tendency of Cultures to Approach the Optimum Concentrations.** CLUZET, ROCHAIX, and KOFMAN (*Compt. rend.*, 1924, **178**, 1638—1639).—Cultures of *Bacillus coli*, *B. paratyphosus* B, and of Ebert's and Flexner's bacilli exhibited optimum and lower and upper limiting concentrations of hydrogen ions, these being different for the different organisms. During normal bacterial growth, the cultures tended to become gradually more alkaline but not to overstep the optimum hydrogen-ion concentration. If development is restricted owing to excessive acidity or alkalinity, the bacteria appear to exert an alkaligenic or acidogenic function, the reaction becoming progressively displaced towards the optimum value.

T. H. P.

**Effect of Iron and Zinc on the Development of *Aspergillus niger* in the Presence of Dextrose.** A. FROUIN (*Compt. rend. Soc. Biol.*, 1923, **89**, 986—988; from *Chem. Zentr.*, 1924, i, 679).—The favourable effect of zinc and ferrous iron on the growth of *Aspergillus* in the presence of sucrose cannot be attributed to the

presence of dextrose. Ferrous iron is unfavourable to the formation of dry mycelial tissue, but favourable to spore formation. G. W. R.

**Transformation of Quinic Acid by Moulds.** W. BUTKEWITSCH (*Biochem. Z.*, 1924, **145**, 442—460).—The coloration observed to develop in cultures of *Citromyces* and *Penicillium* containing sodium quinate (A., 1922, i, 707) is ascribed to the formation of condensation products (with iron) by phenolic compounds into which quinic acid is transformed by the moulds. Protocatechuic acid is the most important of these phenols, but pyrocatechol, quinol, and quinone are supposed also to be formed. The subsequent disappearance of the coloration in old cultures is ascribed to the decomposition of the condensation products with formation of oxalic acid, which is later oxidised to carbon dioxide. Only those moulds which can bring about the formation of the intermediate phenolic compounds from quinic acid are able to utilise it as a source of carbon, and both processes are influenced in the same way when zinc sulphate is added to the culture. Moulds capable of forming phenolic compounds from quinic acid also ferment sugar with formation of citric acid, and a possible correlation of the two processes is suggested. These results are regarded as opposing the view of Kostytshev (A., 1921, i, 83) that quinic acid is first transformed by moulds into sugar.

J. P.

**Comparison of Yields from the Point of View of Energy in the Development of Moulds utilising Carbohydrates or Proteins, and Specific Dynamic Action.** E. F. TERROINE, R. BONNET, R. JACQUOT, and G. VINCENT (*Compt. rend.*, 1924, **178**, 869—872).—*Aspergillus niger* and *A. oryzae* were cultivated in solutions of glucose to which ammonium sulphate had been added, of silk peptone, and of gelatin, the growths being analysed from the thermal point of view. The results, together with those obtained in the course of other investigations (Terroine, Bonnet, and Joessel, *Compt. rend.*, 1923, **177**, 900), lead to the generalisation that in living organisms formation of one carbohydrate from another involves extremely small energy loss, which is increased when carbohydrate is formed from fat and considerably so if from proteins. The energy utilisation coefficients of carbohydrates and proteins are in the ratio of about 100 to 140. H. J. E.

**Metabolism of Acid-fast Bacteria.** I. H. BRAUN, A. STAMATELAKIS, and S. KONDO (*Biochem. Z.*, 1924, **145**, 381—397).—An investigation of the growth of the acid-fast Timothy bacillus, various strains of butyric bacillus, urine and Trumpet bacilli in nutrient media containing various sources of carbon (organic acids, alcohols, and carbohydrates), nitrogen (amino-acids, urea, and uric acid), and inorganic salts.

J. P.

**Susceptibility of Lipases of Various Origin to Toxins.** P. RONA and H. PETOW (*Biochem. Z.*, 1924, **146**, 144—152).—The susceptibility to toxic inactivation (A., 1923, i, 1258) shown by purified pancreatic, liver, and serum lipases is of the same order

as that of the crude aqueous extracts containing these enzymes. The specific reactions of the lipases to quinine and atoxyl are preserved in artificial mixtures of the enzymes, serum lipase being inactivated by quinine, and serum and liver lipases by atoxyl. J. P.

**Kinetics of Trypsin Digestion. II. Conditions Under Which the Reaction is Unimolecular.** J. H. NORTHROP (*J. Gen. Physiol.*, 1924, 6, 417—428).—If certain conditions are observed, the hydrolysis of casein by trypsin is accurately represented by the unimolecular formula  $dx/dt = KE(A-x)$ , where  $K$  is a constant,  $E$  is the quantity of enzyme used,  $A$  is the original concentration of casein, and  $x$  the concentration of casein at the time  $t$ . The conditions are that the temperature is low, to prevent inactivation of the trypsin, that much trypsin is used so that inhibition by the products of the reaction is negligible, and that the course of the reaction is followed by determining the actual amount of casein present at various times so that the effect of consecutive reactions is eliminated. Under these conditions also, the effect of variations in the initial concentration of the trypsin is predicted by the formula, but with increasing casein concentrations the value of  $K$  decreases and ultimately becomes nearly inversely proportional to the casein concentration. It is suggested that this is due to the existence of an equilibrium between casein and water in which casein can be replaced by the first cleavage products, since, if casein is dissolved in a freshly-prepared solution of digested casein, the reaction is typically unimolecular in every respect. W. O. K.

**Kinetics of Trypsin Digestion. III. The Course of the Reaction with Constant Substrate under Conditions causing Inactivation of the Enzyme.** J. H. NORTHROP (*J. Gen. Physiol.*, 1924, 6, 429—437).—When gelatin is hydrolysed in concentrated solution by a large amount of trypsin at 60° and at  $p_H$  6.0, inactivation of the trypsin takes place, and so the reaction is apparently not unimolecular. If, however, determination is made by the method of Northrop and Hussey (*A.*, 1923, ii, 271) of the trypsin present at various times during the course of the reaction, it appears, from theory and experiment, under these conditions, (a) that the rate of reaction is proportional to the concentration of trypsin present at the time, (b) that the reaction is approximately unimolecular if the total hydrolysis observed is taken as the amount of substrate available, (c) that the velocity constant calculated in this way should agree with the constant for the decomposition of the enzyme, and that it should be independent of the concentration of the enzyme instead of proportional to it, and (d) that the total amount of substrate decomposed should be proportional to the amount of trypsin added at the beginning instead of independent of it. W. O. K.

**Kinetics of Trypsin Digestion. IV. The Course of the Reaction when both Substrate and Enzyme Concentrations are Decreasing.** J. H. NORTHROP (*J. Gen. Physiol.*, 1924, 6, 439—452).—When edestin is hydrolysed by trypsin at  $p_H$  7.0 at

40° in the presence of a high concentration of sodium chloride which decreases the activity of the trypsin and increases the solubility of the edestin, rapid inactivation of the trypsin occurs, and the reaction follows the equation  $K = [\log(A_1/A_2)] / (T_1 - T_2) E_t$ , where  $A_1$  and  $A_2$  are the concentrations of the edestin at times  $T_1$  and  $T_2$  respectively and  $E_t$  is the concentration of the enzyme during the interval  $T_1 - T_2$ . If it is assumed that the activity of the enzyme decreases unimolecularly, the theoretical results are obtained when high enzyme and low edestin concentrations are used. With low enzyme and high edestin concentrations, the effects of the products on the reaction become too large to be negligible.

W. O. K.

**Action of Chymosin on the Proteins of Milk. I. Action of Chymosin on Colostrum.** J. ZAYKOWSKY (*Biochem. Z.*, 1924, **146**, 189—197).—From a comparison of the coagulating action of chymosin (rennin) on colostrum and on milk at varying acid concentrations, support is gained for the view that rennin and pepsin are not identical.

J. P.

**Detection of Ferment Processes Conditioned by Immunisation. I.** E. KUPELWIESER (*Biochem. Z.*, 1924, **145**, 492—504).—Using the refractometric method described by Pregl and de Crinis (*Fermentforschung*, 1917, **2**, 58) and in contrast to the findings of these authors, no proteolytic action of serum on placenta proteins could be demonstrated in cases of pregnancy.

J. P.

**Detection of Ferment Processes Conditioned by Immunisation. II.** E. KUPELWIESER and H. WASTL (*Biochem. Z.*, 1924, **145**, 505—513).—The sera of guinea pigs immunised with inactivated ox-serum have no proteolytic action on the antigen (cf. Pfeiffer and Mita, *Z. Immunitätsforsch.*, 1910, **6**, 18; Abderhalden and Pinkussohn, *Z. physiol. Chem.*, 1910, **64**, 100).

J. P.

**Proteinogenous Amines. XVII. Faculty of Normal Intestinal Bacteria to form Toxic Amines. XVIII. Production of Histamine, Tyramine, and Phenol in Laboratory Media by Intestinal Organisms. XIX. Factors involved in the Production of Phenol by the Colon Group. XX. Presence of Histamine in the Mammalian Organism.** M. T. HANKE and K. K. KOESSLER (*J. Biol. Chem.*, 1924, **59**, 835—853, 855—866, 867—877, 879—888. **XXI. Intestinal Absorption and Detoxication of Histamine in the Mammalian Organism.** K. K. KOESSLER and M. T. HANKE (*ibid.*, 1924, **59**, 889—903).—**XVII.**—The action was observed of the mixture of bacteria in human faeces on histidine and tyrosine in a synthetic medium composed of salts and glycerol. Out of a series of twenty-six cases, it was found that 62% decarboxylated histidine, 65% decarboxylated tyrosine, and 46% could do both. Phenol was never produced from tyrosine; in three cases small amounts of *p*-hydroxyphenyl-lactic acid were obtained. During the bacterial

action the hydrogen-ion concentration of the fluid uniformly increased.

XVIII.—The decarboxylating action on histidine and tyrosine of two strains of colon bacilli was studied in milk, blood broth, and ascitic fluid broth. Amines were only produced in media containing carbohydrate and in which an acid reaction was developed. The organism which produced tyramine in an acid medium produced phenol in an alkaline one.

XIX.—An extension of the preceding paper emphasising the authors' view that amine production is a protective mechanism of the bacteria against a rise in hydrogen-ion concentration of the medium.

XX.—Details are given of a method for the colorimetric determination of histamine in mixtures such as intestinal contents. In human faeces, there were found 6—20 mg. of histamine in 500 g. of material, and amounts of the same order of magnitude in caecal contents. No evidence was found of the presence of histamine in the human liver, but it was demonstrated in the liver of the dog.

XXI.—A physiological study was made of the systemic effects observed after the introduction of histamine into different parts of the alimentary canal. A comparison of the rate of absorption, as measured by the disappearance of the substance from the alimentary canal, with the mildness of the resulting systemic effects, leads the authors to conclude that histamine may be detoxicated during its passage through the intestinal wall. C. R. H.

**Culture of Moulds on Amino-acids and Mechanism of the Specific Dynamic Action.** E. F. TERROINE, S. TRAUTMANN, R. BONNET, and R. JACQUOT (*Compt. rend.*, 1924, **178**, 1488—1490).—By growing *Aspergillus niger* and *A. oryzae* on media containing glycoll, alanine, valine, leucine, or glucosamine, it is shown that the energy liberated is constant and independent of the nature of the amino compound or organism. The energy change must therefore be associated solely with de-aminisation. A. B. H.

**Production of Carbamide during Ammonification by the *Microsiphonæ*.** G. GUITTONNEAU (*Compt. rend.*, 1924, **178**, 1383—1385).—When grown in an inorganic solution to which peptone was added as sole organic nutriment, certain of the *Microsiphonæ* produced carbamide in considerable proportions and at the same time ammonium salts neutral to phenolphthalein accumulated in the liquid. The carbamide may be formed as a waste product or may be an intermediate compound in the assimilation of the hydrolytic products of the peptides. As regards its practical significance, carbamide readily enters the general cycle of vegetation owing to its transformation in the soil into ammonium carbonate, and, moreover, most plants secrete urease.

On the other hand, such liberation of carbamide results in loss of gaseous nitrogen if it is produced in contact with the nitrous acid displaced from nitrites by the acid formed in the various

fermentations of carbonaceous material. These phenomena may occur in the soil and also help to explain the enormous losses of nitrogen taking place during the purification of sewage. T. H. P.

**Occurrence of Peroxide in Cultures of *Pneumococcus*.** O. T. AVERY and H. J. MORGAN (*J. Exp. Med.*, 1924, **39**, 275—287).—Peroxide formation was observed with various strains of *Pneumococcus*, *Staphylococcus hæmolyticus*, and *S. mucosus*, but not with *S. aureus*. With the first-named, there must be free access of air, and absence of catalase, peroxylase, etc.; the product is unstable, and conditions leading to its disappearance are mentioned.

CHEMICAL ABSTRACTS.

**Participation of a Peroxylase in the Appearance of Pigment in *Drosophila melanogaster* (Læw.).** DE LUNA (*Compt. rend.*, 1924, **178**, 878—881; cf. this vol., i, 348).—Both an oxydase and a peroxylase play a part in the pigmentation of *Drosophila*; the former is probably tyrosinase, and the distribution of these enzymes is similar to that of the pigment. Rate of pigmentation is a function of temperature, but anæsthetics retard the fixation of oxygen on the colourless matter (A., 1904, ii, 831).

H. J. E.

**Influence of X-Rays on the Catalase of Liver.** A. MAUBERT, L. JALOUSTRE, P. LEMAY, and C. GUILBERT (*Compt. rend.*, 1924, **178**, 889—891; cf. Maubert, Jaloustre, and Lemay, A., 1923, i, 723).—The effect of X-rays is to decrease the activity of liver catalase in proportion to the duration of exposure and the intensity of radiation. Detailed results are given, but comparison is difficult as the catalase preparations used were not identical in each case.

H. J. E.

**Sorptive Power of Metallic Hydroxides [for Invertase].** II. H. VON EULER and R. NILSSON (*Z. physiol. Chem.*, 1924, **134**, 22—38).—Freshly precipitated lanthanum hydroxide adsorbs invertase even more completely than does aluminium hydroxide. It adsorbs more at  $p_H$  8.1 than at  $p_H$  5.6. Its power of adsorption decreases on keeping. The invertase adsorbed by lanthanum hydroxide is not adsorbed irreversibly unless the hydroxide is precipitated in presence of the enzyme, when some inactivation takes place.

W. O. K.

**Coagulation and Vegetable Life.** J. AMAR (*Compt. rend.*, 1924, **178**, 1317—1319; cf. this vol., i, 687; ii, 144).—Experiments on starch, on beans, and on the leaves of the spindle tree are described, the results indicating the marked de-coagulating effects produced by sodium chloride and other sodium salts and hence the importance of such salts in promoting osmotic interchanges and the general health of the vegetable organism.

T. H. P.

**Production of Ozone by Green Plants.** H. COUPIN (*Compt. rend.*, 1924, **178**, 1572—1573).—Some evidence has been obtained

that small quantities of ozone are given off, together with oxygen, from green plants when placed in a damp chamber in the light for 24 or 48 hours. Since in the dark, or with plants devoid of chlorophyll, no ozone is produced, it is concluded that ozone production is probably connected with carbon dioxide assimilation. J. W. B.

**Equilibrium of the Cellular Constituents and Intensity of the Oxidations of the Cell. Imbibition and Oxidation. Case of Reviviscent Plants.** A. MAYER and L. PLANTEFOL (*Compt. rend.*, 1924, 178, 1385—1388).—The authors have investigated the proportions of carbon dioxide formed when *Hypnum triquetrum*, soaked in water to bring it to a reproducible degree of imbibition and then allowed to dry to different extents, is kept in an enclosed space in the dark at 20°. The respiratory intensity either passes through a maximum at 50—60% of water in the moss, or gradually increases to a constant, or passes through a maximum at about 40% of water, according as it is referred to 1 g. of the wet moss, or to 1 g. of the dry matter, or to 1 g. of the water present. It is concluded that, other things being equal, there are definite proportions of water and of the other constituents of the cell for which the cellular oxidations exhibit a maximum intensity. T. H. P.

**"Auximones," and the Growth of the Green Plant.** N. A. CLARK and E. M. ROLLER (*Soil Sci.*, 1924, 17, 193—198).—*Lemna major* was grown in a series of artificial culture solutions and compared with that grown in soil suspensions. Healthy growth and reproduction depended on a requisite proportionality of dissolved salts. Neither "auximones" (Bottomley) nor organic matter were essential. In the absence of these latter, during 4 months closely followed the equation:  $\log_{10} N/N_0 = k(t-t_0)$ , where  $N$ =number of plants present and  $t$ =time. A. G. P.

**Effect of General Anæsthetics on the Respiration of Cereals. I. Carbon Dioxide Production.** E. P. SMITH (*Ann. Bot.*, 1924, 38, 261—272).—Chloroform, ether, and ethyl alcohol in varied concentrations have similar effects on the carbon dioxide output from seedlings of wheat, rice, and oats; the first effect is a decrease in the rate of respiration, followed by an increase to a maximum and a final depression. With chloroform, recovery is possible only after very short exposures, whether continuous or intermittent; with ether recovery can take place even after 6 hours' exposure, provided the respiration does not fall below 60%. Experiments with the corolla of *Ipomœa* indicate that the effect of the anæsthetic on the permeability to carbon dioxide of the plasma membrane must also be taken into account, and that the apparent maximum respiration after treatment with an anæsthetic may be due to a release of carbon dioxide retained during a period of decreased permeability. E. M. C.

**Anaërobic Experiments with Argon.** W. A. CANNON and E. E. FREE (*Carnegie Inst. Yearbook*, 1921, 20, 63).—Experiments with roots and other parts of plants under partial anaërobic conditions show that the amount of oxygen necessary for growth is



the same when nitrogen or argon is used as the diluent gas, but less in the case of helium and hydrogen. The difference is probably concerned with the relative rates of diffusion of oxygen through the gases. A. A. E.

**Carbohydrate-Amino-acid Relation in the Respiration of Leaves.** H. A. SPOEHR and J. M. MCGEE (*Carnegie Inst. Yearbook*, 1921, 20, 60—61).—Carbon dioxide evolved in respiration was determined by a conductivity method. The stimulating effect of amino-acids (glycine, alanine, and asparagine) is most marked with dextrose as the carbohydrate food, noticeable with sucrose but not with mannose, and depressed by lævulose. No explanation is advanced. A. A. E.

**The First Carbohydrates that Originate during the Assimilatory Process. Physiological Study with Variegated Leaves.** T. WEEVERS (*Proc. K. Akad. Wetensch.*, 1924, 27, 46—56).—In ten out of twelve different plants examined, the variegated parts of the leaves contain only sucrose, and the green parts both sucrose and monoses. The presence of monoses in the assimilating leaf-parts and their absence from the non-assimilating full-grown variegated leaves support the view that, in these plants, starch arises from the monoses and that the latter are, in general, the first sugars to be synthesised during the process of carbon assimilation. Confirmation of this view is furnished by the absence of starch as reserve material from three of the species, namely, *Aspidistra*, *Chlorophytum*, and *Ophiopogon*, which contain starch only in the stomata of both the variegated and the green parts of the leaf.

Complete proof has been obtained by depleting the full-grown leaves of the variegated *Pelargonium* of their sugar and starch by keeping the plants in the dark for two or three days and then exposing them to sunlight. Under these conditions, the first sugars to be formed as assimilation takes place are monoses, sucrose and starch appearing only later. Conclusive evidence is not available concerning the character of the initial monose, but in *Pelargonium zonale* lævulose seems to preponderate.

The variegated parts of the plants which contain sucrose contain also invertase, the fact that inversion does not occur in the living tissues being probably due to difference in localisation of the sugar and enzyme in the cell. T. H. P.

**Nitrogenous Metabolism of the Higher Plants. V. Diurnal Variations in the Protein Nitrogen of Runner Bean Leaves.** A. C. CHIBNALL (*Biochem. J.*, 1924, 18, 387—394).—There is a definite fall in the protein content of bean leaves at night, due to the breaking down of the cytoplasmic material. The nitrogenous products of this protein decomposition are translocated away from the leaf. S. S. Z.

**Nitrogenous Metabolism of the Higher Plants. VI. Rôle of Asparagine in the Metabolism of the Mature Plant.** A. C. CHIBNALL (*Biochem. J.*, 1924, 18, 395—404).—The decomposition

products arising from protein metabolism in bean leaves consist in large part of asparagine and other unknown substances containing free amino-nitrogen. Asparagine seems to be the chief agent whereby nitrogen in a form suitable for re-synthesis of protein is conveyed from one part of the plant to another. S. S. Z.

**Nitrogenous Metabolism of the Higher Plants. VII. Leaf Protein Metabolism in Normal and Abnormal Runner Bean Plants.** A. C. CHIBNALL (*Biochem. J.*, 1924, **18**, 405—407).—The protein degradation products of two normal and two abnormal plants are given. S. S. Z.

**Carbon Dioxide Production of Plant Roots as a Factor in the Feeding Power of Plants.** F. W. PARKER (*Soil Sci.*, 1924, **17**, 229—247).—The carbon dioxide evolution of various plant roots differed considerably, but no relationship between this factor and the feeding power of the plant (as determined by plant composition) was found. The removal of carbon dioxide from media by aspiration had no effect on the composition of the plants. The amount of the various nutrient elements absorbed by plants per gram of carbon dioxide excreted by the roots differed with the plant type. A. G. P.

**Variation of the Iodine in *Laminaria flexicaulis* at the Period of the Annual Shooting.** P. FREUNDLER (*Compt. rend.*, 1924, **178**, 1625—1628; cf. this vol., i, 354).—The results of further analyses show that the variations in the iodine content of this alga are influenced by the principal factors which intervene in enzymic reactions. Such variations constitute one of the manifestations of the disturbance of the equilibria between the alga and the sea, and between the alga and the air, and appear to be due to temporary, progressive, and reversible modification in the state of combination of the iodine. T. H. P.

**Extraction of Pectin from the Fruit Rind of the Lime (*Citrus medica acida*).** F. HARDY (*Biochem. J.*, 1924, **18**, 283—290).—Under similar time conditions, the total quantity of pectinogen obtained by extraction from the dried white rind of lime fruits varies directly with the hydrogen-ion concentration of the extracting medium when carried out at temperatures below boiling point. The quantity also varies directly with the temperature if the final reaction of the extract is less acid than  $p_H$  2.0. Alkaline extracts do not contain pectinogen. Autoclave treatment in acid medium hydrolyses the pectinogen. The viscosity of the extracts depends more on the conditions of extraction than on the pectinogen content. S. S. Z.

**Pectins of *Apium graveolens*, of the Tubers of *Stachys tubertifera*, and of the Rind of *Citrus vulgaris*.** Biochemical Method of Characterising Galactose applied to the Study of the Composition of these Pectins. J. CHARPENTIER (*Bull. Soc. Chim. biol.*, 1924, **6**, 142—156).—In the alcoholic extract of the

roots of *Apium graveolens* the presence of sucrose, mannitol, and a small quantity of a reducing sugar was demonstrated. The pectin of the same plant was obtained as a white powder,  $[\alpha]_D +154.5^\circ$ , which was coagulated in aqueous solution by the pectase of lucerne, by lead acetate, calcium and barium hydroxides, and by traces of hydrochloric acid. It yielded mucic acid when treated with nitric acid, and *d*-arabinose on hydrolysis with dilute sulphuric acid. The pectins of *Stachys tuberifera* and of *Citrus vulgaris*, with  $[\alpha]_D +119.8^\circ$  and  $+170.5^\circ$ , respectively, also yielded mucic acid and arabinose and possessed properties similar to those of the pectin of *Apium*. From the hydrolysis product of the pectins of *Apium* and *Citrus*, treated with 70% aqueous ethyl alcohol in the presence of emulsin for 3 months, crystalline  $\beta$ -ethyl galactoside (m. p. 158—159°;  $[\alpha]_D -5.3^\circ$ ) was isolated, yielding on hydrolysis dextrorotatory galactose and on oxidation mucic acid. It is concluded that the latter does not arise from galacturonic acid, and the presence of a galactan in these pectins is established. J. P.

**Chemical Nature of the Cellulose Membrane.** F. M. WOOD (*Ann. Bot.*, 1924, **38**, 273—298).—The author has reinvestigated the methods of preparation and staining of plant-tissues in order to differentiate between cellulose and pectic compounds. The best conditions of preparation for double staining are those giving minimum oxidation and maximum hydration without disintegration. Tests for oxycellulose were made on a large number of stem and root sections both in the fresh state and after the use of many fixatives. Alcohol and glycerin should be avoided on account of their obstinate retention by cellulose and their liability to wash into the pectin and so disturb its reactions to dyes. Pectin is stained by hydrochlorides of amines, and cellulose by alkali salts of the disulphonic acids of compounds containing one or more azo groups. Methylene-blue is uncertain, owing probably to its containing sulphur. The membrane probably consists of cellulose, hydrocellulose, and oxycellulose in equilibrium, the two former generally predominating. E. M. C.

**Nature and Amount of Substances Capable of Hydrolysis by Invertase and by Emulsin contained in Seeds of some Leguminosæ.** H. HÉRISSEY and R. SIBASSIÉ (*Compt. rend.*, 1924, **178**, 884—886).—Seeds of numerous species of *Leguminosæ* were examined. Reducing sugars were not detected and, if present, formed not more than 0.4% of the dry seeds. Aqueous extracts showed different degrees of dextrorotatory power, which was much diminished by the action of invertase; it is inferred that polysaccharides of strong dextrorotatory power are present. Stachyose was isolated from seeds of fenugreek, Provence lucerne, and *Indigofera*, and raffinose from those of *Anthyllis vulneraria* and Spanish sainfoin. Sucrose was present in the majority of the seeds, its presence in Constantinople acacia and in Indian liquorice (*Abrus abrus*) being demonstrated for the first time. Indications of glucosides were obtained with purple broom and *Copaifera officinalis*.

Results obtained in the biological determination of comparative amounts of polysaccharides in thirty varieties of *Phaseolus vulgaris*, six of *Pisum sativum*, and four of *Ervum lens* show that the use of invertase for this purpose is satisfactory. H. J. E.

**New Crystalline Chromogen, Esculetol, extracted from Horse Chestnuts.** G. BERTRAND and (MISS) Y. DJORITCH (*Compt. rend.*, 1924, **178**, 1233—1236).—The authors have isolated from the fruit of the horse chestnut the chromogenic substance which occurs in the envelope of the fruit and is colourless while in the living cells, but under the influence of the laccase present rapidly becomes deep yellow when the cell sap is exposed to the air. This chromogen, named *esculetol*, crystallises from aqueous solution in lustrous, colourless prisms, commonly united in rosettes, and, in a vacuum over sulphuric acid, undergoes dehydration to a powder of irregular lamellæ and slender needles, m. p. (Maquenne block) 275—280°. In the air, it undergoes gradual oxidation and assumes a pink colour, and in aqueous solution it is coloured an intense green by ferric chloride and brownish-yellow by absorption of oxygen or by addition of sodium or potassium hydroxide. It reduces iodic acid and gold chloride in the cold, and silver nitrate and copper acetate when heated. It is not a glucoside, and the extent to which it reduces cupro-potassium solution is not increased by previous treatment with dilute acid. T. H. P.

**The Isoelectric Points of some Plant Proteins.** W. H. PEARSALL and J. EWING (*Biochem. J.*, 1924, **18**, 329—339).—The examination of a representative series of plant proteins shows that the isoelectric point of these compounds is usually about  $p_H$  4.5 or less often about  $p_H$  3.3. Edestin is the only exception. S. S. Z.

**Solanine Content of Potatoes.** A. BÖMER and H. MATTIS (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 97—127).—The methods previously described for determining solanine are subjected to a critical examination. Von Morgenstern's method does not give quantitative results, and the solanine obtained by Meyer's method is on an average only 62.2% pure. The solubility of solanine in ether, acetone, alcohol, and in faintly ammoniacal water has been redetermined. Neither dilute acetic acid, ammonia, nor barium hydroxide decompose solanine appreciably. A simplified method of determining the solanine content of potatoes is given, which gives considerably higher results than that of Meyer or that of von Morgenstern. The original must be consulted for details. The solanine content of a large number of potatoes of various kinds grown under specified conditions as to soil and fertiliser, determined by this method, varied between 2 and 10 mg. %. Potatoes with a content of more than 20 mg. % of solanine appear to be unsafe for consumption. The solanine content of potatoes definitely shown to be prejudicial to health has varied between 25.7 and 58.3 mg. %. Unripe potatoes have a considerably greater con-

tent of solanine than ripe potatoes of the same variety; small potatoes contain more than large ones. An increase in the solanine content occurs on prolonged exposure of potatoes to the light at the same time as the formation of chlorophyll. No connexion could be traced between the use of artificial fertilisers and the solanine content of the potatoes. When potatoes of high solanine content are used as seed, the resulting crop is of normal solanine content, both as regards tops and tubers.

H. C. R.

**Surface Tension of Saponin Solutions.** H. WASTL.—(See ii, 462.)

### Comparative Plant Chemistry. IX. Chemistry of Barks.

I. C. FEINBERG, J. HERRMANN, L. RÖGLSPERGER, and J. ZELLNER (*Monatsh.*, 1924, **44**, 261—276).—Young barks of three species of trees were examined: (1) Field maple (*Acer campestre*, L.); this contained: soluble in light petroleum, 0.56%; ether extract, 1.12%; alcoholic extract, 9.34%; total water-soluble matters, 15.65%; water-soluble mineral matters, 1.11%; tannin, 4.00%; phlobaphens, 3.00%; free acids (as KOH), 1.12%; reducing sugars, trace; sucrose, 1.09%; polysaccharides, 0.55%; total nitrogen, 2.05%; total ash, 11.27%. The light-petroleum extract contained a *phytosterol*, m. p. 128°,  $[\alpha] -24.7^\circ$ , and hydrolysis of the fats yielded ceryl alcohol, arachidic acid, and a mixture of other acids. The ether extract contained an *octadecyl alcohol*, m. p. 75°. The tannin, of the approximate formula  $(C_{10}H_{12}O_5)_n$ , gave protocathechuic acid on fusion with alkali.

(2) Hazel (*Corylus Avellana*, L.) contained: soluble in light petroleum, 4.25%; ether-soluble, 3.45%; alcohol-soluble, 9.34%; total water-soluble, 15.06%; reducing sugars, 2.61%; tannin, 5.23%; free acids (as KOH), 3.96%; polysaccharides, 1.36%; soluble mineral matter, 0.94%; total nitrogen, 0.60%; crude fibre, 48.04%; total ash, 5.97%. The light-petroleum fraction yielded a new substance,  $C_{34}H_{60}O_2$ , termed *corylol*, colourless needles from alcohol, m. p. 240° (decomp.), which gave a cholestol reaction (*acetyl* derivative, m. p. 102°; *benzoyl* derivative, m. p. 136°; *acetyl*bromo derivative, m. p. 115°). *Corylol* is similar to, but not identical with alnulin (*vide infra*), cerin, and friedelin (cf. Istrati and Ostrogovitch, A., 1899, i, 772); the light-petroleum fraction also yielded a substance ( $C_{20}H_{36}O_2$ ), m. p. 199—200°, which gave a cholestol reaction, and a *wax-alcohol*, m. p. 75°. The ether extract gave a *resin acid*, m. p. 272°, and a substance crystallising in needles ( $C_{35}H_{60}O_4$ ?), m. p. 254° (*acetyl* derivative, m. p. 215°), named *coryliresinol*, similar to but differing definitely from corylol.

(3) Grey alder (*Alnus incana*, L.) contained: soluble in light petroleum, 8.97%; ether-soluble, 2.91%; alcohol-soluble, 17.32%; tannins, 9.76%; total water-soluble matters, 27.03%; free acids (as KOH), 1.23%; polysaccharides, 3.15%; total nitrogen, 1.26%; total ash, 2.00%. The light-petroleum fraction afforded long, colourless needles of a substance ( $C_{35}H_{60}O$ ?) termed *alnulin*, m. p. 261° (decomp.) (*acetyl* derivative, m. p. 237°; *bromine additive*

product, m. p.  $210^{\circ}$ ). A second crystalline product was also isolated, termed *alniresinol* ( $C_{34}H_{58}O_3$ ?), m. p.  $179^{\circ}$  (decomp.), which gave a cholestol reaction, *acetyl* derivative, needles, m. p.  $258^{\circ}$ ; it appears to be a resin alcohol. Traces of a third substance,  $C_{34}H_{60}O_3$ , were also obtained, m. p.  $210^{\circ}$ .  
F. A. M.

**Chemical Composition of the Clandestine.** A. GORIS (*Compt. rend.*, 1924, **178**, 1203—1205).—The glucoside, clandestinin, of *Lathrea clandestina*, the extraction of which is described, appears to be identical with meliatin.  
H. J. E.

**Comparative Plant Chemistry. VIII. *Chamaenerium angustifolium*.** K. PÜRINGER (*Monatsh.*, 1924, **44**, 255—260).—The leaves and flowers were examined separately, giving the following results (figures for flowers in brackets): soluble in light petroleum, 4.82% (2.76%); in ether, 4.20% (5.39%); in alcohol, 15.61% (19.77%); total water-soluble, 37.45% (41.04%); water-soluble mineral matter, 5.23% (6.05%); free acids (as KOH), 2.46% (5.32%); reducing sugars, 5.27% (8.47%); tannin, 12.15% (12.67%); phlobaphen, 1.07% (—); total nitrogen, 2.47% (2.26%); protein nitrogen, 2.02% (—); crude fibre, 10.54% (13.53%); ash, 7.70% (6.73%). The general results resemble those obtained with *Knautia* (cf. this vol., i, 816). The plant is used in Russia for adulterating tea. The ether extract contained an amorphous white substance, m. p.  $256$ — $260^{\circ}$  (decomp.),  $[\alpha] +72.75^{\circ}$  in alcohol, which forms an *iodine additive* product, m. p.  $118$ — $120^{\circ}$ , and an *acetyl* derivative, m. p.  $178$ — $180^{\circ}$ ; it is probably a resin alcohol. The alcoholic plant extract contained small amounts of choline and invert-sugar.  
F. A. M.

**Tissue Fluids of Egyptian and Upland Cottons and their  $F_1$  Hybrid.** J. A. HARRIS, Z. W. LAWRENCE, W. F. HOFFMAN, J. V. LAWRENCE, and A. T. VALENTINE (*J. Agric. Res.*, 1924, **27**, 267—328).—The osmotic concentration of the leaf-tissue fluid, as measured by the freezing-point depression, is slightly but definitely greater in Egyptian than in Upland cottons. The electrical conductivity and acidity are also greater in the Egyptian cotton; the average  $p_H$  values varies from 5.26 to 5.40. The osmotic concentration and electrical conductivity are lower in the hybrid than in either of the parents, but the hydrogen-ion concentration falls between those of the parents. As the season advances, the concentrations of total solutes, ionised solutes, and hydrogen ions decrease whilst the differences between the various types of cotton become more marked. Soil conditions and atmospheric conditions during the period of sampling exert a marked influence on the values; the concentration of total solutes is most affected by these environmental factors.  
E. M. C.

**Histological and Chemical Examination of the Seeds of *Ipomœa hederacea*, Jacquin, and of other Species of *Ipomœa*.** H. C. KASSNER (*Pharm. J.*, 1924, **112**, 328—331, 357—359).—The seeds of *Ipomœa hederacea*, Jacq., *I. muricata*, Jacq., *I. pes-tigridis*, L.,

*I. coccinea*, L., *I. pilosa*, Sw., and *I. eriocarpa*, R. Br., all contain a crude resin and a fatty oil as principal constituents. The physical and chemical properties of both these constituents of the different species are given and show that the resins and oils obtained from them were very similar to one another. The seeds of *I. muricata* gave a larger percentage of ether extract after extraction with petroleum spirit, but a smaller quantity of crude resin in the subsequent extraction with alcohol than did those of *I. hederacea*. The seeds of *I. hederacea* contained a larger percentage of the medicinally active resin than those of any of the other species. About 2% of a true resin was isolated from the seeds of *I. hederacea* free from glucosidal matter. The crude resin comprises a mixture of this true resin with a large quantity of glucosidal matter and with a saponin-like substance. Neither the true resin nor the crude resin is identical with convolvulin, the ether-insoluble resin of jalap. The true resin and the crude resin of Kaladana (*I. hederacea*) differ from the jalap and scammony resins in that they are insoluble in ether and give an immediate turbidity on acidifying a boiled alkaline ethereal solution. True Kaladana resin is not precipitated as readily or completely as certain other convolvulaceous resins when its alcoholic solution is poured into water. The true, glucoside-free resin of Kaladana possesses medicinal properties similar to those of jalap resin. The crude resin does not, however, form a wholly satisfactory substitute for jalap resin owing to the presence of a large amount of glucosidal matter which acts as a hygroscopic diluent. The percentage of fatty oils and crude resins in the various species of seeds was 9.23—14.94% and 9.20—15.98%, respectively. *I. coccinea* gave the greatest yield of oil and *I. hederacea* the greatest yield of resin. The monographs on Kaladana in the B.P., 1914, and B.P. Codex, 1923, are inaccurate and need revision.

H. C. R.

**Chemical Factors determining the Quality of Tobacco.** V. GRAHAM and R. H. CARR (*J. Amer. Chem. Soc.*, 1924, 46, 695—702).—There is a relation between the grades of tobacco and their relative solubilities; a high quality cigar tobacco, for instance, has a lower percentage of extractives and nicotine than has a poorer grade. The irritant effect produced by inferior tobaccos is due to the presence of waxes, volatile oils, and loosely combined nicotine, and it is suggested that the quality could be improved by a preliminary extraction with light petroleum. The quality of the tobacco is not so much altered by the use of fertilisers as by changes in the nature of the soil and climatic conditions; of the fertilisers employed superphosphate was found to have the most marked effect in improving the quality. Plants grown on soil containing much lime contained a considerable amount of nicotine-calcium compounds. The best qualities of tobacco are grown on relatively poor sandy and clay soils unsuited for cereals.

C. J. S.

**Comparative Plant Chemistry. VII. *Knautia silvatica*.** J. ZELLNER (*Monatsh.*, 1924, 44, 247—251).—The leaves and

flowers were examined separately and had the following contents (figures for petals in brackets): soluble in light petroleum, 3.21% (2.18%); in ether, 2.13% (3.59%); in alcohol, 25.77% (30.14%); total water-soluble, 40.99% (39.43%); water-soluble mineral matter, 8.27% (6.10%); phlobaphen, 4.68% (6.18%); - tannin, 7.80% (6.85%); free acid (as KOH), 2.51% (2.50%); reducing sugars, 4.43% (5.38%); soluble carbohydrates, 4.03% (2.23%); crude fibre, 14.19% (17.37%); pentosans, 7.68% (10.49%); methylpentosans, 1.02% (1.37%); total nitrogen, 1.96% (2.69%); total ash, 13.42% (8.56%). The tannin yielded protocatechuic acid on fusion with potassium hydroxide; invert-sugar and choline were also present in the alcohol extracts from the leaves. The colloidal carbohydrate contained in the aqueous extract yielded mucic acid and furfuraldehyde as degradation products, and is therefore regarded as a galactopentosan. Attention is directed to the similarity in chemical composition of the leaves and petals.

F. A. M.

**Chemistry of Heterotropic Phanerogams. IV.** J. EINLEGER, J. FISCHER, and J. ZELLNER (*Monatsh.*, 1924, **44**, 277—295).—Mistletoe (*Viscum album*, L.) gave the following results per 100 parts of dried substance (figures for leaves and young stems are given first and figures for berries in brackets): soluble in light petroleum, 5.13% (5.12%); ether-soluble, 3.26% (2.59%); alcohol extract, —, (41.59%); total water-soluble matter, 37.52% (68.08%); water-soluble mineral matter, 7.79% (5.28%); free acids (as KOH), —, (1.19%); reducing sugars, 0.62% (1.33%); pectins 2.05%; soluble polysaccharides, —, (22.4%); tannin, nil (nil); total nitrogen, 2.30% (2.05%); crude fibre, 20.43% (10.85%); ash, 10.40% (5.51%); soluble pentosans, —, (6.58%); insoluble pentosans, —, (3.47%); methylpentosans, —, (0.89%). A new resin alcohol, *visciresinol*,  $C_{15}H_{26}O_2$ , decomp. 274—276°, was isolated from the leaves and stem; it adds on bromine and iodine in acetic acid and can be acetylated; choline was present but phlobaphens were absent. The berries contained a viscous product which after hydrolysis gave a substance decomposing above 280° (*acetyl* derivative, m. p. 250°), possibly identical with visciresinol; a crystalline *wax-alcohol*, m. p. 71°, was also isolated, and an amorphous resin identical with Reinsch's viscine (cf. *Chem. Zentr.*, 1861, 148).

*Loranthus europæus* gave the following analysis per 100 parts of dried berries: soluble in light petroleum, 11.38%; ether-soluble, nil; total water-soluble matter, 48.84%; water-soluble mineral matter, 4.28%; free acids (as KOH), 1.44%; reducing sugars, 20.00%; water-soluble polysaccharides, 5.09%; total nitrogen, 2.57%; crude fibre, 15.83%; total ash, 4.60%. The fatty portions of the leaf extracts yielded *loranthyl alcohol*,  $C_{24}H_{50}O$ , m. p. 71—72° (*acetyl* derivative, m. p. 57—58°, *benzoyl* derivative, m. p. 56—57°). A saturated *hydrocarbon*,  $C_{30}H_{62}$ , was also isolated, m. p. 65°; carotin and phlobaphens were present. Notable amounts of tannin were present which yielded proto-



catechuic acid on alkali fusion. The berries after extraction and hydrolysis yielded cetyl alcohol; an amorphous *resin*,  $(C_{10}H_{18}O)_x$ , was also obtained, m. p. 65–66°,  $[\alpha] +14.5^\circ$ , giving an *acetyl* derivative, m. p. 70–72°. A comparison of the stems of the parasites and their hosts confirmed the results previously found in other cases (cf. Zellner, A., 1920, i, 131) that the parasites had a higher water-content and contained more free acids and soluble nitrogenous compounds than the host, but considerably less reducing sugars. F. A. M.

**Microbiological Analysis of Soil as an Index of Soil Fertility.**

**VII. Carbon Dioxide Evolution.** S. A. WAKSMAN and R. L. STARKEY (*Soil Sci.*, 1924, 17, 141–161).—Methods are described for the measurement of carbon dioxide production in soil. The rate at which soils produce carbon dioxide is suggested as a basis on which soils may be classified, both as to fertility and to number of micro-organisms present. For normal soils, carbon dioxide production was greatest where the percentage of organic matter was high, although no direct proportionality was observed. The rate of evolution of carbon dioxide from acid soils was increased by liming, and in these cases nitrification was increased to an even greater extent. A. G. P.

**Oxidation of Ammonia and Nitrites by Micro-organisms under Different Conditions.** R. N. GAWDA (*Soil Sci.*, 1924, 17, 57–63).—Marked increases in the rates of oxidation of sodium nitrite and ammonium sulphate in culture solutions of nitrifying organisms were observed when an air current was drawn through the liquid. This rate was further considerably increased by allowing the solution to drip through a column of broken limestone on the surface of which a culture of the organisms was established and through which an air current was passed. Nitrite-bacteria were most active in media with  $p_H$  8.0 and nitrate-forming organisms with  $p_H$  8.5–8.8. Magnesium carbonate used as a base during ammonia oxidation proved devoid of toxic effects. A. G. P.

**Sulphur Oxidation in Oregon Soils.** W. V. HALVERSEN and W. B. BOLLEN (*Soil Sci.*, 1923, 16, 479–490).—Attempts to correlate factors concerned in the use of sulphur as a fertiliser are described. An approximate proportionality was found between the sulphur-oxidising power of soils and their sulphate contents. The total sulphur content of soils bore no apparent relationship to either the sulphur-oxidising power or the sulphate content. The rate of sulphur-oxidation can be increased by a previous treatment with sulphur and by the use of inoculated sulphur. Oxidation was favoured by aëration and temperature increases. In heavy soils with high buffer capacities, sulphur oxidation was considerably slower than in light sandy soils having small buffer capacity. The sulphur-oxidising power of a soil was in no way connected with its hydrogen-ion concentration. A. G. P.

**Biochemical Conditions of a Soil treated with Different Organic Manures.** E. HASELHOFF and O. LIEHR (*Landw. Versuchs.-Stat.*, 1924, 102, 43—59). **Carbon Dioxide Content of the Soil Atmosphere.** E. HASELHOFF and O. LIEHR (*ibid.*, 60—72). **Nitrogen Economy of Arable Soil.** E. HASELHOFF (*ibid.*, 73—89). **Ammonia and Nitric Acid Content of the Soil.** E. HASELHOFF and F. HAUN (*ibid.*, 90—103). **Effect of Fallow, Dung, and Green Manures in Conjunction with Mineral Manures.** E. HASELHOFF (*ibid.*, 104—121).—This series of papers contains a detailed discussion of an investigation of the soil from a large number of plots, over a period of 10 years, on which a rotation of wheat, potatoes, rye, and oats followed green manuring with serradella, peas, and clover. Other plots received dung or were fallowed. The whole rotation was repeated twice. Determinations are recorded of bacterial numbers, and ammonifying, nitrifying, and nitrogen-fixing powers of soil samples; the carbon dioxide content of the soil atmosphere at depths of 25 and 50 cm.; the total nitrogen recovered in the crops; the ammonia and nitric acid of the soil, as determined colorimetrically in aqueous extracts; and the crop yields with green manures and ammonium sulphate. Reference should be made to the original papers, since the results do not allow any definite conclusions to be given briefly.

E. M. C.

**Moisture Relationships in an Ideal Soil.** B. A. KEEN (*J. Agric. Sci.*, 1924, 14, 170—177).—The views of a number of soil physicists are discussed in a theoretical paper, on the basis of the mathematical relationships of soil and water in an ideal soil.

A. G. P.

**Imbibitional Soil Moisture.** E. A. FISHER (*J. Agric. Sci.*, 1924, 14, 204—220).—In continuation of former papers (see *Ann. Repts.*, 1923, 20, 202), the nature of imbibitional or “gel” water is discussed, particularly in respect of its effect on the movement of water in soils. The imbibitional process may be due to the attainment of a Donnan equilibrium within the “swollen” colloidal particles of the soil. The possible effects of imbibition on the movement of soil-water are discussed mathematically. A. G. P.

**Measurement of Hydrogen-ion Concentration in Soil by means of the Quinhydrone Electrode.** E. BILLMANN (*J. Agric. Sci.*, 1924, 14, 232—239).—Apparatus is described for the determination of hydrogen-ion concentrations of soil-water suspensions by means of an electrode vessel containing quinhydrone as the source of hydrogen. Rapid equilibrium is attained, and the results are in close agreement with those yielded by the colorimetric method and the standard hydrogen electrode. A. G. P.

**Electrical Conductivity of Extracts from Soils of Various Types and its Use in Detecting Infertility.** W. R. G. ATKINS (*J. Agric. Sci.*, 1924, 14, 198—203).—The electrical conductivity of

aqueous soil extracts increased with the period of extraction in the case of rich soils, but reached its maximum quickly in the case of infertile soils and peats. High conductivity does not necessarily indicate a good soil, but a rapid increase with extended extraction period appears to be characteristic of fertility. A. G. P.

**Modifications in Soil Dried in the Air.** A. LEBEDIANTZEV (*Compt. rend.*, 1924, 178, 960—963).—The proportions of organic matter, total nitrogen, and ammoniacal nitrogen extractable from soil by water and acid solutions are greatly increased by preliminary drying of the soil in the air. At the same time, the extractable phosphoric acid increases appreciably and the extractable mineral matter slightly, whilst the bacteria present undergo considerable diminution. These effects are due, not to the action of oxygen or light, but to the loss of water and to the rise of temperature caused by the sun's rays. T. H. P.

**Determination of Carbonic Acid present as Carbonate in Soils.** P. B. SANYOL (*Agric. Res. Inst. Pusa, Bull.* No. 151).—Carbonates in the soil are decomposed by treatment with cold hydrochloric acid in a vessel containing a stirrer. When no more gas is evolved the carbon dioxide dissolved in the liquid is completely driven out by the generation of hydrogen from aluminium foil. The rate of hydrogen generation is regulated by the addition of a copper sulphate solution. A. G. P.

**Calcium Content of Soil in Relation to Absolute Reaction.** C. O. SWANSON, P. L. GAINES, and W. L. LATSHAW (*Soil Sci.*, 1924, 17, 181—191).—Analyses of a large number of soils indicate that in similar types of soil a close relationship exists between the  $p_H$  value of the soil and the amount of calcium present in a form soluble in cold *N*-hydrochloric acid solution. A. G. P.

**Adsorption and Absorption of Bases by Soils.** C. P. JONES (*Soil Sci.*, 1924, 17, 255—273).—Experiments are described in support of the view that the adsorption of bases by soil colloids is but a preliminary or accessory factor to the absorption of bases, which is a chemical reaction between the soil constituents and added substances. The latter phenomenon is considered of the greater importance and is governed by the chemical nature of the reactive soil constituents and by those factors limiting the extent of the hydrolysis of the reacting substance. The absorption of basic ions is greater as the degree of ionisation decreases. The absorption of the base of sparingly soluble substances is dependent on their fineness of division. A. G. P.

## Organic Chemistry.

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**Refractive Indices of Hexanes and Hexenes.** H. VAN RISSEGHEM (*Bull. Soc. chim. Belg.*, 1924, **33**, 115—119; cf. A., 1922, i, 313).—The following corrected values are given.  $\beta\beta$ -Dimethylbutane,  $n_D^{15}$  1.3716,  $n_{H\beta}^{15}$  1.3762,  $n_{H\gamma}^{15}$  1.3801; isohexane,  $n_{H\alpha}^{15}$  1.3725,  $n_{H\beta}^{15}$  1.3792,  $n_{H\gamma}^{15}$  1.3829;  $\gamma$ -methylpentane,  $n_D^{15}$  1.3793,  $n_{H\beta}^{15}$  1.3841,  $n_{H\gamma}^{15}$  1.3878;  $\beta\gamma$ -dimethylbutane,  $n_{H\beta}^{15}$  1.3855,  $n_{H\gamma}^{15}$  1.38935.  
H. J. E.

**Photochlorination of Aliphatic Compounds in Carbon Tetrachloride.** A. BENRATH and E. HERTEL (*Z. wiss. Phot.*, 1924, **23**, 30—40).—The amount of chlorine dissolved in technical or in pure carbon tetrachloride (Kahlbaum) continuously diminishes when the solution is subjected to the action of light. If, however, the carbon tetrachloride has been previously subjected at its boiling point to the prolonged action of chlorine and then purified by treatment with nitric acid followed by sodium carbonate and chlorine again dissolved in it, the chlorine titre no longer diminishes but increases when the solution is subjected to light. Perfectly purified and dried carbon tetrachloride was shown to contain free chlorine after several days' exposure to light. The amount of decomposition is not sufficiently great to hinder the use of carbon tetrachloride as a medium in which to study the photochlorination of various aliphatic compounds. The chlorine solutions employed contained about 0.05 g. of chlorine in 10 g. of solution. In some of the compounds investigated, one atom of hydrogen was displaced, in others two. The reaction was generally preceded by an induction period. The amount of chlorination, in some cases, was proportional to the time and in others to the logarithm of the time. If two atoms of hydrogen are displaced, the reaction takes place in distinct steps. The second displacement frequently takes place with a rapidity much greater than that at the end of the first, and is preceded by a new induction period. Chloroform, after an induction period of about 30 mins., absorbs about 70% of the chlorine required for its conversion into carbon tetrachloride. The reaction is not reversible. Tetrachloroethane was not attacked by chlorine in 3 hours. Acetic acid was converted into monochloroacetic acid with very little tendency for the reaction to proceed further. Acetyl chloride and isobutyric acid behave similarly to acetic acid. With propionic acid and ethyl malonate the reaction commenced slowly and then continued at a rate proportional to the time until one atom of hydrogen was displaced. The second atom reacted at a much slower rate and in accordance with the logarithmic law. Two atoms of hydrogen were displaced in the case of *n*-butyric acid, both at the logarithmic rate, the two steps of the reaction being markedly

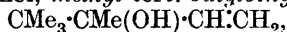
distinct. The chlorination of ethyl ether proceeded linearly during the displacement of one atom, then, after a slowing up, a second atom was displaced at the logarithmic rate. The induction period was long in the case of acetic anhydride and the reaction was in two phases, but the rate was neither linear nor according to the logarithmic law. A. C.

**tert.-Butyl Alcohol.** R. R. READ and F. PRISLEY (*J. Amer. Chem. Soc.*, 1924, **46**, 1512—1515).—The vapour of isobutyl alcohol is passed over pumice coated with aluminium oxide, contained in an iron tube, at 500—520°, and the isobutylene formed is freed from water and unchanged alcohol, and hydrated to tert.-butyl alcohol by absorption in 50% sulphuric acid, either directly or from its solution in kerosene. The yield is improved by using a glass catalyst tube at 450—475°. The use of phosphoric acid on coke as the dehydrating catalyst (cf. King, T., 1919, **115**, 1404), even at 210—230°, led to the loss of half the total hydrocarbon by polymerisation. F. G. W.

**Preparation of Dialkylethinyl Carbinols.** R. LOCQUIN and S. WOUSENG (*Bull. Soc. chim.*, 1924, [iv], **35**, 597—604; cf. A., 1922, i, 617).—The sodium derivatives of ketones may be obtained with a minimum of condensation by reactions by adding finely-powdered sodamide gradually to a mixture of the ketone (1 part) and dry ether (4—5 parts) kept thoroughly agitated and cooled for several hours, the ammonia being removed under reduced pressure.  $\gamma$ -Ethyl- $\Delta^{\alpha}$ -pentinene- $\gamma$ -ol,  $\text{OH}\cdot\text{C}(\text{Et})_2\cdot\text{C}:\text{CH}$ , obtained from sodium diethyl ketone and acetylene by the method previously described, forms an *allophanate*,  $\text{Et}_2\text{C}(\text{C}:\text{CH})\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , fine needles, m. p. 130—131°.  $\gamma\zeta$ -Diethyl- $\Delta^{\delta}$ -octinene- $\gamma\zeta$ -diol,  $\text{OH}\cdot\text{C}(\text{Et})_2\cdot\text{C}:\text{C}(\text{Et})_2\cdot\text{OH}$ , m. p. 76°, b. p. 132—135°/14 mm., is formed in small quantity along with the ethinylcarbinol. On distillation with a little solid potassium hydroxide, it is decomposed quantitatively into acetylene and diethyl ketone.  $\alpha$ -cycloHexyl- $\Delta^{\alpha}$ -propinene- $\gamma$ -ol has m. p. 22°, b. p. 73—75°/15 mm.; *allophanate*, m. p. 197°.  $\zeta$ -Methyl- $\gamma$ -isobutyl- $\Delta^{\alpha}$ -heptinene- $\gamma\delta$ -diol,  $\text{C}_4\text{H}_9\cdot\text{CH}(\text{OH})\cdot\text{C}(\text{OH})(\text{C}_4\text{H}_9)\cdot\text{C}:\text{CH}$ , has m. p. 101—102°.  $\alpha$ -Phenyl- $\gamma$ -propyl- $\Delta^{\alpha}$ -hexinene- $\gamma$ -ol,  $\text{PhC}:\text{C}\cdot\text{CPr}_2\cdot\text{OH}$ , b. p. 153—158°/10 mm., is obtained by the action of phenylacetylene on the sodium derivative of dipropyl ketone. F. G. W.

**Methylpropylethinylcarbinol [ $\gamma$ -Methyl- $\Delta^{\alpha}$ -hexinene- $\gamma$ -ol] and its Derivatives.** R. LOCQUIN and S. WOUSENG (*Bull. Soc. chim.*, 1924, [iv], **35**, 604—606).— $\gamma$ -Methyl- $\Delta^{\alpha}$ -hexinene- $\gamma$ -ol,  $\text{OH}\cdot\text{CMePr}\cdot\text{C}:\text{CH}$ , obtained by the action of acetylene on sodium methyl *n*-propyl ketone, has b. p. 137°; *allophanate*, m. p. 133°.  $\delta\eta$ -Dimethyl- $\Delta^{\alpha}$ -decinene- $\delta\eta$ -diol,  $\text{OH}\cdot\text{CMePr}\cdot\text{C}:\text{C}\cdot\text{CMePr}\cdot\text{OH}$ , m. p. 60°, b. p. 130—135°/10 mm., is formed in small quantity along with the carbinol. The latter substance combines with water in presence of acid mercuric sulphate with formation of  $\gamma$ -methyl-hexan- $\gamma$ -ol- $\beta$ -one, b. p. 166—168° (*semicarbazone*, m. p. 163—164°). F. G. W.

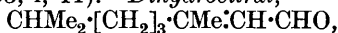
**Action of Acetylene on Sodium Compounds of Ketones. Isomeric Transformation of Dialkylvinylcarbinols into  $\beta\beta$ -Dialkylallyl Alcohols.** S. WOUSENG (*Ann. Chim.*, 1924, [x], 1, 343—416).—The sodium compound of a ketone, obtained by using sodamide, reacts in ethereal suspension with acetylene under a water-pressure of 500—600 cm. to yield an acetylenic alcohol (cf. Locquin and Wouseng, A., 1922, i, 617, 710; 1923, i, 302). Pinacolin thus affords *methyl-tert.-butylethinylcarbinol* [ $\gamma\delta\delta$ -trimethyl-pentinene- $\gamma$ -ol],  $\text{CMe}_3\cdot\text{CMe}(\text{OH})\cdot\text{C}:\text{CH}$ , an oil with a mint-like odour, b. p.  $144^\circ$ ,  $d_4^{20}$  0.8806,  $n_D^{20}$  1.4441; this forms a crystalline hydrate of low m. p., an *allophanate* (cf. Behal, A., 1919, ii, 301), needles, m. p.  $156^\circ$  (after drying at  $110^\circ$ ), and an *acetate*, b. p.  $156$ — $159^\circ$ . Two, or three, by-products, all presumably stereoisomeric forms of the *glycol*,  $\text{CMe}_3\cdot\text{CMe}(\text{OH})\cdot\text{C}:\text{C}\cdot\text{CMe}(\text{OH})\cdot\text{CMe}_3$  (cf. Dupont, A., 1914, i, 134), are also formed, the viscous oily mixture of b. p.  $148$ — $150^\circ/14$  mm. being separable into scales, m. p.  $88$ — $89^\circ$ , rhomboidal tablets, m. p.  $78^\circ$ , and another substance (?), m. p.  $67$ — $68^\circ$ . The saturated alcohol, *methylethyl-tert.-butylcarbinol*, obtained from the acetylenic compound by treatment with hydrogen in presence of platinum black, or directly from pinacolin and magnesium ethyl iodide, has b. p.  $152^\circ$ , and yields an *allophanate*, m. p.  $134$ — $135^\circ$ . Partial hydrogenation of the acetylenic compound to the ethylenic alcohol, *methyl-tert.-butylvinylcarbinol*,



b. p.  $144$ — $146^\circ$ ,  $d_4^{20}$  0.8576,  $n_D^{20}$  1.4452, which also possesses a strong mint-like odour, was best effected by the action of hydrogen in presence of reduced nickel (in methyl-alcoholic solution). This substance also forms a *hydrate* of low m. p. and gives an *allophanate*, needles, m. p.  $167$ — $168^\circ$  (decomp.). When treated with acetic anhydride at  $140^\circ$ , or boiling glacial acetic acid, it undergoes a molecular transformation analogous to that of linalool into geraniol and nerol (Forster and Cardwell, T., 1913, 103, 1338 etc.), thus demonstrating (cf. also the results described below) that this change is a general one for tertiary vinylcarbinols. The primary alcohol so obtained,  $\gamma\delta\delta$ -trimethyl- $\Delta^{\beta}$ -pentinol, separated as the hydrogen phthalate (cf. Stephan, A., 1899, i, 68), has b. p.  $84^\circ/12$  mm., and yields an *allophanate*, m. p.  $180$ — $181^\circ$ . When it is oxidised by a chromic-sulphuric acid mixture, or by atmospheric oxygen and metallic silver, it is converted into  $\beta\gamma\gamma$ -trimethyl- $\Delta^{\alpha}$ -pentaldehyde, b. p.  $75$ — $78^\circ/15$  mm., the *semicarbazone* of which has m. p.  $204$ — $205^\circ$ . This aldehyde is also obtained by direct oxidation of the above ethylenic alcohol,  $\gamma\delta\delta$ -trimethyl- $\Delta^{\beta}$ -pentinol, by chromic-sulphuric acid, in a manner exactly analogous to the formation of geraniol and citral from linalool. Further oxidation affords the *acid*,  $\text{CMe}_3\cdot\text{CMe}:\text{CH}\cdot\text{CO}_2\text{H}$ , m. p.  $85$ — $86^\circ$ , which when treated with warm 80% sulphuric acid is converted into the *lactone* of  $\gamma\gamma$ -dimethyl- $\beta$ -hydroxymethylvaleric acid (cf. Petshnikoff, A., 1902, i, 338), which is also obtained when *ethyl  $\gamma\gamma$ -dimethylvalerate*, b. p.  $96$ — $99^\circ/10$  mm., prepared from pinacolin and ethyl bromoacetate, is heated with formic acid, no dehydration to the corresponding derivative of acrylic acid taking place in this case.

Dipropyl ketone, treated with sodamide and acetylene, yields  $\gamma$ -propyl- $\Delta^a$ -hexinen- $\gamma$ -ol,  $\text{CPr}^a_2(\text{OH})\cdot\text{C}\equiv\text{CH}$ , b. p. 69—71°/12 mm.,  $d^{20}_4$  0.8691,  $n^{20}_D$  1.4443, the acetyl derivative of which has b. p. 82—83°/10 mm., and the allophanate, m. p. 143°. As a by-product, the glycol,  $\text{CPr}_2\cdot\text{C}(\text{OH})\cdot\text{C}\equiv\text{C}\cdot\text{C}(\text{OH})\cdot\text{CPr}_2$  (Dupont, *loc. cit.*), is formed. By reduction as described above, ethyldipropylcarbinol (Tschebotarev and Saytzev, A., 1886, 437) is formed, whilst partial reduction affords dipropylvinylcarbinol, b. p. 75—76°/12 mm., the allophanate of which has m. p. 102—103°. When this ethylenic tertiary alcohol is boiled with acetic acid and the product saponified, the primary isomeride is obtained, exactly as described above; purified through its hydrogen phthalate,  $\gamma\gamma$ -dipropylallyl alcohol has b. p. 99—101°/12 mm., and gives an allophanate, m. p. 147—148°. When reduced with hydrogen and platinum black, it yields  $\gamma$ -propylhexyl alcohol, b. p. 107—108°, which yields an allophanate, needles, m. p. 133—134°, and a pyruvic ester, b. p. 140—145°/20 mm., the semicarbazone of which has m. p. 116—117°. This saturated alcohol is identical in all respects with that obtained by condensing butyrene with ethyl bromoacetate (by the Grignard reaction), dehydrating the product, ethyl  $\beta$ -hydroxy- $\beta$ -propylhexoate, b. p. 160—165°/85 mm., by heating with formic acid and reducing the resulting ethyl  $\beta$ -propyl- $\Delta^a$ -hexenoate, b. p. 122—128°/30 mm., with sodium and alcohol.  $\beta$ -Propyl- $\Delta^a$ -hexenaldehyde is obtained by regulated oxidation either of  $\gamma$ -propylhexenol, or of the parent dipropylvinylcarbinol; it has b. p. 75—76°/12 mm., and gives a semicarbazone, m. p. 171—173°.

$\zeta$ -Methyl- $\beta$ -heptanone (Bouveault and Locquin, A., 1905, i, 18) yields  $\gamma\eta$ -dimethyloctinene- $\gamma$ -ol,  $\text{CHMe}_2\cdot[\text{CH}_2]_3\cdot\text{CMe}(\text{OH})\cdot\text{C}\equiv\text{CH}$ , which has b. p. 187—188°, or 83—85°/10 mm.; this gives an allophanate, needles, m. p. 114—115°. Stereoisomeric glycols are produced as by-products and are isolated first as an oil of b. p. 183—184°/12 mm., from which crystals of m. p. 66—68° may be separated, and the second component forms the main proportion of a pasty mass melting at about 35°.  $\beta\zeta$ -Dimethyloctan- $\zeta$ -ol, identical with Barbier and Locquin's preparation (A., 1914, i, 833), is obtained by reduction of the acetylenic derivative, whilst regulated reduction produces methylisohexylvinylcarbinol, b. p. 89—91°/15 mm., which, like its analogues, is readily converted by treatment with hot acetic acid, and subsequent purification through the hydrogen phthalate, into  $\gamma\eta$ -dimethyl- $\Delta^b$ -octen- $\alpha$ -ol,  $\text{CHMe}_2\cdot[\text{CH}_2]_3\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ , b. p. 110°/12 mm. When this is reduced, a tetrahydrogeraniol is formed, the allophanate of which has m. p. 117°, the pyruvate, b. p. 140—145°/12 mm., and the semicarbazone of the latter, m. p. 118°. This tetrahydrogeraniol was identical with the product obtained via ethyl  $\beta$ -hydroxy- $\beta\zeta$ -dimethyloctoate (cf. Bouveault and Blanc, A., 1905, i, 11). Dihydrocitril,



obtained by oxidising either the vinylcarbinol or its primary isomeride, yields a semicarbazone, m. p. 164°. The above results show that no conclusion can be drawn from the results of a chromic-sulphuric acid oxidation as to the presence of a primary alcoholic

grouping; catalytic oxidation, on the other hand, gives trustworthy results. The author discusses the mechanism of these isomeric transformations and describes experiments which indicate that Tiemann's explanation (A., 1894, i, 83) is unsatisfactory. W. A. S.

**Constitution of Farnesol. Synthesis of Dihydrofarnesol, a new Aliphatic Sesquiterpene Alcohol.** A. VERLEY (*Bull. Soc. chim.*, 1924, [iv], 35, 606—608).—Farnesol, obtained by the oxidation of farnesol with chromic acid, yields, on boiling with 10% potassium carbonate solution, acetaldehyde and dihydro- $\psi$ -ionone, and on reducing the glycidic ester of this compound or that of  $\psi$ -ionone with sodium and amyl alcohol, *dihydrofarnesol*,

$\text{CH}_2\cdot\text{CMe}\cdot[\text{CH}_2]_3\cdot\text{CMe}\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ ,  
is obtained as an oily, amber liquid with an odour of cedar wood.  
F. G. W.

**Stereoisomerism among Trisubstituted  $\alpha\beta$ -Glycols and the Production of Stereoisomerides by inverting the Order of Introduction of the Substituent Radicals.** M. TIFFENEAU and J. LEVY (*Compt. rend.*, 1924, 178, 1724—1726).—The products obtained by treating ketols of the general formula  $\text{CHPh}(\text{OH})\cdot\text{CO}\cdot\text{R}$  with magnesium alkyl bromides,  $\text{MgR}'\text{Br}$ , are different from those formed when  $\text{MgRBr}$  acts on  $\text{CHPh}(\text{OH})\cdot\text{CO}\cdot\text{R}'$ . The former (R being smaller than R') are provisionally termed  $\alpha$ , the latter  $\beta$ . The  $\alpha$ -variety of  $\alpha\beta$ -dihydroxy- $\alpha$ -phenyl- $\beta$ -methylbutane has m. p.  $85^\circ$ ; the  $\beta$ -variety, m. p.  $73^\circ$ . Similarly, the  $\alpha$ - and  $\beta$ -forms of  $\alpha\beta$ -dihydroxy- $\alpha$ -phenyl- $\beta$ -ethylhexane have m. p.  $88^\circ$  and  $81^\circ$ , and the  $\alpha$ - and  $\beta$ -ethylhydrobenzoin have m. p.  $105^\circ$  and  $117^\circ$  respectively. The isomeric forms of these substances yield the same product when dehydrated with concentrated sulphuric acid. W. A. S.

**Replacement of Acid Radicals in Glycerides.** K. H. BAUER (*Ber.*, 1924, 57, [B], 897—899).—The action of *m*-nitrobenzoyl chloride on glyceryl  $\alpha$ -benzoate dissolved in cold chloroform and quinoline (cf. Fischer, A., 1920, i, 808) leads to the production of *glyceryl tri-m-nitrobenzoate*, m. p.  $160$ — $161^\circ$  after softening at  $158^\circ$ , in yield which varies with the experimental conditions. H. W.

**Preparation of Ethers from Secondary Alcohols by Dehydration with a Sulphonic Acid.** R. VERNIMMEN (*Bull. Soc. chim. Belg.*, 1924, 33, 96—101).—The preparation is easily effected in presence of *p*-toluenesulphonic acid; a high temperature and too great an excess of catalyst should be avoided in order to obviate the formation of ethylenic hydrocarbons. In the aliphatic series, dehydration is more difficult, as the alcohols must be heated nearly to boiling point. The following are described: Di- $\beta$ -*n*-hexyl ether (cf. Wanklyn and Erlenmeyer, T., 1863, 221), b. p.  $200^\circ/760$  mm.,  $d_{20}^{20}$  0.7889,  $n_D^{20}$  1.4152; di- $\beta$ -*n*-amyl ether, b. p.  $160$ — $163^\circ/760$  mm.,  $d_{20}^{20}$  0.7830,  $n_D^{20}$  1.4078; di( $\alpha$ -phenyl- $\alpha$ -propyl) ether, b. p.  $164^\circ/14$  mm.,  $d_{20}^{20}$  1.0043,  $n_D^{20}$  1.5420 (cf. Oddo and Rosso, A., 1911, i, 443); di( $\alpha$ -phenyl- $\alpha$ -*n*-butyl) ether, b. p.  $178$ — $179^\circ/13$  mm.,



$d_{20}^{20}$  0.9769,  $n_D^{20}$  1.5275 (cf. Oddo, *loc. cit.*); di( $\alpha$ -phenyl- $\alpha$ -n-amy) ether, b. p. 199°/14 mm.,  $d_{20}^{20}$  0.9574,  $n_D^{20}$  1.5175. H. J. E.

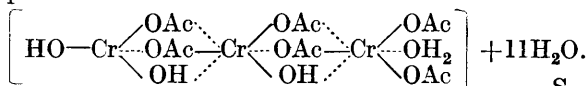
**Derivatives of  $\gamma$ -Chloro- $n$ -propyl Alkyl Ethers.** W. DULIÈRE (*Bull. Soc. chim.*, 1924, [iv], 35, 584—590).— $\alpha\gamma$ -Dichloropropyl alkyl ethers (this vol., i, 258) react vigorously with magnesium organohalides with formation of  $\alpha$ -substituted  $\gamma$ -chloropropyl alkyl ethers. Of the following compounds described, which are all colourless, strong-smelling oils, the aromatic derivatives are viscous and distil badly under reduced pressure. They are all stable to dilute sodium hydroxide and only slowly attacked by silver nitrate, the mobility of the chlorine atom increasing with increasing molecular weight.  $\gamma$ -Chloro- $\alpha$ -phenyl- $n$ -propyl methyl ether,  $\text{Me}\cdot\text{O}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , b. p. 110°/12 mm.,  $d_{20}^{20}$  1.097,  $n_D^{20}$  1.52219;  $\gamma$ -chloro- $\alpha$ -phenyl- $n$ -propyl ethyl ether, b. p. 120°/11 mm.,  $d_{20}^{20}$  1.066,  $n_D^{20}$  1.51502;  $\gamma$ -chloro- $\alpha$ -phenyl- $n$ -propyl  $n$ -propyl ether, b. p. 130°/12 mm.,  $d_{20}^{20}$  1.044,  $n_D^{20}$  1.50492;  $\gamma$ -chloro- $\alpha$ -phenyl- $n$ -propyl isobutyl ether, b. p. 137°/11 mm.,  $d_{20}^{20}$  1.024,  $n_D^{20}$  1.50118;  $\gamma$ -chloro- $\alpha$ -phenyl- $n$ -propyl isoamyl ether, b. p. 145°/13 mm.,  $d_{20}^{20}$  1.019,  $n_D^{20}$  1.50212; methyl  $\gamma$ -chloro- $\alpha$ -methyl- $n$ -propyl ether, b. p. 35°/10 mm.; methyl  $\gamma$ -chloro- $\alpha$ -ethyl- $n$ -propyl ether, b. p. 40°/10 mm., 147°/atmospheric pressure,  $d_{22}^{22}$  0.964,  $n_D^{22}$  1.42501; ethyl  $\gamma$ -chloro- $\alpha$ -methyl- $n$ -propyl ether, b. p. similar,  $d_{22}^{22}$  0.971,  $n_D^{22}$  1.42751; methyl  $\gamma$ -chloro- $\alpha$ -isopropyl- $n$ -propyl ether, b. p. 47°/11 mm.,  $d_{20}^{20}$  0.951,  $n_D^{20}$  1.43096.  $\alpha$ -Benzyl- $n$ -propyl methyl ether, fine white needles, odour of aniseed, m. p. 34°, b. p. 130°/12 mm.,  $d_{24}^{24}$  0.983,  $n_D^{24}$  1.54998, was obtained by the action of magnesium benzyl bromide on methyl  $\alpha\gamma$ -dichloro- $n$ -propyl ether, instead of the expected  $\gamma$ -chloro derivative. F. G. W.

**Alkyl Ethers of Ethylene Glycol.** L. H. CRETCHER and W. H. PITTENGER (*J. Amer. Chem. Soc.*, 1924, 46, 1503—1504).—Ethylene oxide or ethylene chlorohydrin (1.1 mols.) is added to a solution of sodium (1 mol.) in the appropriate alcohol, the glycol monoalkyl ether being separated by fractionation after removal of the sodium chloride. *Monoisopropyl*, b. p. 144°/743 mm.; *monopropyl*, b. p. 150°/743 mm.; *monoisobutyl*, b. p. 158.8°/743 mm.; *monobutyl*, b. p. 170.6°/743 mm., and *monoamyl glycol ether*, b. p. 181°/745 mm., are described. F. G. W.

**Manganese Acetate.** A. F. G. CADENHEAD and W. H. VINING (*Can. Chem. Met.*, 1924, 8, 64—65).—Manganese acetate,  $\text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ , rose-pink plates or flat, monoclinic prisms, dissolves to the extent of 64.5 g. in 100 g. of water at 5°.

#### CHEMICAL ABSTRACTS.

**Space Significance of the Co-ordination Number in Polynuclear Compounds. II. Constitution of the Violet Chromic Acetate.** H. REIHLEN (*Z. anorg. Chem.*, 1924, 133, 82—90; cf. A., 1921, ii, 193).—The violet chromic acetate is considered to be a compound of co-ordination number 10 :—



S. K. T.

**Electrolysis of Mixtures of Acetates and Trichloroacetates.**

R. E. GIBSON (*Proc. Roy. Soc. Edin.*, 1924, **44**, 140—152).—In the electrolysis of an aqueous solution of potassium acetate and trichloroacetate containing 2 mols. of the former salt to 1 mol. of the latter, the main products are those from single molecules of either acid, namely, ethylene, formaldehyde, and hydrochloric acid. Smaller amounts of derivatives from 2 mols. of either acid, namely, ethane, trichloromethyl trichloroacetate, and hexachloroethane, and from 1 mol. of each acid, trichloromethyl acetate, were also obtained. All reactions resulted in the liberation of carbon dioxide, whilst the formation of carbon monoxide was also observed.

A. COUSEN.

**Action of Acetic Anhydride on Hydrated Metallic Salts.**

“Acetylated” Salts. A. RECOURA (*Compt. rend.*, 1924, **178**, 2217—2221).—The action of acetic anhydride on certain hydrated metallic salts is primarily one of dehydration which, in some cases, is complete, but in others certain molecules of water remain combined with the salt and by means of their residual valencies attack molecules of the anhydride. The anhydrous salts do not combine with acetic anhydride. The acetylated salts are generally only stable in an atmosphere of acetic anhydride, and in air rapidly lose their acetic anhydride and unite with water to form the original hydrated salt. The acetylated salt which has lost some acetic anhydride by short exposure to air slowly recombines with it to form the normal acetylated salt when replaced in an atmosphere of the acetic anhydride. When placed over quicklime in a desiccator, they lose the whole of their acetic anhydride but retain their water, so that the anhydride is not combined with the water in the form of acetic acid. Copper sulphate yields the compound  $\text{CuSO}_4 \cdot \text{H}_2\text{O} \cdot 2\text{Ac}_2\text{O}$ . Nickel sulphate yields the compound  $\text{NiSO}_4 \cdot \text{H}_2\text{O} \cdot 2\text{Ac}_2\text{O}$ , which on placing in a desiccator over quicklime loses only 1 mol. of acetic anhydride, leaving the compound  $\text{NiSO}_4 \cdot \text{H}_2\text{O} \cdot \text{Ac}_2\text{O}$ . Magnesium sulphate yields the compound  $\text{MgSO}_4 \cdot 1.3\text{H}_2\text{O} \cdot 2\text{Ac}_2\text{O}$  which also loses only 1 mol. of acetic anhydride by the action of quicklime.

J. W. B.

**Salts of isoValeric Acid and  $\alpha$ -Bromoisovaleric Acid with Organic Bases.**

H. GOLDSCHMIDT and O. NEUSS (D.R.-P. 386616; from *Chem. Zentr.*, 1924, i, 1713).—It is claimed that neutral salts of diethylenediamine with isovaleric acid and  $\alpha$ -bromoisovaleric acid may be prepared. Diethylenediamine isovalerate has m. p. 136°. Diethylenediamine  $\alpha$ -bromoisovalerate sinters at 136° and decomposes at higher temperatures.

G. W. R.

**Synthesis of Normal Fatty Acids from Stearic Acid to Hexacosanoic Acid.**

P. A. LEVENE and F. A. TAYLOR (*J. Biol. Chem.*, 1924, **59**, 905—921).—The syntheses were carried out by the series of reactions:  $\text{R} \cdot \text{CO}_2\text{R} \rightarrow \text{R} \cdot \text{CH}_2 \cdot \text{OH} \rightarrow \text{R} \cdot \text{CH}_2\text{I} \rightarrow \text{R} \cdot \text{CH}_2 \cdot \text{CN} \rightarrow \text{R} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ . The following compounds are recorded: Ethyl stearate, m. p. 32.5—33.5°; b. p. 152°/0.18 mm. Ethyl n-nonadecoate, m. p. 37—38°; b. p. 166—

168°/0.27 mm. *Ethyl n-eicosoate*, m. p. 41.5–42.5°; b. p. 177°/0.28 mm. *Ethyl n-heneicosoate*, m. p. 45–46°. *Ethyl n-docosoate*, m. p. 48.5–49.5°; b. p. 184–185°/0.20 mm. *Ethyl n-tricosoate*, m. p. 52–53°; b. p. 198–199°/0.27 mm. *Ethyl n-tetracosoate*, m. p. 55.5–56.5°; b. p. 198–199°/0.24 mm. *Ethyl n-pentacosoate*, m. p. 58–59°; b. p. 216–217°/0.50 mm. *Methyl stearate*, m. p. 38.5–39.5°. *Methyl n-nonadecoate*, m. p. 39.5–40.5°. *Methyl n-eicosoate*, m. p. 46–47°. *Methyl n-heneicosoate*, m. p. 48–49°. *Methyl n-docosanoate*, m. p. 53–54°. *Methyl n-tricosoate*, m. p. 55–56°. *Methyl n-tetracosoate*, m. p. 59–60°. *Methyl n-pentacosoate*, m. p. 61–62°. *n-Nonadecanol*, m. p. 62–63°; b. p. 166–167°/0.32 mm. *n-Eicosanol*, m. p. 65.5–66.5°; b. p. 178°/0.40 mm. *n-Heneicosanol*, m. p. 68–69°. *n-Docosanol*, m. p. 70.5–71.5°; b. p. 180°/0.22 mm. *n-Tricosanol*, m. p. 73.5–74.5°; b. p. 191–193°/0.7 mm. *n-Tetracosanol*, m. p. 76.5–77.5°; b. p. 210–210.5°/0.40 mm. *n-Pentacosanol*, m. p. 78.5–79.5°; b. p. 214–216°/0.36 mm. *n-Octadecyl iodide*, m. p. 34.5–35.5°; b. p. 164°/0.22 mm. *n-Nonadecyl iodide*, m. p. 42.5–43.5°; b. p. 174–174.5°/0.22 mm. *n-Eicosyl iodide*, m. p. 42–43°. *n-Heneicosyl iodide*, m. p. 49–50°. *n-Docosyl iodide*, m. p. 48.5–49.5°; b. p. 198°/0.23 mm. *n-Tricosyl iodide*, m. p. 55–56°; b. p. 205°/0.45 mm. *n-Tetracosyl iodide*, m. p. 54.5–55.5°; b. p. 207–209°/0.35 mm. *n-Pentacosyl iodide*, m. p. 60–61°. *n-Octadecyl cyanide*, m. p. 42.5–43.5°. *n-Nonadecyl cyanide*, m. p. 49.5–50.5°. *n-Eicosyl cyanide*, m. p. 48.5–49.5°. *n-Heneicosyl cyanide*, m. p. 55.5–56.5°. *n-Docosyl cyanide*, m. p. 53.5–54.5°. *n-Tricosyl cyanide*, m. p. 61–62°. *n-Tetracosyl cyanide*, m. p. 58–59°. *n-Pentacosyl cyanide*, m. p. 61–62°. *Stearic acid*, m. p. 70.5–71.5°. *n-Nonadecoic acid*, m. p. 69–70°. *n-Eicosanoic acid*, m. p. 76–77°. *n-Heneicosoic acid*, m. p. 75–76°. *n-Docosoic (behenic) acid*, m. p. 81–82°. *n-Tricosoic acid*, m. p. 80–81°. *n-Tetracosoic acid*, m. p. 85–86°. *n-Pentacosoic acid*, m. p. 84–85°. *n-Hexacosic acid*, m. p. 88–89°. C. R. H.

**Action of Alcoholic Iodine Solutions on Unsaturated Fatty Acids and Fatty Oils. Influence of Water and Potassium Iodide on the Course of the Reaction.** B. M. MARGOSCHES, W. HINNER, and L. FRIEDMANN (*Ber.*, 1924, 57, [B], 996–1001; cf. this vol., i, 487).—The action of alcoholic iodine solutions on oleic acid is not confined to the alcoholic solution, but proceeds, especially if the period of reaction is short, after diluting the mixture with water preparatory to titrating the excess of iodine; the addition of hypoiodous acid is apparently almost instantaneous at the moment of dilution. The presence of potassium iodide hinders the reaction, probably on account of its tendency to reverse the reaction:  $I_2 + H_2O \rightarrow I(OH) + HI$  (cf. also Ingle, A., 1902, i, 528; 1904, ii, 456). Experiments in which the addition of water was omitted, or its influence restricted by the prior addition of carbon tetrachloride, gave lower iodine values after 1 hour's contact with the iodine solution, and it thus appears that the quickening of the reaction is due to the water itself. Similar results were obtained

with castor, sesamé, poppy-seed, and linseed oils in alcoholic solution. The free acid liberated in these experiments corresponds with about 50% of the iodine consumed, except in the case of castor oil, when it amounts to 60—65%.  
R. B.

**Autoxidation of Fats.** G. R. GREENBANK and G. E. HOLM (*Ind. Eng. Chem.*, 1924, **16**, 598—601).—The presence of water and water vapour seems to retard the autoxidation of fats, and to a greater or less extent the formation of those compounds that are responsible for the tallowy odour. Fatty acids act probably indirectly as catalysts for autoxidation, through the liberation of unsaturated acids (especially oleic acid) which are strongly catalytic in this reaction. The resistance of butter fat to autoxidation may be increased by thorough washing of the fat or by passing steam through it, but prolonged heating or steam treatment has the opposite effect. The results of experiments at 95° on the rate of absorption of oxygen by butter fat in the dry condition and mixed with water, oleic acid, and butyric acid, respectively, are given graphically. The addition of water increases the period of induction before the absorption of oxygen begins. Once the absorption commences, the shape of the curves is almost identical whether fatty acid or water is present or not. The presence of free fatty acids decreases the period of induction, oleic acid being more effective in this respect than butyric acid.  
H. C. R.

### I. Oxidation of Sodium Lactate by Hydrogen Peroxide.

**II. Effect of Cystine and Glycine on the Oxidation of Sodium Lactate by Hydrogen Peroxide.** G. B. RAY (*J. Gen. Physiol.*, 1924, **6**, 509—523, 525—529).—I.—The reaction between hydrogen peroxide and sodium lactate was studied by observing the rate of production of carbon dioxide and by titrating the amount of peroxide present at various stages. In the early stages of the reaction there was found an increased amount of peroxide when the experiment was performed in the presence of air, but not in its absence. In the latter case, the end-product of the reaction was acetaldehyde. From these results and from the observations on the carbon dioxide production, the author concludes that the reaction is of an auto-catalytic type and that the increased peroxide observed in the presence of air is due to the formation of acetyl peroxide from the acetaldehyde which is the first product of reaction. Ferric chloride increases the production of carbon dioxide if added to the peroxide solution first, but inhibits it if added first to the sodium lactate.

II.—The rate of production of carbon dioxide in the reaction above described is augmented considerably by the presence of cystine and slightly by glycine. Since it is influenced by the presence of the sulphhydryl group, the process is probably one of dehydrogenation.  
C. R. H.

**Aliphatic Hydroxy-acids.** I. M. ASANO (*J. Pharm. Soc. Japan*, 1924, No. 504, 75—86).—Heptoyl chloride was converted into ethyl heptoylacetoacetate from which the acetyl group was removed with ammonia and the product reduced with sodium  
ff\*

amalgam to  $\beta$ -hydroxypelargonic acid, m. p. 59–60°. *Ethyl hydrogen azelate*, b. p. 169–170°/2 mm., 178°/4 mm., 193°/9 mm., m. p. 26–27°, was prepared by heating a mixture of azelaic acid (1 mol.) and anhydrous ethyl alcohol (2.5 mols.) or a mixture of ethyl azelate (1 mol.) and water (2.5 mols.) in a sealed tube at 150° during 6 hours. The yields in both the methods do not exceed 50%, but no resinous substance is produced. Ethyl hydrogen pimelate, b. p. 166°/5 mm., 155°/2 mm., is prepared by the same method. By the action of zinc propyl iodide on ethyl azelate chloride, *ω*-butyroyloctoic acid,  $C_3H_7 \cdot CO \cdot [CH_2]_7 \cdot CO_2H$ , m. p. 56°, is produced; *semicarbazone*, m. p. 131°. A small amount of *α*-dibutyroylheptane,  $(C_3H_7 \cdot CO)_2[CH_2]_7$ , m. p. 71°, was produced as a by-product; the *disemicarbazone* melts at 166°. The conversion of the ketonic acid into its chloride did not proceed smoothly.

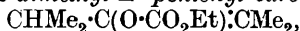
K. K.

**Influence of the Base on the Degree of Conversion of Primary Salts of Dibasic Acids in Aqueous Solution.** T. SABALITSCHKA and G. KUBISCH (*Z. anorg. Chem.*, 1924, **134**, 79–86).—The authors have determined the acid content of ethereal extracts of aqueous solutions of the primary salts of camphoric, oxalic, succinic, fumaric, and maleic acids with potassium, sodium, lithium, ammonium, aniline, carbamide, and benzamide. For the primary camphorates, oxalates, succinates, and fumarates of potassium, sodium, lithium, and ammonium, similar amounts of free acid pass into the ethereal layer. In some cases, *e.g.*, in the case of benzamide oxalate and maleate, the ether dissolves some of the salt. The greater free acid content of the ether in the case of the primary salts of aniline, carbamide, and benzamide than in that of alkali and ammonium salts is conditioned by hydrolytic decomposition. The relation of acid transference, aniline salt < carbamide < benzamide, is for aniline and carbamide in agreement with the known dissociation constants. Camphoric and fumaric acids liberated from the primary alkali and ammonium salts pass completely into the ethereal layer, succinic acid less completely, and oxalic and maleic acids only very slightly. The conversion of the acid salt depends on the distribution of the free acid between ether and water and the ratio of the dissociation constant of both hydrogen atoms. The degree of conversion of the acid salt to normal salt and free acid in aqueous solution is for the individual salts of that acid the same so long as the salt undergoes no appreciable hydrolytic decomposition. The degree of decomposition is independent of the base so long as it is sufficiently strong to give salts which are not appreciably hydrolysed.

J. B. F.

**Syntheses using Sodamide. XII. Action of Ethyl Chloroformate on the Sodium Compounds of certain Ketones.** A. HALLER and E. BAUER (*Ann. Chim.*, 1924, [x], **1**, 275–297).—After treatment with sodamide, phenyl isopropyl ketone interacts with ethyl chloroformate to yield chiefly  $\alpha$ -phenyl- $\beta$ -methyl- $\Delta^{\alpha}$ -propenyl ethyl carbonate,  $CMe_2 \cdot CPh \cdot O \cdot CO_2Et$ , m. p. 41–42°, b. p. about 135°/10 mm.; the product is hydrolysed to the original ketone,

gives no oxime, and generally is quite different from its isomeric *C*-derivative, ethyl  $\alpha$ -benzoylisobutyrate (Blaise and Courtot, A., 1906, i, 794). When the *oxime* of the latter (needles, m. p. 135—136°) is subjected to hydrolysis, or prepared directly in alkaline solution, it is converted into 3-phenyl-4 : 4-dimethylisooxazolone, m. p. 70—71°. The sodium compound of phenyl ethyl ketone and ethyl chloroformate produces two compounds, viz.,  $\alpha$ -phenyl- $\Delta^{\alpha}$ -propenyl ethyl carbonate, b. p. 140—145°/11—12 mm., and the ethyl carbonic ester of ethyl  $\beta$ -hydroxy- $\alpha$ -methylcinnamate,  $\text{CO}_2\text{Et}\cdot\text{O}\cdot\text{CPh}\cdot\text{CMe}\cdot\text{CO}_2\text{Et}$ , b. p. 182—185°/11 mm., which, on hydrolysis, affords ethyl  $\alpha$ -benzoylpropionate (Perkin and Calman, T., 1886, 49, 156); this interacts with hydroxylamine in alkaline solution to form 3-phenyl-4-methylisooxazolone, needles, m. p. 123—124°. From phenyl propyl ketone are similarly obtained  $\alpha$ -phenyl- $\Delta^{\alpha}$ -butenyl ethyl carbonate, b. p. 143°/10 mm., and the ethyl carbonic ester of ethyl  $\beta$ -hydroxy- $\alpha$ -ethylcinnamate, m. p. 35°, b. p. 183—184°/10 mm., which yields, when hydrolysed, ethyl  $\alpha$ -benzoylbutyrate. The *oxime* of the latter forms scales or needles, m. p. 80—81°; Hantzsch and Miolati's product (A., 1893, i, 583), m. p. 90—91°, is 3-phenyl-4-ethylisooxazolone, not the simple oxime. Acetophenone, treated with sodamide followed by ethyl chloroformate, yields ethyl benzoylmalonate (Bernhard, A., 1895, i, 93), a compound,  $\text{C}_{11}\text{H}_{14}\text{O}_4$ , b. p. 128—129°/11 mm., and the ethyl carbonic ester of ethyl  $\beta$ -hydroxy-cinnamate (Bernhard, *loc. cit.*). Diisopropyl ketone similarly yields chiefly ethyl  $\beta\delta$ -dimethyl- $\Delta^{\beta}$ -pentenyl carbonate,



b. p. 86°/15 mm., whilst pentamethylacetone, from the above isobutyronone, sodamide, and methyl iodide, gives ethyl  $\beta\delta\delta$ -trimethyl- $\Delta^{\beta}$ - $\gamma$ -pentenyl carbonate, b. p. 104—107°/24—25 mm. cyclo-Hexanone, by similar treatment, is converted into a mixture of  $\Delta^1$ -cyclohexenyl ethyl carbonate, b. p. 108—110°/20 mm., and biscyclohexenehexanone (Wallach, A., 1897, i, 160). W. A. S.

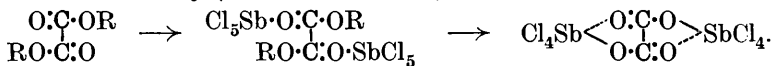
**Bismuth Oxalates.** E. MOLES and R. PORTILLO (*Anal. Fis. Quím.*, 1924, 22, 187—197; cf. this vol., i, 9).—According to the method of preparation, bismuth oxalate monohydrate is obtained with colours varying from brick-red to pink. The velocity with which water is absorbed on exposure in a moist atmosphere differs with the colour of the monohydrate. The red monohydrate absorbs water more quickly than the pink monohydrate, and when dried over sulphuric acid loses 3 of the 6 mols. of water thus absorbed, whilst in the case of the pink monohydrate 5 mols. of water are taken up, of which 3 are lost on drying over sulphuric acid. It is supposed that the single molecule of water in the monohydrate is more closely associated with the nucleus than the molecules which are absorbed from a moist atmosphere. Four hydrates are mentioned containing, respectively, 6, 5, 3, and 2 mols. of water in addition to the single molecule associated with the nucleus. G. W. R.

**Thermal Decomposition of Calcium Oxalate.** E. MOLES and C. DÍAZ VILLAMIL (*Anal. Fis. Quím.*, 1924, 22, 174—186).—When traces of moisture are present, the initial temperature of

decomposition of anhydrous calcium oxalate is  $380^{\circ}$ ; carbon monoxide and carbon dioxide are evolved together with water vapour, and the residue of calcium carbonate is grey in colour and contains carbon and traces of formic acid. Using perfectly dry anhydrous calcium oxalate, the decomposition also begins at  $380^{\circ}$ , and is represented by the equation,  $\text{CaC}_2\text{O}_4 \rightleftharpoons \text{CaCO}_3 + \text{CO}$ . The decomposition is thus incomplete and the residue contains calcium oxalate. At higher temperatures ( $470$ — $480^{\circ}$ ), the decomposition is represented by the equation  $7\text{CaC}_2\text{O}_4 = 7\text{CaCO}_3 + 5\text{CO} + \text{CO}_2 + \text{C}$ .

G. W. R.

**Reaction between Antimony Pentachloride and Ethyl Oxalate.** P. PFEIFFER (*Z. anorg. Chem.*, 1924, **133**, 101—106).—The behaviour of antimony pentachloride towards *o*-hydroxyketones is exactly analogous to that of stannic chloride (A., 1913, i, 879). Two mols. of the ketone combine with 1 mol. of the halide and, on warming, 1 mol. of ketone and 1 mol. of hydrogen chloride are eliminated. Thus  $\beta$ -acetyl- $\alpha$ -naphthol reacts to give  $\beta$ -acetyl- $\alpha$ -naphthoxy-antimony tetrachloride,  $\text{Ac}\cdot\text{C}_{10}\text{H}_6\cdot\text{O}\cdot\text{SbCl}_4$ . Ethyl oxalate behaves similarly (cf. A., 1902, i, 358):



S. K. T.

**Stereoisomerism and Steric Transformations among  $\alpha$ -Thio- and  $\alpha$ -Sulpho-di[alkyl]carboxylic Acids.** R. AHLBERG (*J. pr. Chem.*, 1924, [ii], **107**, 241—329; cf. Lovén and Ahlberg, A., 1921, i, 223; Loven, A., 1908, i, 714, and earlier papers).—Sodium  $\alpha$ -bromobutyrate and sodium sulphide interact in aqueous solution to give almost equimolecular proportions of *meso*- $\alpha$ -thiodibutyric acid,  $\text{S}(\text{CHEt}\cdot\text{CO}_2\text{H})_2$ , m. p.  $109^{\circ}$  (Lovén, *loc. cit.*), and the *racemic* isomeride, m. p.  $82^{\circ}$ . The *potassium hydrogen* salt is described. The acid is resolved with the help of the active phenylethylamines. 1-Phenylethylammonium 1-thiodibutyrate, m. p.  $142$ — $143^{\circ}$ ,  $[\alpha]_D -46.0^{\circ}$ , and d-phenylethylammonium d-thiodibutyrate,  $[\alpha]_D +43.6^{\circ}$ , are described. 1- $\alpha$ -Thiodibutyric acid forms prisms, m. p.  $35^{\circ}$ ,  $[\alpha]_D -152^{\circ}$ ; the d-variety has  $[\alpha]_D +145^{\circ}$ . Slow racemisation takes place in aqueous solution at  $100^{\circ}$ . The normal *silver*, *potassium hydrogen*, and d-phenylethylammonium *hydrogen meso*- $\alpha$ -thiodibutyrate were prepared. In preparing the  $\alpha$ -thiodiisovaleric acid, it was found better to treat ethyl  $\alpha$ -bromoisovalerate with alcoholic sodium sulphide; the crude ethyl  $\alpha$ -thiodiisovalerate obtained had b. p.  $165$ — $168^{\circ}/17$  mm. It was hydrolysed and converted into the strychnine salt, which, fractionally crystallised, gave *meso*- $\alpha$ -thiodiisovaleric acid, m. p.  $136^{\circ}$  (cf. Lovén, *loc. cit.*), and small quantities of the *racemic* variety. The latter is also obtained by heating the *meso*-form at  $200$ — $210^{\circ}$ , and in considerable proportion when the diethyl ester (b. p.  $160$ — $162^{\circ}/13$  mm.) of the latter is hydrolysed. The *potassium*, *sodium*, *magnesium*, *barium*, *calcium*, *strontium*, *copper*, *silver*, *strychnine*, *brucine*, and 1- $\alpha$ -phenylethylammonium salts of *meso*- $\alpha$ -thiodiisovaleric acid were prepared.

The *ethyl* ester has b. p. 160—162°/13 mm. The *potassium hydrogen, potassium sodium, magnesium, barium, copper, and silver* salts of the *r*-acid are described. The acid is resolved into optically active components by means of *l*-phenylethylamine or brucine. *d*- $\alpha$ -Thiodiisovaleric acid has m. p. 80.5—81°,  $[\alpha]_D +129^\circ$ ; the *lævo* isomeride has m. p. 81—81.5° and  $[\alpha]_D -126.5^\circ$ . The brucine salts were isolated. The solubilities of all these acids and of many of their salts are recorded, and also the affinity constants, from conductivity measurements, for the acids. It is shown that, for the series  $\alpha$ -thiodiacetic acid— $\alpha$ -thiodiisovaleric acid, the racemic form in every case is the stronger acid, whilst the optical activity (for the three acids possessing the property) decreases with rise in molecular weight for the acids, but increases for their salts. *meso*- $\alpha$ -Thiodibutyric acid oxidised with alkaline permanganate yields the sulphone, *r*- $\alpha$ -sulphodibutyric acid (Lovén, *loc. cit.*); *l*- $\alpha$ -thiodibutyric acid similarly oxidised gives a *lævorotatory* product which, even in cold aqueous solution, rapidly loses its optical activity and the same product as from the inactive thio acid can be isolated. Optically active acids were, nevertheless, isolated from the brucine salts of the racemic sulphone acid, but rapid racemisation prevented their characterisation in any other way than by the optical activity of the solutions; *d*- $\alpha$ -sulphodibutyric acid crystallises but has no definite m. p. The *potassium hydrogen* salt of the *meso* variety is described. *r*- $\alpha$ -Thiodiisovaleric acid carefully oxidised with alkaline permanganate gives *r*- $\alpha$ -sulphoxydiisovaleric acid, m. p. 152—152.5°. The *meso*-thio acid, further oxidised, yields a little of this, together with a mixture of *racemic* (Lovén, *loc. cit.*) and *meso*- $\alpha$ -sulphodiisovaleric acids, m. p. 131—133°; the *sodium, potassium, magnesium, zinc, calcium, barium, cinchonine, brucine, and strychnine* salts are described. The *potassium hydrogen* and *barium* salts of the corresponding *r*-acid were prepared. Oxidation of the optically active  $\alpha$ -thiodiisovaleric acids yields optically active products which rapidly racemise, but they can be isolated by fractionally crystallising the brucine and cinchonine salts of the racemic variety. The brucine salt of *l*- $\alpha$ -sulphodiisovaleric acid has m. p. 139° and the free acid  $[\alpha]_D -30.6^\circ$ ; the cinchonine salt of the *d*-variety (decomp. 115°) similarly gives an acid,  $[\alpha]_D +30.2^\circ$ . Both rapidly racemise in warm aqueous solution. The author discusses at length the mechanism of the racemisation and the conversion of the *meso* into the racemic forms. The reactions are unimolecular and evidently depend on enolisation, either through the carboxy or the sulpho group, or both. W. A. S.

### “Alcoholic Fermentation” of Formaldehyde by Osmium.

II. E. MÜLLER (*Z. physikal. Chem.*, 1923, **107**, 347—356; cf. A., 1922, i, 110).—Osmium catalyses the reduction of formaldehyde to methyl alcohol only when present in the colloidal or highly dispersed condition. The metal is obtained in this condition by adding to the formaldehyde an osmium compound, such as osmic acid, which is then reduced to the metal in a highly active form. An examination of the catalytic reaction at 100° shows that the



gas evolved is not entirely carbon dioxide as the equation  $3\text{H}\cdot\text{CHO} + \text{H}_2\text{O} = \text{CO}_2 + 2\text{CH}_3\cdot\text{OH}$  demands, but contains hydrogen and methane in addition, and sometimes, although in very small quantities, carbon monoxide. The formation of hydrogen and methane is due to the changes,  $\text{H}\cdot\text{CHO} + \text{H}_2\text{O} = 2\text{H}_2 + \text{CO}_2$  and  $2\text{H}\cdot\text{CHO} = \text{CH}_4 + \text{CO}_2$ . Experiments show that an increasing evolution of methane is accompanied by a decreasing evolution of hydrogen and that as the ratio, volume of aldehyde solution: weight of osmium, increases the amount of methane formed decreases, the reaction producing the alcohol always predominating. The time taken for the catalytic action and the gas evolution to reach a maximum is increased by increasing  $p_{\text{H}}$ , and the magnitude of the maximum is reduced. The induction period before the catalytic action begins appears to be the same whether the formaldehyde is heated with the osmium compound or kept cold, and the catalysis differs little whether the osmium is added in the form of the tetroxide, potassium osmate, or potassium chloro-osmate. The volume relations of the gases evolved are about the same in all cases, and when the reaction is concluded the osmium is present in the colloidal condition. The similarity between the present reaction and fermentation by yeast is pointed out. J. F. S.

**Formaldehyde.** H. VON WARTENBERG, A. MUCHLINSKI, and G. RIEDLER (*Z. angew. Chem.*, 1924, **37**, 457—459).—The heat of combustion of formaldehyde and its polymerides has been redetermined as follows:  $\text{CH}_2\text{O}_{\text{gas}} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}_{\text{liq.}} + 15.88 \pm 0.033$  Cal.;  $\text{CH}_2\text{O}_{\text{para.}} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}_{\text{liq.}} + 12.21 \pm 0.0085$  Cal.;  $\frac{1}{3}(\text{CH}_2\text{O})_3 + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}_{\text{liq.}} + 10.95 \pm 0.007$  Cal. From this it follows that the heat of transformation of formaldehyde into paraformaldehyde and  $\alpha$ -trioxymethylene is as follows:  $\text{CH}_2\text{O}_{\text{gas}} \rightarrow \text{CH}_2\text{O}_{\text{para.}} + 36.7$  Cal.  $\rightarrow \frac{1}{3}(\text{CH}_2\text{O})_3 + 1.26$  Cal. and the heat of formation of gaseous formaldehyde from its elements is  $\text{C}_{\text{diamond}} + \frac{1}{2}\text{O}_2 + \text{H}_2 = \text{CH}_2\text{O}_{\text{gas}} + 4.0 \pm 0.3$  Cal. Attempts to synthesise formaldehyde by subjecting mixtures of carbon monoxide and hydrogen to the silent electric discharge at pressures up to 30 atms. gave only the merest trace of the substance. A mixture of carbonyl chloride with 15 times its volume of hydrogen yielded 3.6% of the theoretical amount of formaldehyde when passed over nickelised pumice at  $300^\circ$ . A maximum yield of 2% of formaldehyde based on the methane content of a mixture of methane and ozone was obtained when the mixture was passed over silver or lead chromate at  $650^\circ$ ; at higher temperatures the yield rapidly fell to zero. A. R. P.

**Rate of Oxidation of Aldehydes.** M. SEIJOO (*Anal. Asoc. Quím. Argentina*, 1923, **11**, 151—171).—Data are given for the velocity of oxidation of formaldehyde, acetaldehyde, and benzaldehyde, respectively, by potassium permanganate and sulphuric acid. The reaction is found to be unimolecular when very dilute solutions of potassium permanganate are used. G. W. R.

**Tautomerism of Ethyl Acetoacetate and Acetylacetone. Absorption Spectra of These and Related Compounds.** P. GROSSMANN (*Z. physikal. Chem.*, 1924, **109**, 305—352).—The pro-

portion present of the enolic form of ethyl acetoacetate and acetylacetone in various solvents, both pure and mixed in varying proportions, has been determined by titration with bromine and by quantitative absorption spectra measurements. The proportion found may vary slightly with concentration even for very dilute solutions, but no explanation of this is suggested. The velocity of the isomeric change was studied in various solvents, but in spite of careful purification, the reaction proved too susceptible to catalytic influence for reproducible results. In several cases, determinations were made at 0° and 25° and the heats of reaction calculated, but these varied with the solvent. Alkaline solutions were studied by a slight modification of the usual practice. Instead of acidifying the solution before treating with bromine, with consequent ketisation, acid bromine solution was added direct and excess bromine removed by aniline hydrochloride. Results were confirmed by spectroscopic measurements. Excess of alkali favours the enolic form. Similar results were obtained with acetylacetone. With still greater excess of alkali, the results are even higher, corresponding with the presence of a dienol. Analogous results are afforded by acetylacetone.

On warming alkaline solutions of ethyl acetoacetate, ketonic fission takes place, but, in the cold, hydrolysis occurs slowly and quantitatively. The course of hydrolysis was followed simultaneously with the proportion present of the enolic form. The resulting solution of sodium acetoacetate is only 0.2% enolic if the ester and alkali are mixed in equivalent proportions, but with excess alkali this is increased and, in great excess of alkali, may attain 5%. In spite of the complication of formation of enol, the reaction is bimolecular. Acetylacetone hydrolyses to acetone and sodium acetate quantitatively: the reaction corresponds with the simultaneous hydrolysis of the ketonic and enolic (and perhaps the dienolic) forms at different rates. In both cases, the conductivity scarcely alters during hydrolysis, so the enolic forms must be ionised about as highly as sodium acetate, and complex formation is excluded.

The ultra-violet absorption spectra of ethyl acetoacetate and acetylacetone and other substances of similar composition in various solvents are given quantitatively. That of ethyl acetoacetate in the vapour state at room temperature was also studied and found closely to resemble that of the pure liquid. It is deduced that 5% must be in the enolic form. A ring structure in the gaseous state is excluded, as the band is continuous and cannot be resolved into the fine lines characteristic of unsaturated ring compounds.

L. J. H.

**Keto-enolic. Desmotropy. III. Determination of Enols by Titration with Thiocyanogen.** H. P. KAUFMANN and G. WOLFF (*Ber.*, 1924, 57, [B], 934—937).—Experiments with ethyl acetoacetate, acetyldibenzoylmethane, ethyl diacetylsuccinate, and ethyl formylphenylacetate show that the equilibrium of keto-enolic desmotropes can be determined by titration with thiocyanogen if the rate of transformation is sufficiently slow; nitromethane is particularly suitable as a solvent. From the points of view of

convenience and general applicability, the method is inferior to Meyer's bromine titration method. H. W.

**Compounds of Quadrivalent Nickel with Dimethylglyoxime.** F. FEIGL.—(See ii, 504.)

**Colour Reaction between Cobalt Salts and Dimethylglyoxime in the Presence of Sulphides.** F. FEIGL and L. VON TUSTANOWSKA.—(See ii, 504.)

**Oxidation of Carbohydrates with Air.** H. A. SPOEHR (*J. Amer. Chem. Soc.*, 1924, **46**, 1494—1502).—Methylene-blue is reduced by dextrose in solutions containing disodium phosphate, the rate of reduction being proportional to the concentration of the latter from 0.025 to 0.75*M*, and to that of the dextrose from 0.05 to 0.5*M*. On drawing a stream of air through the solution, the blue colour is restored and carbon dioxide formed. Lævulose reacts similarly, from five to eight times as rapidly as dextrose. The rate of production of carbon dioxide is increased threefold by the addition of a trace of a solution of ferric phosphate in sodium citrate ("soluble ferric phosphate"). The methylene-blue is gradually consumed, possibly on account of production of hydrogen peroxide. Sodium ferropyrophosphate,  $\text{Na}_6\text{Fe}_2(\text{P}_2\text{O}_7)_3$ , catalyses the above reaction, and also brings about atmospheric oxidation of dextrose alone, the rate of formation of carbon dioxide first increasing rapidly and then slowly diminishing. Sodium ferripyrophosphate,  $\text{Na}_6\text{Fe}_2(\text{P}_2\text{O}_7)_3$ , is less active, and sodium manganopyrophosphate shows only about 0.1% of the activity of iron. Prior aëration of the catalyst has no effect on its activity. Maximum oxidation was attained at  $p_{\text{H}}$  7.2. *d*-Mannose, *d*-galactose, sucrose, trehalose, and mannitol are also oxidised in presence of sodium ferropyrophosphate, disodium phosphate, and potassium dihydrogen phosphate, the oxidation of sucrose also proceeding in solution of  $p_{\text{H}}$  6.8. Evidence of hydrolysis of sucrose and trehalose prior to oxidation was not obtained. The oxidation of dextrose is probably accompanied by partial conversion into lævulose and ketoses, and some formation of saccharic acid.

F. G. W.

**Behaviour of Sugars in Dilute Alkaline Solutions. I. Cause of the Transformation of Dextrose in Dilute Solutions of Potassium Hydroxide.** J. GROOT (*Biochem. Z.*, 1924, **146**, 72—90).—The lowering of rotation of dextrose solutions of various concentrations from 0.16*M* to 0.66*M*, in the presence of potassium hydroxide varying between 0.05*N* and 1.0*N* has been studied quantitatively. For various concentrations of dextrose the extent to which the rotation is lowered increases with increasing hydroxide concentration, the limiting value being about 2/9 of the rotation of the original dextrose solution at equivalent dilution. For any given concentration of dextrose the velocity of the decrease in rotation increases with increasing hydroxide concentration, until a limiting value is reached beyond which further increases in the hydroxide concentration produce no effect on the velocity of the change of rotation. The latter attains its maximum when the ratio of dextrose to potassium hydroxide is unimolecular, and this is independent of

the original dextrose concentration. The results resemble the de Bruyn-van Ekenstein transformation and are interpreted as representing the conversion of dextrose into a mixture of this and other hexoses which proceeds as a unimolecular reaction, the following equation being deduced as applying within the limits between which  $K$  varies with  $N$ :  $K = 12.8M/N$  (at  $25^\circ$ ), where  $K$ =velocity constant with a maximum value of 12.8,  $M$ =molar concentration of dextrose, and  $N$ =normality of the potassium hydroxide. In a theoretical discussion of the results the view is expressed that the cause of the changes observed is the formation of potassium glucosate,  $C_6H_{11}O_6K$ , and the instability of this compound in aqueous solution. J. P.

**Fluoro-acetyl Derivatives of Sugars. III. Optical Rotation and Atomic Dimension.** D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1924, **46**, 1484—1488).—*Fluorotriacetyl-l-arabinose* forms brilliant needles, m. p.  $117-118^\circ$ ,  $[\alpha]_D^{20} +138.18^\circ$  in chloroform. Chlorotriacetyl-*l*-arabinose has  $[\alpha]_D^{20} +244.32^\circ$  (cf. Chavanne, A., 1902, i, 346; Ryan and Mills, T., 1901, **79**, 706), and bromotriacetyl-*l*-arabinose has m. p.  $138-139^\circ$ ,  $[\alpha]_D^{20} +287.11^\circ$  (cf. Chavanne, *loc. cit.*). *Iodotriacetyl-l-arabinose*, prepared similarly to iodo-tetra-acetylglucose (E. and H. Fischer, A., 1910, i, 716), forms colourless crystals,  $[\alpha]_D^{20} +339.06^\circ$ . The differences in specific rotations of the above compounds are approximately proportional to the differences in atomic diameters of the halogen atoms, and are in agreement with similar relationships previously found for analogous derivatives of other carbohydrates. F. G. W.

**Halogen Compounds of Starch.** M. BERGMANN and S. LUDEWIG (*Ber.*, 1924, **57**, [B], 961—963).—Starch acetates, obtained by short treatment of starch with a saturated solution of hydrogen chloride in acetic anhydride at  $0^\circ$ , retain the typical affinity of starch towards mixtures of iodine and potassium iodide and the power of absorbing bromine, thus lending support to the authors' view (this vol., i, 618) that the formation of halogen compounds is attributable to certain bridge oxygen atoms of starch. H. W.

**Alkoxy Groups of the Wood and Lignin of the Pine.** E. HÄGGLUND and B. SUNDRÖS (*Biochem. Z.*, 1924, **146**, 221—225).—From determinations of the alkoxy content of pine wood and of the lignins prepared from it, by the Zeisel and Feist-Willstätter methods, and since the latter method yields only phenyltrimethylammonium iodide or tetramethylammonium iodide, it is concluded that the alkoxy groups consist wholly of methoxyl. J. P.

**Ammonia and Amine Compounds of Stannic Dialkyl Halides.** P. PFEIFFER (*Z. anorg. Chem.*, 1924, **133**, 91—100).—Stannic dialkyl halides combine with quinoline or aniline to give crystalline additive compounds which are unstable towards heat and have indefinite melting points (cf. A., 1911, i, 747). Dry ammonia combines with stannic dialkyl halides at the ordinary temperature to form additive ammonia compounds in which the co-ordination number of the tin is probably 8 (cf. A., 1923, ii, 867).

*Diquinoline stannic dimethyl chloride*,  $\text{SnMe}_2\text{Cl}_2 \cdot 2\text{C}_9\text{H}_7\text{N}$ , forms white crystals, m. p.  $40-60^\circ$ , unstable in moist air; the corresponding *bromide*, m. p.  $80-115^\circ$ , behaves similarly. *Dianiline stannic dimethyl chloride*,  $\text{SnMe}_2\text{Cl}_2 \cdot 2\text{PhNH}_2$ , when dissolved in pyridine, yields the corresponding pyridine compound; the *iodide* forms unstable, pale yellow crystals. *Dianiline stannic diethyl chloride* and the *bromide*,  $\text{SnEt}_2\text{X}_2 \cdot 2\text{PhNH}_2$ , *monoaniline stannic diethyl bromide* and *dianiline stannic dipropyl bromide* were also prepared.

The *ammonia* compounds,  $\text{SnR}_2\text{X}_2 \cdot 4\text{NH}_3$ , were prepared, where  $\text{R}=\text{Me}$ ,  $\text{X}=\text{Cl}$ ,  $\text{Br}$  and  $\text{I}$ ;  $\text{R}=\text{Et}$ ,  $\text{X}=\text{Br}$  and  $\text{I}$ ;  $\text{R}=\text{Pr}$ ,  $\text{X}=\text{Cl}$  and  $\text{Br}$ . The compound with  $\text{R}=\text{Et}$  and  $\text{X}=\text{Cl}$  contained only  $3\text{NH}_3$ .  
S. K. T.

**Organic Silver Complexes.** F. G. PAWELKA (*Z. Elektrochem.*, 1924, **30**, 180—186).—By the use of the method described by Bödlander, the complexity of a number of additive derivatives of organic substances and silver nitrate has been determined. If the complexes are considered to be of the general type,  $[\text{Ag}_m\text{R}_n](\text{NO}_3)_m$ , then  $m=1$  and  $n/m=2$  in the case of the following silver derivatives: sodium thiosulphate, dimethylamine, diethylamine, triethylamine, hexamethylenetetramine, glycine, acetonitrile, propionitrile, ethylene cyanide, and toluidine. In the case of thiocarbamide,  $m=1$  and  $n/m=3$ .  
H. T.

**Preparation of *p*-Aminobenzoyl Derivatives of  $\delta$ -Methyl- $\beta$ -dimethyl(diethyl)aminopentan- $\alpha$ -ol.** CHEMISCHE FABRIK FLORA (Brit. Pat. 200810).— $\delta$ -Methyl- $\beta$ -dimethyl(diethyl)aminopentan- $\alpha$ -ol (cf. Karrer and others, this vol., i, 168) is converted into the *p*-nitrobenzoic ester and the latter is reduced.  *$\delta$ -Methyl- $\beta$ -diethylaminoamyl *p*-nitrobenzoate hydrochloride*, m. p.  $163^\circ$ , and  *$\delta$ -methyl- $\beta$ -diethylaminoamyl *p*-aminobenzoate hydrochloride*, m. p.  $190^\circ$ , are described. The latter substance has valuable therapeutic properties.  
W. T. K. B.

**Mixed Crystals, consisting of 2 Mols. of Glycine, or 2 Mols. of Alanine, or 1 Mol. of Glycine and 1 Mol. of Alanine, combined with 1 Mol. of Hydrochloric Acid.** E. ABDERHALDEN and H. SICKEL (*Z. physiol. Chem.*, 1924, **135**, 29—31).—From the strongly acidified mother-liquors of a tyrosine preparation the authors isolated crystals of *glycinealanine monohydrochloride*, rectangular needles, m. p.  $177^\circ$  after softening at  $105^\circ$ ,  $[\alpha]_D^{25} +4.42^\circ$ . Recrystallisation from water gave rhombic crystals of *diglycine monohydrochloride*, m. p.  $178^\circ$ . The crystals, together with *dialanine monohydrochloride*, m. p.  $214^\circ$ ,  $[\alpha]_D^{25} +9.13^\circ$ , were also prepared directly from the amino-acids and hydrochloric acid by slow evaporation.  
E. M. C.

**Action of Sulphuric Acid on some Amino-acids and on the Vinasse from the Distillation of Molasses.** P. G. KRONACKER (*Bull. Soc. chim. Belg.*, 1924, **33**, 217—231).—Determinations have been made of the proportions of nitrogen convertible into ammonium sulphate by the action of sulphuric acid on various amino-acids known to be present in sugar juices. The whole of the nitrogen in glycine, asparagine, aspartic acid, glutamic acid, and leucine

was converted by treatment with sulphuric acid (66%). In the case of betaine it was necessary to use 95% acid with permanganate or mercury. It is suggested that dehydration causes betaine to form a stable ring compound. On treatment with 66% acid, tryptophan gave a low result which is ascribed to the formation of a stable tautomeric form; the theoretical value was obtained when the Stolzenberg-Kjeldahl method was used. Arginine gave a low result when treated with 66% acid. F. B.

**Sulphamic Ester and its Isomerisation to Compounds of the Betaine Type.** W. TRAUBE, H. ZANDER, and H. GAFFRON (*Ber.*, 1924, 57, [B], 1045—1051).—An attempt to prepare methyl sulphamate by the action of diazomethane on the acid led to the production of a *substance*, m. p. 239°, which is also obtained, in 93% yield, by the action of methyl iodide on dry silver sulphamate at the ordinary temperature. On account of its difference in properties from the dimethylsulphamic esters prepared by Behrend

(A., 1884, 285), the constitution,  $\text{NMe}_3 \cdot \text{SO}_2 \cdot \text{O}$ , is ascribed to the substance, which is thus *anhydrotrimethylsulphamic acid*. The isomeric *methyl dimethylsulphamate*, pale or yellow oil, obtained by the action of sodium methoxide on dimethylsulphamyl chloride, undergoes conversion into the trimethylsulphamic acid even at the ordinary temperature, and is probably produced intermediately in the formation of trimethylsulphamic acid. The reaction with silver sulphamate proceeds according to the equation  $3\text{NH}_2 \cdot \text{SO}_3 \text{Ag} +$

$3\text{MeI} = \text{NMe}_3 \cdot \text{SO}_2 \cdot \text{O} + 2\text{NH}_2 \cdot \text{SO}_3 \text{H} + 3\text{AgI}$ , two-thirds of the silver sulphamate being found as free sulphamic acid. The course of this reaction depends on the weight of the alkyl radical participating. Thus with ethyl iodide the product is *ethyl diethylsulphamate*,  $\text{NEt}_2 \cdot \text{SO}_3 \text{Et}$ , in 80% of the theoretical yield, whilst with benzyl chloride in chloroform solution the product is *benzyl benzylsulphamate*, m. p. 90°. R. B.

**Determination of the Constitution of the Eutectic Mixture of Methyl, Ethyl, and isoButyl Oxamates.** A. PRAETORIUS (*Z. anal. Chem.*, 1924, 64, 96—102).—By thermal analysis, the results of which are plotted on a triangular diagram, the eutectic mixture, m. p. 56°, of methyl, ethyl, and *isobutyl* oxamates was found to consist of 16.5% of the methyl, 24.5% of the ethyl, and 59% of the *isobutyl* ester. The error in calculating the result from the analytical figures for carbon and nitrogen amounted to 10%. A. R. P.

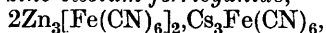
**Chlorides of Thiocyanogen.** H. P. KAUFMANN and J. LIEPE (*Ber.*, 1924, 57, [B], 923—928).—Thiocyanogen dissolved in cold chloroform reacts with chlorine in three ways, yielding, respectively, *thiocyanogen monochloride*,  $(\text{SCN})\text{Cl}$ , sulphur chloride and cyanuric chloride, and *thiocyanogen trichloride*,  $(\text{SCN})\text{Cl}_3$ . The monochloride crystallises in colourless needles which become yellow at about 150° and darken, without melting, at a higher

temperature. It is comparatively stable towards water, by which it is ultimately hydrolysed to sulphur, hydrocyanic, hydrochloric, thiocyanic, and sulphuric acids. The trichloride, which is more conveniently prepared in ethyl bromide solution, is a yellow liquid with a very unpleasant odour, b. p.  $54-56^{\circ}/20$  mm.,  $152-153^{\circ}/760$  mm. It is slowly decomposed by cold water into sulphur, thiocyanic, hydrocyanic, hydrochloric, and sulphuric acids and by sodium hydroxide solution (10%) into hydrocyanic, thiocyanic, hydrochloric, sulphurous, thiosulphuric, and sulphuric acids, hydrogen sulphide, carbon dioxide, and ammonia. H. W.

**Titration with Free Thiocyanogen.** H. P. KAUFMANN and P. GAERTNER (*Ber.*, 1924, 57, [B], 928-934).—Solutions of thiocyanogen in organic media can be accurately titrated by agitation with at least twice the equivalent quantity of potassium iodide dissolved in water and determination of the liberated iodine. In cases in which the end-point is obscured by the separation of thiocyanogen compounds, alcoholic sodium iodide solution may replace aqueous potassium iodide. The application of thiocyanogen in volumetric analysis is restricted by the necessity of using anhydrous solvents and dry vessels to avoid hydrolysis, and by the limited stability of such solutions owing to the tendency towards polymerisation. With a sufficient excess of sodium thiosulphate or hydrogen sulphide, respectively, thiocyanogen reacts quantitatively according to the equations  $2\text{Na}_2\text{S}_2\text{O}_3 + (\text{CNS})_2 = 2\text{NaSCN} + \text{Na}_2\text{S}_4\text{O}_6$  and  $(\text{SCN})_2 + \text{S}'' = 2\text{SCN}' + \text{S}$ . In carbon tetrachloride solution, antipyrine reacts rapidly and quantitatively with an excess of thiocyanogen, whereas  $\alpha$ - and  $\beta$ -naphthols react similarly, but more slowly. Thymol dissolved in nitromethane is moderately rapidly transformed into 4-thiocyano-6-isopropyl-m-cresol, yellow needles, m. p.  $108-109^{\circ}$ . H. W.

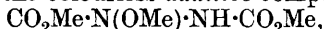
**Thiocyanatocobaltous Acid and its Alkali Salts.** F. J. ALLEN and A. R. MIDDLETON (*Proc. Indiana Acad. Sci.*, 1922, 153-158).—Experiments on the partition of sulphuric acid, thiocyanic acid, and cobalt between water and a 1:4-mixture of ethyl alcohol and ethyl ether showed the ether layer to contain equivalent proportions of cobalt and thiocyanate, and larger amounts of thiocyanic acid, but practically no cobalt thiocyanate or potassium thiocyanate; they do not elucidate the composition of the blue compounds obtained by Rosenheim and Cohn (A., 1901, i, 455), which probably consist of one or more complex acids,  $\text{H}_{2x}\text{Co}(\text{SCN})_{4x}$ , containing cobalt in the anion. Both the blue complex alkali thiocyanatocobaltites and the purple compound,  $\text{Co}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ , can be prepared by double decomposition in aqueous solution from cobalt sulphate, the alkali sulphate being removed with ethyl alcohol, thus avoiding the use of unstable thiocyanic acid. The form of the compounds,  $\text{K}_2\text{Co}(\text{SCN})_4$  and  $(\text{NH}_4)_2\text{Co}(\text{SCN})_4$  stable in air is the trihydrate (cf. Treadwell, A., 1901, ii, 284). The purple salt,  $\text{Co}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$ , on exposure to warm air, yields the yellowish-brown hemihydrate. CHEMICAL ABSTRACTS.

**Double Salt of Zinc and Cæsium Ferricyanides.** I. M. KOLTHOFF and E. J. A. H. VERZIJL (*Rec. trav. chim.*, 1924, **43**, 394—396).—In the potentiometric titration of a zinc salt with potassium ferrocyanide containing a little ferricyanide, addition of cæsium chloride causes a considerable fall in the potential of the electrode (cf. this vol., ii, 501). This is due to the formation of a very sparingly soluble *zinc cæsium ferricyanide*,



the precipitation of which increases the ratio ferrocyanide:ferricyanide on which the electrode potential depends. E. H. R.

**Addition of Mono- and Poly-hydric Alcohols and Mercaptans to Azodicarboxylic Ester.** O. DIELS and C. WULFF (*Annalen*, 1924, **437**, 309—318; cf. A., 1922, i, 774, 1194; 1923, i, 391; this vol., i, 673).—Azodicarboxylic ester reacts with alcohols and mercaptans with varying velocity, yielding additive compounds of 1 mol. of alcohol with 1 mol. of ester (2 mols. of ester in the case of glycols). In the presence of potassium acetate the additive compounds are decomposed, yielding nitrogen, hydrazo ester, and the alkyl carbonate. Methyl alcohol and methylazodicarboxylate yield the colourless *additive* compound,



a colourless, viscous oil,  $d_4^{20}$  1.3024;  $n_{\text{H}_a}^{20}$  1.44475,  $n_{\text{D}}^{20}$  1.44887. Similarly, ethyl alcohol and methyl azodicarboxylate yield the *compound*,  $\text{CO}_2\text{Me}\cdot\text{N}(\text{OEt})\cdot\text{NH}\cdot\text{CO}_2\text{Me}$ , a bright, viscous, highly refracting oil, decomposing on distillation into nitrogen, hydrazo ester, and methyl ethyl carbonate. *iso*Butyl alcohol in 4—6 weeks yields the *compound*,  $\text{C}_8\text{H}_{16}\text{O}_5\text{N}_2$ , and amyl alcohol in 8 weeks the *compound*,  $\text{C}_9\text{H}_{18}\text{O}_5\text{N}_2$ , colourless, viscous, highly refracting oils. With ethyl mercaptan, methyl azodicarboxylate yields in 24 hours the *compound*,  $\text{C}_6\text{H}_{12}\text{O}_4\text{N}_2\text{S}$ , a thick, colourless oil,  $d_4^{20}$  1.2537,  $n_{\text{H}_a}^{20}$  1.48330,  $n_{\text{H}_B}^{20}$  1.49410, which with fuming hydrochloric acid is decomposed into nitrogen, methyl hydrazodicarboxylate, and ethyl disulphide. Ethylene glycol and methyl azodicarboxylate in cold ethereal solution in the presence of a little potassium acetate yield in 2—3 days a little dimethyl ethylene dicarbonate, and the *additive* compound,  $\text{C}_{10}\text{H}_{18}\text{O}_{10}\text{N}_4$ ,  $d_4^{20}$  1.3296,  $n_{\text{H}_a}^{20}$  1.44918,  $n_{\text{H}_B}^{20}$  1.45734, which dissociates in acetone yielding ethylene carbonate and hydrazo ester, whilst with potassium acetate reaction takes place, yielding nitrogen, methyl hydrazodicarboxylate, and *dimethyl ethylene dicarbonate*,  $(\text{CH}_2\cdot\text{O}\cdot\text{CO}_2\text{Me})_2$ , ester-like oil, b. p. 215—220°/760 mm., which on boiling in ether yields ethylene and dimethyl carbonates. R. B.

**Catalytic Decomposition of Hexahydro-aromatic and Saturated Aliphatic Hydrocarbons.** The Cracking of Petroleum. V. GRIGNARD and R. STRATFORD (*Compt. rend.*, 1924, **178**, 2149—2152).—The effect of aluminium chloride as a catalyst in the cracking of hydrocarbons was studied at temperatures between 120° and 150°, the proportion of catalyst used being 20—30%. *cyclo*Hexane and methyl*cyclo*hexane remained unchanged, whilst *o*-dimethyl- and, less readily, *p*-dimethyl-*cyclo*-



hexane were transformed into the *m*-compound. With derivatives having a side-chain of 2 or 3 carbon atoms, branched or not, about 1—5% was cracked, giving a saturated aliphatic hydrocarbon and polymerised *cyclohexene*, the remainder forming polymethyl*cyclohexanes* with the methyl groups in the meta positions to each other. *m*-Diethyl*cyclohexane* was chiefly converted into tetramethyl*cyclohexane* with some butane. The three butyl*cyclohexanes* were cracked to the extent of 13—15%, the normal and secondary compounds producing *n*-butane, the tertiary, a mixture of butanes. The uncracked portion gave tetramethyl*cyclohexanes*. Amyl- and isoamyl-*cyclohexanes* decompose to the extent of 70% and 42%, respectively, into methyl*cyclohexane* and butane, the rest isomerising to tetra- and penta-methyl*cyclohexanes*. *n*-Octane,  $\beta\zeta$ -dimethylhexane, *n*-decane,  $\beta\eta$ -dimethyloctane, and heptadecane all gave *n*-butane, the longer chains being broken at both ends simultaneously. A. COUSEN.

**0 : 1 : 3-dicycloHexane.** N. ZELINSKY and M. OUCHAKOFF (*Bull. Soc. chim.*, 1924, [iv], 35, 484—487).—0 : 1 : 3-dicycloHexane,  $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH} \\ \text{CH}_2 \cdot \text{CH} \end{smallmatrix} > \text{CH}_2$ , the simplest example of a combined three-

and five-membered ring, is prepared by reduction, with sodium and alcohol, of ethyl 2-ketocyclopentanecarboxylate to the corresponding glycol. The dibromide is formed by heating the latter under pressure with phosphorus tribromide at 100°, and by treatment with zinc powder gives dicyclohexane, b. p. 78—79.5°/745 mm. It is not affected by bromine. A. B. H.

**X-Ray Diffraction Patterns from Crystalline and Liquid Benzene.** E. D. EASTMAN.—(See ii, 448.)

**Sulphonation of *m*-Dinitrobenzene.** R. H. GRIFFITH (*J. Chem. Soc.*, 1924, 125, 1401—1402).—The direct sulphonation of *m*-dinitrobenzene with fuming sulphuric acid (18%  $\text{SO}_3$ ) at 150—160° in the presence of mercury yields 3 : 5-dinitrobenzenesulphonic acid (A., 1903, i, 407) in 38% of the theoretical yield. The product is sensitive to alkali, and apparently changes readily to a nitro-hydroxybenzenesulphonic acid. R. B.

**s-Tribromobenzyl Chloride and some of its Transformations.** M. HENRAUT (*Bull. Soc. chim. Belg.*, 1924, 33, 132—138).—Addition of benzyl chloride and bromine to anhydrous aluminium bromide yields 2 : 4 : 6-tribromobenzyl chloride, yellow crystals, m. p. 153—154°, which when oxidised by nitric acid under pressure is converted into 2 : 4 : 6-tribromobenzoic acid. The chloride reacts with potassium cyanide to form 2 : 4 : 6-tribromophenylacetoneitrile, a brown solid, m. p. 138—139°, which on hydrolysis at 150° with alcoholic potassium hydroxide affords 2 : 4 : 6-tribromophenylacetic acid, m. p. 157—158°, of which the chloride and the amide, m. p. 162—163°, were prepared. H. J. E.

**Polarity Effects in Aromatic Halogen Compounds.** J. B. SHOESMITH, A. C. HETHERINGTON, and R. H. SLATER (*J. Chem. Soc.*, 1924, 125, 1312—1319).—The hydrolysis of the isomeric

$\omega$ -bromotoluic acids in alcohol is in accordance with the principle of induced alternate polarities (T., 1922, **121**, 1392; 1923, **123**, 2828), the meta-isomeride being more readily hydrolysed than the para-, whilst with hydrogen iodide the para- is more readily reduced than the meta-isomeride. The behaviour of the ortho-compound is abnormal in both cases, owing to phthalide formation due to spatial influences. Since benzyl bromide is more readily hydrolysed than any of the  $\omega$ -bromotoluic acids, the introduction of the carboxyl group has stabilised the molecule as a whole. The hydrolysis of the nitrobenzyl bromides follows the same rule, the *m*-isomeride being the most readily hydrolysed, but the introduction of the nitro group into a very reactive molecule such as *p*-methoxybenzyl bromide diminishes the reactivity of the latter to the order of that of the unsubstituted compound. 3-Nitro-4-hydroxybenzyl bromide is more readily hydrolysed by aqueous alcohol than 3-nitro-4-methoxybenzyl bromide. The order of reduction of the halogenated phenols with hydriodic acid in acetic acid solution: *p*-iodo > *o*-iodo > *p*-bromo > *o*-bromo > *p*-chloro, is also in accordance with the theory. The *m*-isomerides showed no tendency to be reduced, and of the chlorophenols only the *p*-compound showed any reduction.  $\omega$ -Bromo-*p*-toluoyl bromide, b. p. 160—165°/14 mm., m. p. 39—40°, prepared by Davies and Perkin's method (T., 1922, **121**, 2202), yields  $\omega$ -bromo-*p*-toluic acid, m. p. 223° (Zalkind, A., 1914, i, 957), on warming with formic acid.  $\omega$ -Bromo-*m*-toluoyl bromide has b. p. 160—165°/14 mm., m. p. 23—25°. *o*-Nitrobenzyl bromide, light yellow plates, m. p. 45·5°, was obtained from *o*-nitrobenzyl chloride and phosphorus pentabromide. 3-Nitro-4-hydroxybenzyl bromide, yellow, prismatic needles, m. p. 82°, was obtained from dry hydrogen bromide and the alcohol in benzene solution. 3-Nitro-4-methoxybenzyl bromide, pale yellow needles, m. p. 108°, was similarly obtained from 3-nitro-4-methoxybenzyl alcohol. *m*-Bromophenol distils at 125—127°/12 mm. (cf. Diels and Bunzl, A., 1905, i, 431).

R. B.

**Solubility of 2 : 4 : 6-Trinitrotoluene, "Tetryl," and Tetra-nitroaniline in Organic Solvents.** L. DESVERGNES (*Mon. Sci.*, 1924, **14**, 121—130).—A detailed résumé of previous work by Taylor and Rinkenbach is given (A., 1923, i, 315, 320, 672). The solubility of 2 : 4 : 6-trinitrotoluene in 95% alcohol is 1·26 at 15°, 20·45 at 78·5°, and of trinitrophenylmethylnitroamine (tetryl) in water, 0·007 at 15°, 0·017 at 30°, 0·020 at 50°, 0·051 at 80°, 0·116 g. at 100°, per 100 g. of solvent in each case.

A. C.

**Specific Heats of Trinitrotoluene, "Tetryl," Picric Acid, and their Molecular Complexes.** C. A. TAYLOR and W. H. RINKENBACH (*J. Amer. Chem. Soc.*, 1924, **46**, 1504—1510).—The following specific heats were determined by means of the Dewar liquid oxygen calorimeter, using lead as the standard of comparison. Tetryl, 0°, 0·213; 125°, 0·235; picric acid, 0°, 0·234; 120°, 0·337; trinitrotoluene, 0°, 0·309; 80°, 0·374; tetryl-picric acid compound, 0°, 0·254; 80°, 0·311; tetryl-trinitrotoluene compound, 0°, 0·287; 60°, 0·349. Intermediate specific heats

are tabulated at  $10^\circ$  intervals, and equations deduced for the temperature-mean specific heat curves from  $-182.8^\circ$  to the highest temperature used for each substance. Kopp's law does not hold for trinitrotoluene, "tetryl," or picric acid. F. G. W.

### Specific Heat and Thermal Diffusivity of certain Explosives.

III. A. M. PRENTISS (*Army Ordnance*, 1924, 4, 242—246; cf. *ibid.*, 1923, 4, 184).—For trinitrotoluene, trinitroxylenes, and trinitrophenylmethylnitroamine, respectively, the specific heats are:  $0.3776$  ( $-200^\circ$  to  $+50^\circ$ ),  $0.3950$  ( $+20^\circ$  to  $50^\circ$ ),  $0.4233$  ( $+20^\circ$  to  $50^\circ$ ); the coefficients of conductivity at  $25^\circ$  are:  $0.00043$ ,  $0.00057$ ,  $0.00088$ , and the coefficients of diffusivity at  $25^\circ$ ,  $0.00197$ ,  $0.00225$ , and  $0.00388$ , respectively.

### CHEMICAL ABSTRACTS.

### Derivatives of Tetrahydro- and Decahydro-naphthalenes.

E. BÖDTKER and O. RAMBECH (*Bull. Soc. chim.*, 1924, [iv], 35, 631—638).—The authors confirm the observation of Schroeter (D.R.-P. 333158) that aluminium chloride reacts with tetrahydronaphthalene at the ordinary temperature with formation of benzene and octahydro-anthracene and -phenanthrene, and demonstrate that the reaction is reversible. Methyltetrahydronaphthalene could not be obtained by the Friedel-Crafts reaction, but tetrahydro-2-ethylnaphthalene (b. p.  $244^\circ$ ) was obtained in small yield. 2-isopropyltetrahydronaphthalene, b. p.  $255$ — $256^\circ$ ,  $d_4^{25}$   $0.9518$ ,  $n_D^{25}$   $1.5352$ , is obtained similarly from *n*-propyl chloride and tetrahydronaphthalene. The formation of 2-tert.-butyltetrahydronaphthalene, b. p.  $265.5$ — $266.5^\circ$ ,  $d_4^{25}$   $0.9463$ ,  $n_D^{25}$   $1.5348$ , is accompanied by evolution of isobutane. 2-tert.-amyltetrahydronaphthalene has b. p.  $149.2$ — $150^\circ/12$  mm.,  $d_4^{25}$   $0.9478$ ;  $n_D^{25}$   $1.5332$ , b. p.  $280^\circ/760$  mm., with partial decomposition. When decahydronaphthalene is boiled with aluminium chloride, a mixture of saturated hydrocarbons,  $C_{10}H_{18}$ , b. p.  $157$ — $250^\circ$ , is obtained.

F. G. W.

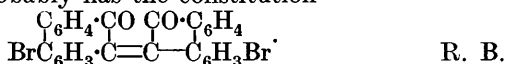
### Bromine Compounds of Phenanthrene. III. H. HENSTOCK

(*J. Chem. Soc.*, 1924, 125, 1296—1299).—The bromination of potassium phenanthrene-2-sulphonate in aqueous solution yields a product giving a brilliant dark green barium salt, which in the absence of ammonium chloride changes almost instantaneously to a brown powder, normal barium 10-bromo-9-hydroxyphenanthrene-2-sulphonate. The green barium salt on acidifying with hydrochloric acid yields an acid,  $C_{14}H_9OBr \cdot SO_3H$ , bright blue, amorphous powder, which is much more stable than the salt and probably

possesses the constitution: 
$$\begin{array}{c} C_6H_4 \cdot CO \\ | \\ SO_3H \cdot C_6H_3 \cdot CHBr \end{array}$$
 With dry bromine

vapour, potassium phenanthrene-2-sulphonate is converted into an orange-yellow dibromide,  $C_{14}H_9Br_2 \cdot SO_3K$ , fuming in air through loss of hydrogen bromide, which on heating yields the yellow potassium 10-bromo-9-hydroxyphenanthrene-2-sulphonate. The free acid, granular, white powder, obtained from the silver salt, yields a colourless, doubly-refracting jelly with concentrated hydrochloric acid, and the bromine is therefore in position 10 (cf. Sandqvist, A., 1919, i, 120; 1920, i, 300). Sodium, ferric, ammonium, basic

barium,  $C_{14}H_7(OH)Br \cdot SO_3Ba(OH)$ , normal and basic lead salts,  $[C_{14}H_7(OH)BrSO_3]_8Pb_3$ , are described. 9:10-Dibromophenanthrene-2-sulphonyl bromide, yellow, amorphous powder, has m. p.  $204^\circ$ . The scarlet substance previously obtained by treating 2:10-dibromophenanthrene with alcoholic potassium hydroxide (T., 1921, 119, 59) has the composition  $C_{28}H_{14}O_2Br_2$ , yields *p*-bromodiphenic acid, m. p.  $237-238^\circ$  (cf. Schmidt and Junghans, A., 1904, i, 1033) on oxidation, and probably has the constitution



**Space Lattice of Triphenylmethane.** K. BECKER; H. MARK and K. WEISSENBERG.—(See ii, 449.)

**Triphenylmethyl Fluoride.** F. F. BLICKE (*J. Amer. Chem. Soc.*, 1924, 46, 1515—1518).—Triphenylmethyl fluoride, m. p.  $102-104^\circ$ , was obtained by the action of acetyl fluoride on triphenylcarbinol suspended in benzene. It is much less reactive than the corresponding compounds of the other halogens, remaining unaffected after shaking for 24 hours in benzene solution, with 10 mols. of molecular silver, mercury, zinc, copper, bronze, or magnesium, and on boiling with excess of silver in benzene for 6 hours in an atmosphere of nitrogen. It is reduced by zinc chloride in ether, and oxidised by potassium permanganate in acetone, with quantitative formation of triphenylmethane and triphenylcarbinol, respectively. It condenses slowly with amines, and with magnesium phenyl bromide yields triphenylmethyl, triphenylcarbinol, and a red oil, but no tetraphenylmethane. F. G. W.

**Action of Formaldehyde on Formylated Aromatic Amines and on Isatin.** A. REISSERT and A. HÄNDELER (*Ber.*, 1924, 57, [B], 989—996).—Formanilide is slowly converted by formaldehyde in aqueous alkaline solution into formic acid, and formylmethylenedianiline,  $CHO \cdot NPh \cdot CH_2 \cdot NPh$ , m. p.  $93^\circ$ , the constitution of which is established by its reduction with sodium amalgam to aniline, methylaniline, and formic acid; the benzoyl derivative has m. p.  $119^\circ$ . Boiling, aqueous potassium cyanide solution transforms formylmethylenedianiline into aniline, anilinoacetamide, m. p.  $141^\circ$ , anilinoacetic acid, and anilinodiaceticmonoamide,  $CO_2H \cdot CH_2 \cdot NPh \cdot CH_2 \cdot CO \cdot NH_2$ , m. p.  $217^\circ$ . Formylmethylenedio-toluidine has m. p.  $108-109^\circ$  (benzoyl derivative, m. p.  $130^\circ$ ). Formylmethylenedi-p-toluidine has m. p.  $92-93^\circ$  (benzoyl derivative, m. p.  $120-121^\circ$ ).

1-Hydroxymethylisatin, red crystals, m. p.  $156-157^\circ$ , is the main product of the interaction of equimolecular proportions of isatin and formaldehyde in boiling aqueous solution. The oxime, reddish-yellow needles, m. p.  $138^\circ$  (decomp.), phenylhydrazone, m. p.  $180-181^\circ$ , acetate, m. p.  $112-113^\circ$ , and benzoate, m. p.  $124-125^\circ$ , are described. Methylenedi-isatin,  $\left[ CO \begin{array}{c} \diagup CO \\ \diagdown C_6H_4 \end{array} \diagup N \right]_2 CH_2$ , a yellow, crystalline powder, decomp.  $287^\circ$  [dioxime, m. p.  $230-231^\circ$  (decomp.)]; monophenylhydrazone, decomp.  $289-290^\circ$  is obtained as a by-product in the preparation of 1-hydroxymethylisatin. Isatic

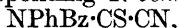
acid is converted by ice-cold formaldehyde solution into "*methylene-di-isatin hydrate*,"  $C_{17}H_{12}O_5N_2$ , decomp.  $262-264^\circ$ , after darkening at  $230^\circ$ , the constitution of which has not been elucidated. It yields a *monoxime*, m. p.  $208^\circ$ , and is converted by boiling methyl alcohol into methylenedi-isatin.

H. W.

### Action of Potassium Cyanide on Aromatic Mustard Oils.

A. REISSERT and K. BRÜGGEMANN (*Ber.*, 1924, 57, [B], 981—989).  
—An extension of previous work (Reissert, A., 1904, i, 990).

Thio-oxanilonitrile is converted by benzoyl chloride and sodium carbonate into the corresponding *N*-benzoyl derivative,



red needles, m. p.  $103^\circ$ , which is mixed with the *amide*, yellow needles, m. p.  $218^\circ$ , if sodium hydroxide is substituted for the carbonate. *Methylthio-oxanilonitrile* is a viscous, orange-coloured liquid, b. p.  $160^\circ/23$  mm., from which methylaniline is obtained by the action of alkalis. Thio-oxanilothioamide, m. p.  $98^\circ$ , is readily prepared by the action of yellow ammonium sulphide on thio-oxanilonitrile. The latter substance is transformed by ethyl alcohol and hydrogen chloride in the presence of an inert solvent into *ethyl imidothio-oxanilate*,  $NHPh \cdot CS \cdot C \cdot NH(OEt)$ , yellow needles, m. p.  $73^\circ$ ; the corresponding *hydrochloride*, m. p.  $166^\circ$ , is converted by alcohol into ethyl thio-oxanilate, m. p.  $38-40^\circ$ . Thio-oxanilonitrile is converted by aniline in boiling benzene into *phenylimido-oxanilonitrile*,  $NHPh \cdot C(CN) \cdot NPh$ , m. p.  $137^\circ$ , the yield being poor. *Thio-oxalo-o-toluidinonitrile*,  $C_7H_7 \cdot NH \cdot CS \cdot CN$ , orange-coloured needles, m. p.  $64^\circ$ , is converted into the corresponding *benzoyl* derivative, m. p.  $103^\circ$ , the *amide*, yellow needles, m. p.  $117^\circ$ , and the *thioamide*, pale red needles, m. p.  $90^\circ$ . *Thio-oxalo-p-toluidinonitrile*, yellow needles, m. p.  $127-128^\circ$ , is converted by the methods used with the phenyl compound into the *benzoyl* derivative, m. p.  $123^\circ$ , *amide*, m. p.  $169^\circ$ , *thioamide*, m. p.  $128^\circ$ , *ethyl imidothio-oxalo-p-toluidinate*,  $C_7H_7 \cdot NH \cdot CS \cdot C \cdot NH(OEt)$ , m. p.  $73^\circ$  (*hydrochloride*, m. p.  $166-167^\circ$ ), *ethyl thio-oxalo-p-toluidinate*, m. p.  $82^\circ$ , and *thio-oxalo-p-toluidinic acid*, m. p.  $130^\circ$ . *Thio-oxalo-m-xylydinonitrile*, yellow needles, m. p.  $98^\circ$ , yields the corresponding *amide*, m. p.  $147^\circ$ , *thioamide*, m. p.  $136^\circ$ , and *benzoyl* derivative, m. p.  $104^\circ$ . *Thio-oxalo- $\alpha$ -naphthylaminonitrile*, pale red needles, m. p.  $136^\circ$ , gives rise to the corresponding *amide*, m. p.  $199^\circ$ , and *thioamide*, m. p.  $147^\circ$ ; the *benzoyl* derivative, red needles, m. p.  $135^\circ$ , is converted by exposure to sunlight into the colourless *dimeride*, m. p.  $165-166^\circ$ . *Thio-oxalo- $\beta$ -naphthylaminonitrile* crystallises in yellow needles, m. p.  $157^\circ$ .

The action of hydrogen peroxide on the thionitriles leads mainly to the production of derivatives of oxamide. The thioamides are converted by potassium ferricyanide into thiazole derivatives, of which the following are described: 3-methylbenzthiazole-1-carboxyl-*amide*, m. p.  $163^\circ$ , and the corresponding *acid*, m. p.  $110-111^\circ$ ; 5-methylbenzthiazole-1-carboxyl-*amide*, m. p.  $243^\circ$ , the corresponding *acid*, m. p.  $110-111^\circ$  (decomp.), and its *silver* salt and *methyl* ester, m. p.  $96^\circ$ ; 3:5-dimethylbenzthiazole-1-carboxyl-*amide*, m. p.  $192^\circ$ ,

and the corresponding *acid*, m. p.  $114^{\circ}$ ;  $\alpha$ -*naphththiazole-1-carboxylamide*, m. p.  $210^{\circ}$ , and  $\alpha$ -*naphththiazole-1-carboxylic acid*, m. p.  $129-130^{\circ}$ .  
H. W.

**Salts of Phenyldiguanidine.** E. ROMANI (*Caoutchouc et Gutta-Percha*, 1923, **20**, 12005—12008).—An investigation of the utility of derivatives of guanidine as accelerators for the vulcanisation of caoutchouc.  $\alpha$ -*Phenyldiguanidine carbonate*,  $R_2H_2CO_3$  [where  $R = NH \cdot C(NHPh) \cdot NH \cdot C(NH_2) \cdot NH$ ], has m. p.  $128-130^{\circ}$ ; *carbamide*, m. p.  $216-218^{\circ}$ ; *hydrosulphide*,  $R_2H_2S$ , m. p.  $155^{\circ}$ ; *polysulphide*,  $R_2H_2S_2$ , m. p.  $209-210^{\circ}$ ; *thiocyanate*,  $R_2HSCN$ , nacreous, m. p.  $232^{\circ}$ ; *thiocarbamide*, m. p.  $142-143^{\circ}$ . *Phenyldiguanidinoethylthiocarbamide* has m. p.  $246^{\circ}$ ; *phenyldiguanidinophenylthiocarbamide* was prepared. *Phenyldiguanidine dithiocarbamate* has m. p.  $106^{\circ}$ ; *dithiophenylcarbazinate*, m. p.  $142^{\circ}$ ; *piperidylthiocarbamate*, m. p.  $94-95^{\circ}$ ; *phenyldithiocarbamate*, m. p.  $140^{\circ}$ ; *ethylxanthate*, pale yellow, m. p.  $128^{\circ}$ ; *dithiopyromucate*, garnet red, m. p.  $158^{\circ}$ ; *mercaptobenzthiazole* compound, yellow, m. p.  $160$ ; *zincate* (cf. Cohn, A., 1911, i, 928).

## CHEMICAL ABSTRACTS.

**Action of Carbon Dioxide on Phenoxides.** H. MEYER (*Z. anal. Chem.*, 1924, **64**, 72—81).—The passage of carbon dioxide through solutions of alkali phenoxides at  $0^{\circ}$  produces crystalline precipitates consisting of definite compounds of the free phenol with the alkali phenoxide. Some of these substances may be purified by recrystallisation from organic solvents whilst others are decomposed in these media into the phenol which dissolves and the alkali phenoxide which remains insoluble. The following compounds have been prepared:  $PhOK \cdot 3PhOH$ , long, thin, colourless needles, m. p.  $114^{\circ}$ ;  $p\text{-}C_6H_4Me \cdot OK \cdot 3p\text{-}Me \cdot C_6H_4 \cdot OH$ , m. p.  $148^{\circ}$ ;  $o\text{-}NO_2 \cdot C_6H_4 \cdot OK \cdot o\text{-}NO_2 \cdot C_6H_4 \cdot OH, 3H_2O$ , golden-yellow leaflets,  $o\text{-}NO_2 \cdot C_6H_4 \cdot ONa \cdot o\text{-}NO_2 \cdot C_6H_4 \cdot OH, 6H_2O$ , red crystals, and  $o\text{-}NO_2 \cdot C_6H_4 \cdot ONH_4 \cdot o\text{-}NO_2 \cdot C_6H_4 \cdot OH, H_2O$ , yellowish-brown leaflets;  $m\text{-}NO_2 \cdot C_6H_4 \cdot OK \cdot 2m\text{-}NO_2 \cdot C_6H_4 \cdot OH, 5H_2O$ , brown crystals decomposed on warming;  $p\text{-}NO_2 \cdot C_6H_4 \cdot OK \cdot p\text{-}NO_2 \cdot C_6H_4 \cdot OH, 3H_2O$ , short, thick, ochre-yellow needles, m. p.  $170^{\circ}$  (decomp.),  $2p\text{-}NO_2 \cdot C_6H_4 \cdot ONa \cdot 3p\text{-}NO_2 \cdot C_6H_4 \cdot OH, 3H_2O$ , thick, brownish-yellow needles, m. p.  $156^{\circ}$  (decomp.),  $p\text{-}NO_2 \cdot C_6H_4 \cdot ONH_4 \cdot p\text{-}NO_2 \cdot C_6H_4 \cdot OH, H_2O$ , small yellow leaflets, m. p.  $126-130^{\circ}$  (decomp.); from 3-nitro-*p*-cresol,  $NO_2 \cdot C_7H_6 \cdot OK \cdot 5NO_2 \cdot C_7H_6 \cdot OH, 8H_2O$ , reddish-brown crystals, m. p.  $53^{\circ}$ ,  $NO_2 \cdot C_7H_6 \cdot ONa \cdot 7NO_2 \cdot C_7H_6 \cdot OH, 8H_2O$ ,  $NO_2 \cdot C_7H_6 \cdot ONH_4 \cdot 2NO_2 \cdot C_7H_6 \cdot OH, 4H_2O$ , yellow powder, m. p.  $140^{\circ}$  (decomp.);  $\alpha\text{-}C_{10}H_7 \cdot OK \cdot 4\alpha\text{-}C_{10}H_7 \cdot OH, 5H_2O$ , green, amorphous powder;  $\beta\text{-}C_{10}H_7 \cdot OK \cdot 2\beta\text{-}C_{10}H_7 \cdot OH, 5H_2O$ , colourless crystals; from pyrocatechol,  $OH \cdot C_6H_4 \cdot OK \cdot C_6H_4(OH)_2, 2H_2O$ , colourless crystals,  $2OH \cdot C_6H_4 \cdot ONa \cdot C_6H_4(OH)_2, 6H_2O$ , colourless, glistening crystals; from quinol, colourless crystals,  $OH \cdot C_6H_4 \cdot OK \cdot 7C_6H_4(OH)_2$

and  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{ONa}, 4\text{C}_6\text{H}_4(\text{OH})_2$ ; from guaiacol,  
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OK}, \text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OH}, 1.5\text{H}_2\text{O}$ ,  
 large colourless needles, m. p.  $186^\circ$  (decomp.),  
 $2\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{ONa}, 5\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OH}, 2\text{H}_2\text{O}$ ,  
 colourless crystals, m. p.  $139^\circ$ ; from 4-nitroguaiacol,  
 $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\text{OK}, \text{OMe}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{OH}, 3\text{H}_2\text{O}$ ,  
 yellow crystals, m. p.  $169\text{--}171^\circ$ ; from 5-chloroguaiacol,  
 $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{OK}, \text{OMe}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{OH}, 2\text{H}_2\text{O}$ ,  
 yellowish-white, very stable needles, m. p.  $146^\circ$ . In purifying  
 phenols by the carbon dioxide method, the substance should be  
 dissolved in sodium hydroxide and the gas passed through the  
 warm solution for a prolonged period to avoid contamination of  
 the precipitate by complex compounds. A. R. P.

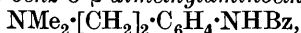
**Sulphonation of *m*-Cresol and its Methyl Ether.** R. D. HAWORTH and A. LAPWORTH (*J. Chem. Soc.*, 1924, **125**, 1299—1307; cf. T., 1923, **123**, 2982).—The sulphonation of *m*-cresol with concentrated sulphuric acid at  $30\text{--}35^\circ$  yields *m*-cresol-4- and -6-sulphonic acids in the ratio 1 : 2.7; the 6-sulphonic acid is also the main product at  $120^\circ$  (cf. Claus and Krauss, A., 1888, 280). The acids were separated by means of their barium salts and identified by methylation of the potassium salts to the corresponding 3-methoxytoluenesulphonates.

[With M. L. WILSON.]—Sulphonation with chlorosulphonic acid (1 mol.) in carbon disulphide at  $-15^\circ$  yields potassium *m*-tolyl sulphate (Verley, A., 1901, i, 143) and potassium *m*-cresol-6-sulphonate. In the presence of pyridine, 70% of the theoretical yield of potassium *m*-tolyl sulphate was obtained. On heating the mixture at  $100^\circ$ , after distilling off the carbon disulphide, *m*-cresol-6-sulphonic acid alone was obtained. The *barium* (decomp.  $180^\circ$ ), *ammonium*, *ferrous*, *zinc*, and *potassium* salts of *m*-cresol-6-sulphonic acid are described, and the *barium* (decomp.  $150^\circ$ ), *copper*, and *potassium* salts of *m*-cresol-4-sulphonic acid. With 2 or 3 mols. of chlorosulphonic acid below  $35^\circ$  *m*-cresol yields *m*-cresol-4 : 6-disulphonic acid (*barium* salt), the product, after distilling off the carbon disulphide, being heated at  $100^\circ$  to ensure migration of the sulphonic group to the nucleus. No *m*-cresolsulphonyl chloride was produced. Sulphonation of *m*-tolyl methyl ether with chlorosulphonic acid at  $-15^\circ$  gave only 3-methoxytoluene-6-sulphonic acid in good yield. Nitration of potassium *m*-cresol-6-sulphonate in acetic acid gives *potassium 4-nitro-m-cresol-6-sulphonate*, pale yellow prisms, potassium 6-nitro-*m*-cresol-4-sulphonate being similarly obtained from the 4-sulphonate. Both nitro compounds on heating with hydrochloric acid in a sealed tube yield the corresponding nitrocresol. Oxidation of potassium 3-methoxytoluene-6-sulphonate with potassium permanganate yields the *potassium hydrogen 3-methoxy-6-sulphobenzoate*, whereas oxidation of the corresponding sulphonamide yields 5-methoxy-*o*-benzoic sulphinide, m. p.  $242^\circ$ , also prepared from the potassium hydrogen salt. Potassium 3-methoxytoluene-4-sulphonate similarly yields the *potassium hydrogen 3-methoxy-4-sulphobenzoate* and 3-methoxy-4-sulphamido-

*benzoic acid*, m. p. 254—255°, which is also obtained by the oxidation of 3-methoxytoluene-4-sulphonamide with alkaline permanganate. 3-Methoxytoluene-2-sulphonamide similarly yields 3-methoxy-*o*-benzoic acid, m. p. 227—228° (decomp.).

R. B.

***o*-Hordenine** [***o*- $\beta$ -Dimethylaminoethylphenol**]. J. VON BRAUN and O. BAYER (*Ber.*, 1924, 57, [B], 913—914).—Benz-*o*- $\beta$ -chloroethyl-anilide is converted by dimethylamine in benzene solution at 100° into benz-*o*- $\beta$ -dimethylaminoethyl-anilide,



m. p. 95°; the hygroscopic *hydrochloride* and the *picrate*, m. p. 160°, are described. It is hydrolysed by hydrochloric acid at 150° to *o*- $\beta$ -dimethylaminoethyl-aniline, b. p. 129°/12 mm., m. p. 45°, which yields a very hygroscopic *hydrochloride* and a *chloroplatinate*, decomp. 209°. The base is converted through the diazonium compound into *o*- $\beta$ -dimethylaminoethylphenol, a pale yellow liquid, b. p. 136—137°/13 mm., which could not be caused to crystallise; the hygroscopic *hydrochloride*, *chloroplatinate*, m. p. 144°, *sulphate*, *picrate*, m. p. 142°, and quaternary methiodide, m. p. 218°, are described. The physiological action of *o*- $\beta$ -dimethylaminoethylphenol is much weaker than that of hordenine.

H. W.

#### Catalytic Hydrogenation of *p*- and *o*-Hydroxydiphenyl.

J. RANEDO and A. LEÓN (*Anal. Fis. Quím.*, 1924, 22, 222—232; cf. A., 1923, i, 909).—Catalytic perhydrogenation of *p*-hydroxydiphenyl in presence of platinum black yields two isomerides identical with those obtained from *o*-cyclohexylphenol by Schrauth and Görig (A., 1923, i, 1084). Perhydrogenation of *o*-hydroxydiphenyl yields a cyclohexylcyclohexanol having b. p. 172—177°/75 mm., m. p. 63°. By oxidation a ketone is obtained identical with that obtained by Schrauth and Görig from the oxidation of the above isomerides.

G. W. R.

#### Lichen Products. IV. Synthesis of Divarinol.

A. SONN and B. SCHEFFLER (*Ber.*, 1924, 57, [B], 959—961).—Methyl 3 : 5-dimethoxybenzoate is condensed with ethyl acetate and sodium to ethyl 3 : 5-dimethoxybenzoylacetate, b. p. 189—191°/28 mm., which is methylated with sodium ethoxide and methyl sulphate and then submitted to simultaneous ketonic fission and reduction by Clemmensen's method, thus yielding 3 : 5-dimethoxypropylbenzene, b. p. 147—148°/29 mm. (cf. Mauthner, this vol., i, 524). The latter substance is more readily obtained by treating the fraction of beechwood tar, b. p. 265—295°, with hot potassium hydroxide solution, whereby a mixture of the potassium salts of 5-*n*-propylpyrogallol mono- and di-methyl ethers separates. This, on methylation, gives 5-*n*-propylpyrogallol trimethyl ether, b. p. 263—265°, which is reduced by sodium and alcohol to 3 : 5-dimethoxypropylbenzene, b. p. 145—147°/27 mm. The latter substance is converted by hydriodic acid (*d* 1.7) into divarinol. Myristicin is also converted by sodium and alcohol into divarinol. The introduction of the aldehydic group into divarinol by Gattermann's method gives a substance, b. p. 184—185°.

H. W.



**Effect of Temperature and of Medium in the Dehydration of  $\alpha$ -Phenylethyl Alcohol.** R. DESCAMPS (*Bull. Soc. chim. Belg.*, 1924, **33**, 139—145; cf. Wuyts, A., 1921, i, 506).—In the dehydration of  $\alpha$ -phenylethyl alcohol by means of *p*-toluenesulphonic acid in the absence of a solvent, the proportion of styrene obtained decreases with temperature, *e.g.*, 7.31% at 82.6°, 0.8% at 48.4°. Camphorsulphonic acid under similar conditions produces a smaller proportion of the hydrocarbon, whilst in presence of benzene as solvent the proportion is increased. In presence of carbon disulphide at 48.4°, the proportion of alcohol converted into styrene is 0.58%. The yield of ether in all the cases studied was good.

H. J. E.

**Tervalent Carbon. II. Conversion of the Ethers of Tertiary Alcohols into Organic Potassium Compounds and Hexa-substituted Ethane Derivatives.** K. ZIEGLER and B. SCHNELL (*Annalen*, 1924, **437**, 227—255; cf. this vol., i, 308).—

The reaction of triphenylmethyl alkyl ethers with potassium (A., 1923, i, 921) has now been utilised in the conversion of tertiary ethers into hexa-substituted ethanes. Diphenylalkylcarbinols,  $\text{OH}\cdot\text{CPh}_2\text{R}$ , in cold methyl-alcoholic solution in the presence of 2% of sulphuric acid (cf. this vol., i, 509) are converted into the corresponding methyl ethers. At higher temperatures the ethers are converted into ethylene derivatives, showing that this is the final stage of the reaction. Confirmation of this conclusion is found in the fact that  $\alpha\alpha$ -diphenylpropylene is unchanged by methyl alcohol. With phenyldialkylcarbinols the reaction is slower and the ethers must be prepared at higher temperatures with consequent loss of yield. When the corresponding chloride is available, *e.g.*,  $\beta$ -phenylisopropyl chloride, the ether can be obtained in good yield by the action of methyl alcohol. On shaking with potassium in cold ethereal solution, the diphenyl tertiary ethers are converted into potassium compounds:  $\text{CPh}_2\text{R}\cdot\text{OMe} \rightarrow \text{CPh}_2\text{R}\cdot\text{K}$ . Phenyl tertiary ethers, *e.g.*, phenyldibenzylmethyl methyl ether,



and  $\beta$ -phenylisopropyl methyl ether,  $\text{CPhMe}_2\cdot\text{OMe}$ , react less readily and ethers such as *tert.*-butyl methyl ether, terpeneol methyl ether, and camphene hydrate methyl ether, in which no phenyl group is attached to the tertiary carbon atom, are not attacked by potassium. On treatment with tetramethylene dibromide, these potassium compounds are decomposed, yielding hexa-substituted ethanes:  $\text{CPh}_2\text{R}\dots\text{K} \rightarrow (\cdot\text{CPh}_2\text{R})_2$ , and in some cases the reverse reaction takes place on treating the substituted ethane with potassium. The dissociation capacity of the substituted ethanes is discussed in relation to the valency considerations advanced by Wieland, Meerwein, and Skraup.

$\alpha\alpha$ -Diphenylethyl methyl ether,  $\text{CPh}_2\text{Me}\cdot\text{OMe}$ , white needles, m. p. 35—36°, yields potassium  $\alpha\alpha$ -diphenylethyl, brick-red powder, which with carbon dioxide gives 80—90% of the theoretical yield of  $\alpha\alpha$ -diphenylpropionic acid, and with benzyl chloride yields  $\alpha\beta\beta$ -triphenylpropane,  $\text{CPh}_2\text{Me}\cdot\text{CH}_2\text{Ph}$ , dense prisms, m. p. 116—117°.

With tetramethylene dibromide in the cold, the potassium compound yields  $\beta\beta\gamma\gamma$ -tetraphenylbutane, m. p. 126—127°. On heating, its carbon tetrachloride solution becomes unsaturated and takes up bromine, yielding  $\beta\beta$ -diphenylvinyl bromide, in consequence of decomposition into  $\alpha\alpha$ -diphenylethane and  $\alpha\alpha$ -diphenylethylene.  $\alpha\alpha$ -Diphenylpropyl methyl ether,  $\text{CPh}_2\text{Et}\cdot\text{OMe}$ , dense, triangular plates, m. p. 68—69°, yields potassium  $\alpha\alpha$ -diphenylpropyl, red oil, converted into  $\alpha\alpha$ -diphenylbutyric acid by carbon dioxide.  $\gamma\gamma\delta\delta$ -Tetraphenylhexane, m. p. 85—86°, obtained from this potassium compound, gradually dissociates in solution but no satisfactory reaction constant was obtained. The cold, freshly-prepared solution in carbon disulphide is saturated, but gradually becomes unsaturated and 1 mol. of bromine is taken up.  $\alpha\alpha\beta$ -Triphenylethyl methyl ether,  $\text{CH}_2\text{Ph}\cdot\text{CPh}_2\cdot\text{OMe}$ , flat, sword-like cusps or radial prisms, m. p. 93—94°, gives potassium  $\alpha\alpha\beta$ -triphenylethyl, small, brown crystals with blue lustre, yielding  $\alpha\alpha\beta$ -triphenylpropionic acid (this vol., i, 171) with carbon dioxide and  $\alpha\beta\beta$ -triphenylpropane on treatment with methyl iodide. Attempts to obtain  $\alpha\beta\beta\gamma\delta$ -hexaphenylbutane were unsuccessful, and only resinous substances were formed, evidently mixtures of the two decomposition products  $\alpha\alpha\beta$ -triphenylethane and  $\alpha\alpha\beta$ -triphenylethylene. Diphenylcyclohexylmethyl methyl ether,  $\text{C}_6\text{H}_{11}\cdot\text{CPh}_2\cdot\text{OMe}$ , laminated prisms, m. p. 69—70°, yields potassium diphenylcyclohexylmethyl, bright red, which with alcohol is converted into diphenylcyclohexylmethane and with carbon dioxide gives diphenylcyclohexylacetic acid, microcrystalline powder, m. p. 202—203°. Tetramethylene dibromide converts the potassium compound into a sparingly soluble colourless substance which is probably  $\alpha\alpha\beta\beta$ -tetraphenyl- $\alpha\beta$ -dicyclohexylethane. This substance in chloroform solution readily absorbs bromine, iodine, and oxygen, yielding in the latter case a thick oil, probably a peroxide. Treatment with potassium-sodium alloy yields the original potassium diphenylcyclohexylmethyl.  $\alpha\beta\beta'$ -Triphenylisopropyl methyl ether, lustrous needles, m. p. 105—106°, gives a brownish-violet potassium  $\alpha\beta\beta'$ -triphenylisopropyl, which with carbon dioxide yields  $\alpha\beta\beta'$ -triphenylisobutyric acid,



m. p. 125—126°, and with tetramethylene dibromide,  $\alpha\beta\gamma\delta$ -tetraphenyl- $\beta\gamma$ -dibenzylbutane, m. p. 126—127°, which shows no tendency to dissociate in solution.  $\beta$ -Phenylisopropyl methyl ether, from  $\beta$ -phenylisopropyl chloride, colourless oil, b. p. 78°/13 mm., with an odour resembling camphor and peppermint, gives the deep red potassium  $\beta$ -phenylisopropyl, which with carbon dioxide yields  $\alpha$ -phenylisobutyric acid.

R. B.

### Thiophenols. VI. Thiophenol Ethers of Triphenylmethane and the Bathochromic Action of Alkylthiol Groups.

K. BRAND and O. STALLMANN (*J. pr. Chem.*, 1924, [ii], 107, 358—382). —The corresponding carbinol (A., 1921, i, 664) is reduced by zinc and acetic acid to *o*-methylthioltriphenylmethane, colourless tablets, m. p. 111°. This combines with methyl sulphate to form a *sulphonium methyl sulphate*,  $\text{CHPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{SMe}_2\cdot\text{SO}_4\text{Me}$ , colourless scales,

m. p. 163°; the corresponding *iodide* is very unstable. *o*-Methylthioltriphenylmethyl chloride, formed when the carbinol is treated with ethereal hydrogen chloride, crystallises in needles, m. p. 126°, and yields unstable coloured compounds with ferric and stannic chlorides. *oo'*-Dimethylthioltriphenylmethane, m. p. 100·5°, was obtained satisfactorily by reducing the corresponding carbinol, not with zinc and acetic acid, but with alcoholic hydrogen chloride (Kaufmann, A., 1912, i, 351). The corresponding *chloride* forms fine needles, m. p. 164° (decomp.), and also yields unstable compounds with ferric and stannic chlorides. *oo'o''*-Trimethylthioltriphenylcarbinol is formed by interaction of magnesium *o*-methylthiolphenyl bromide and methyl *o*-methylthiolbenzoate; it crystallises from alcohol in prisms, m. p. 180°, but from chloroform or benzene in octahedra, m. p. 190°. It yields the corresponding *methane* derivative, m. p. about 176°, and *chloride*, colourless rods, m. p. 140° (decomp.).

*p*-Methylthioltriphenylcarbinol is formed together with much *pp'*-dimethylthioldiphenyl, by interaction of magnesium *p*-methylthiolphenyl bromide and benzophenone (cf. Bistrzycki and Kuba, A., 1922, i, 33). By methods analogous to those described above, the following *p*-substituted derivatives were prepared: *pp'*-dimethylthioltriphenylcarbinol, forming needles, m. p. 110—111°, and yielding a *perchlorate*, bronzy needles, m. p. 195° (decomp.), and *double chlorides* with mercuric chloride (green needles, m. p. 122°, decomposed by water) and stannic chloride (green needles, m. p. 205—207°, unstable); *pp'*-dimethylthioltriphenylmethane, needles, m. p. 63°; *pp'*-dimethylthioltriphenylmethyl chloride, m. p. 122°; *pp'p''*-trimethylthioltriphenylcarbinol (the requisite methyl *p*-methylthiolbenzoate was obtained from *p*-cyanophenyl methyl sulphide), colourless needles, m. p. 128°, yielding a *perchlorate*, bright bronze rods, m. p. 220° (decomp.), and *double salts* with mercuric chloride (bronzy-green needles, m. p. 163—165°) and stannic chloride (prisms, m. p. about 210°). The corresponding *methane* forms colourless needles, m. p. 95·5°; *chloride*, m. p. 152°. Various colour reactions of all these substances are described.

*oo'*-Dimethylthioldiphenyl was prepared by treating *o*-iodophenyl methyl sulphide with copper bronze at 200—250°; it forms feathery crystals, m. p. 158·5°. W. A. S.

**Thiophenols. VII. Simple Method of preparing *p*-Methylthiol- and *pp'*-Dimethylthiol-triphenylcarbinols.** K. BRAND and W. VOGT (*J. pr. Chem.*, 1924, [ii], 107, 383—390).—By reactions resembling those of Döbner's malachite-green synthesis, phenyl methyl sulphide heated with benzophenone chloride and aluminium chloride in carbon disulphide solution yields *p*-methylthioltriphenylcarbinol, and with benzotrichloride and zinc chloride, *pp'*-dimethylthioltriphenylcarbinol (cf. preceding abstract). When equimolecular proportions of phenyl methyl sulphide and benzotrichloride are used, the product is *p*-methylthiolbenzophenone, m. p. 72—73°, which yields two *oximes*, m. p. 138° and 105°, respectively.

*p*-Methylthioltriphenylcarbinol gives violet-red, and *pp'*-dimethylthioltriphenylcarbinol bluish-green salts with mineral acids.

W. A. S.

**Action of Organo-magnesium Compounds on Nitriles.** E. ECTORS (*Bull. Soc. chim. Belg.*, 1924, **33**, 146—159).—Benzonitrile acts on magnesium methyl bromide with formation of acetophenone (80% yield) together with *s*-triphenylpyridine; with magnesium ethyl bromide it yields phenyl ethyl ketone, no other product being isolated. With magnesium benzyl chloride, it forms phenyl benzyl ketone, the dimeride of phenyl benzyl ketimine, and a third substance,  $C_{21}H_{18}N_2$ . The dimeride is shown to be 3:4:5:6-tetraphenylhexahydro-1:2-diazine, fine needles, m. p. 192°, whilst the third product proved to be 3:4:5-triphenylpyrazoline, m. p. 152°, *hydrochloride*, m. p. 221° (decomp.). Benzonitrile is differentiated from aliphatic compounds such as phenylacetone in its action on organo-magnesium compounds by the formation of such condensation products in addition to the high yield of ketone obtained (cf. Blaise, A., 1912, i, 164). H. J. E.

**Reaction Velocity of Rearrangement of Potassium Dibenzhydroxamate.** G. DOUGHERTY and L. W. JONES (*J. Amer. Chem. Soc.*, 1924, **46**, 1535—1539).—The rearrangement of potassium dibenzhydroxamate (5.5 g. per litre) under the influence of an equivalent of potassium hydroxide, at 25°, is unimolecular for the last 75% of the reaction period, and is represented by the scheme  $COPh \cdot NK \cdot O \cdot COPh \rightarrow COPh \cdot OK + COPh \cdot N:$ ;  $COPh \cdot N: \rightarrow NPh \cdot C:O$ . The apparent deviation during the first 25% of the reaction time is due to the hydrolysis of the dibenzhydroxamic acid to monobenzhydroxamic and benzoic acids, the consequent increase in acidity of the reaction mixture, above that required by the actual rearrangement, ceasing as the unimolecular reaction constant assumes a steady value. F. G. W.

**Correlation of Additive Reactions with Tautomeric Change.** III. **The Cyano-imino Additive Process.** E. H. INGOLD (*J. Chem. Soc.*, 1924, **125**, 1319—1322).— $\alpha$ -Cyano- $\beta$ -imino- $\alpha$ -phenyl- $\beta$ -*o*-tolylethane on treatment with alcoholic sodium ethoxide readily undergoes degradation to phenylacetone nitrile and *o*-toluonitrile:  $C_7H_7 \cdot C(NH) \cdot CHPh \cdot CN \rightarrow CH(H)Ph \cdot CN + C_7H_7 \cdot CN$ , a balanced reaction resulting. Some cyanobenzylidene was also obtained from the hydrochloric acid extract. Ethyl  $\alpha$ -cyano- $\beta$ -imino- $\beta$ -phenylpropionate similarly yields ethyl cyanoacetate and benzonitrile, but the equilibrium between ethyl cyanoacetate and ethyl cyanoiminoglutarate is disturbed by reactions leading to ethyl  $\alpha$ -cyano- $\beta$ -iminobutyrate:  $2CH_2(CN) \cdot CO_2Et \rightleftharpoons CO_2Et \cdot CH_2C(NH) \cdot CH(CN) \cdot CO_2Et \rightarrow Me \cdot C(NH) \cdot CH(CN) \cdot CO_2Et$ . This reversibility of the cyano-imino additive process is in accordance with Usherwood's views of tautomeric change (T., 1923, **123**, 1717).

R. B.

**Reduction Products of *o*-Nitromandelonitrile.** A. REISSERT and K. HESSERT (*Ber.*, 1924, **57**, [B], 964—972).—Reinvestigation

of the substance obtained by Heller (A., 1906, i, 585) by the reduction of *o*-nitromandelonitrile and regarded by him as a compound of the quinhydrone type composed of  $\text{N}(\text{OH})_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CN}, \text{HCl}$  and  $\text{OH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CN}, \text{HCl}$ , leads the authors to the conclusion that it is *o*-hydroxylaminomandelamide hydrochloride.

The mode of preparation and the properties of the compound are in complete harmony with Heller's description. The substance is decomposed by warm water into isatin and *anthroxanamide*, m. p. 211—212° (considered erroneously by Heller as nitrosomandelonitrile); with acetylating agents, it yields isatin and 1-acetoxyisatin in varying amount, whilst with phenylhydrazine it gives isatin-1- and -2-phenylhydrazones and 1-hydroxyisatin-3-phenylhydrazone. The formation of derivatives of 1-hydroxyisatin is completely in accord with Heller's conception of the partial reduction of the nitro group; since, however, exactly two atomic proportions of hydrogen are used, it appears reasonable to attribute their production to intermolecular oxidation, which should therefore be accompanied by the formation of dihydroxyindole as observed by Heller and Sourlis (A., 1908, i, 208), but not by the authors.

*o*-Hydroxylaminomandelamide hydrochloride is converted by sodium carbonate and sodium hydroxide into *isatin-2-imide*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \text{NH} \end{smallmatrix} \text{C}:\text{NH}$ , golden-yellow needles, m. p. 147—148° (decomp.). It is readily hydrolysed by dilute acids into isatin and ammonia, and by alkali hydroxide to isatic acid and by aniline into isatin-2-anilide. It is easily converted into *isatin-2-phenylhydrazone*, m. p. 222°, *isatin-2-semicarbazone*, m. p. 235—236°, and *isatindioxime*, m. p. 182—183° (decomp.). Treatment of *o*-hydroxylaminomandelamide or isatin-2-imide with sodium acetate and acetic anhydride gives a *diacetyl* compound, m. p. 224—225° (decomp.) after darkening at 200°, which is regarded as an isatol derivative,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OAc}) \\ | \\ \text{N} \end{smallmatrix} \text{C}:\text{NAc}$  or  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OAc}) \\ \diagup \text{N} \end{smallmatrix} \text{C}:\text{NAc}$ . It is hydrolysed in well-marked stages to a *monoacetyl* compound, m. p. 281—282° (decomp.) after darkening at 240°, which does not exhibit ketonic properties, and ultimately to isatin.

*o*-Hydroxylaminobenzoic acid (cf. Bamberger and Pyman, A., 1909, i, 573) is conveniently prepared by treating *o*-nitrobenzaldehyde with sodium hydrogen sulphite and potassium cyanide and subsequently warming the solution at 60°.

Cautious oxidation of Kalle's "anhydrohydroxylaminomandelic acid" (cf. Heller, *loc. cit.*) appears to lead to the formation of 1-hydroxyisatin, which, however, could be isolated only as the phenylhydrazone.  
H. W.

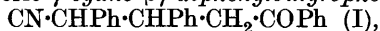
**Constitution of and Method of preparing Hydroxyphenylhomocampholic Acid.** A. HALLER and L. PALFRAY (*Compt. rend.*, 1924, **178**, 1647—1652).—From dibenzoylcamphor, 1-hydroxy-2-benzoylcamphene (Forster, T., 1901, **79**, 987) was prepared and either fused with potassium hydroxide at 195—200° (yield about

30% of theory) or heated at 200—220° with alcoholic sodium hydroxide (yield about 60%) or with a mixture of acetic and hydrochloric acids (yield about 50%) or with 50% sulphuric acid; it was thus converted (cf. cyanocamphor, Haller and Weimann, A., 1907, i, 278) into benzoylcampholic acid. This also is obtained directly, together with hydroxybenzoylcamphene, by treating dibenzoylcamphor with alcoholic sodium hydroxide (2 mols.) at 200—210°. The product is identical in all respects with that obtained from methyl cyanocampholate (*loc. cit.*). When reduced with sodium amalgam, it gives phenylhydroxyhomocampholic acid, identical with Haller and Minguin's product (A., 1900, i, 452). The hydroxy group is thus again proved to be attached to the same carbon atom as the phenyl radical, not to the adjacent one, as stated by Rupe and Blechschmidt (A., 1918, i, 222).

W. A. S.

### **δ-Ketonic Nitriles and their Relation to Cyclic Compounds.**

**III.** E. P. KOHLER and C. F. H. ALLEN (*J. Amer. Chem. Soc.*, 1924, **46**, 1522—1534).—Phenylacetonitrile condenses with phenyl styryl ketone in presence of sodium methoxide with formation of two stereoisomeric  $\gamma$ -cyano- $\beta\gamma$ -diphenylbutyrophenones,



prisms, m. p. 118° (a), and 109° (b), respectively, (b) being converted into (a) on saturating a solution of the former in chloroform or carbon tetrachloride with hydrogen bromide. The *methyl* esters of the corresponding stereoisomeric *acids* form needles, m. p. 150° and 139° respectively, and are both hydrolysed to the same  $\gamma$ -benzoyl- $\alpha\beta$ -diphenylbutyric acid, needles, m. p. 239°, which on re-esterification gives only the ester of m. p. 150°. The action of alcoholic potassium hydroxide on the nitriles (I) affords a *substance*,  $\text{C}_{38}\text{H}_{31}\text{O}_2\text{N}$ , microscopic needles, m. p. 257°, which is also formed together with (I) in the above condensation. On saturating a solution of either of the isomerides (I) in glacial acetic acid with hydrogen bromide, 2-*keto*-3 : 4 : 6-*triphenyltetrahydropyridine*, needles, m. p. 173°, was obtained, and this yielded 2-*hydroxy*-3 : 4 : 6-*triphenylpyridine*, fluorescent prisms, m. p. 263°, on treatment with sodium nitrite in glacial acetic acid. Bromination of the isomeride (b) in glacial acetic acid afforded 2-*bromo*-3 : 4 : 6-*triphenylpyridine*, fluorescent needles, m. p. 110°, from which, by the action of sodium butoxide, 2-*butoxy*-3 : 4 : 6-*triphenylpyridine*, small needles, m. p. 94°, was obtained. In chloroform, bromination yielded, together with the above product, 2-*bromo*-6-*hydroxy*-3 : 4 : 6-*triphenyl-5 : 6-dihydropyridine*, colourless needles, m. p. 100° (benzoyl derivative, pointed rods, m. p. 137°), together with 2-*bromo*-3 : 4 : 6-*triphenylpyridine*, the latter being also formed by the action of methyl-alcoholic potassium acetate solution or hydrogen bromide in glacial acetic acid. The nitrile (b) when brominated in chloroform gave  $\gamma$ -*bromo*- $\gamma$ -cyano- $\beta\gamma$ -diphenylbutyrophenone,  $\text{CN}\cdot\text{CBrPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COPh (IV)}$ , in two stereoisomeric forms, plates, m. p. 172° and 131°, respectively. The latter was slowly converted into the former by the action of hydrogen bromide

in glacial acetic acid, further action yielding 2-bromo-3:4:6-triphenylpyridine. On boiling (IV) with methyl-alcoholic potassium acetate solution, two stereoisomeric 2-cyano-1-benzoyl-2:3-diphenyl cyclopropanes, prisms, m. p. 172° and 143°, respectively, were produced, a third isomeride, fine needles, m. p. 178°, b. p. 275°/29 mm., being obtained by prolonged action. The cyano group is completely inactive in all three isomerides. The isomeride of m. p. 172° was reduced to the nitrile (*b*) by the action of zinc dust in glacial acetic acid, the other isomerides yielding the nitrile (*a*). The action of methyl-alcoholic potassium hydroxide produced two stereoisomeric  $\beta$ -cyano- $\gamma$ -hydroxy- $\beta\gamma$ -diphenylbutyrophenones, stout needles, m. p. 156° (*c*) and 218° (*d*), respectively, the former being obtained from the isomeride of m. p. 172°, the latter from the others. The compound (*c*) was converted into (*d*) by solution in glacial acetic acid, the reverse change being effected by the action of methyl-alcoholic hydrogen chloride. Both isomerides yielded the hydrated acetate,  $C_{25}H_{21}O_3N \cdot H_2O$ , stout needles, m. p. 121°, which yielded the anhydrous acetate,  $C_{25}H_{21}O_3N$ , microcrystalline plates, m. p. 142°, on boiling with acetyl chloride. On oxidation,  $\alpha$ -cyano- $\alpha\beta$ -dibenzoyl- $\alpha$ -phenylethane, prisms, m. p. 206°, was produced.  $\beta$ -Cyano- $\gamma$ -hydroxy- $\beta\gamma$ -diphenylbutyrophenone, m. p. 218°, was also synthesised by condensing benzaldehyde with the nitrile (I) in presence of potassium methoxide. The action of magnesium methoxide on methyl 3-cyano-2-benzoyl-1-phenylcyclopropane-3-carboxylate (A., 1923, i, 54) afforded methyl  $\alpha$ -cyano- $\beta$ -benzoyl- $\gamma$ -phenyl- $\Delta^{\beta}$ -butenoate,  $CHPh \cdot C(COPh) \cdot CH(CN) \cdot CO_2Me$ , prisms, m. p. 104°.

F. G. W.

**Study of the Freezing of Solutions as a Method of Investigating some problems in Pure Chemistry. I. Systems containing sec.-Butyl Alcohol and its Derivatives.** R. H. LOMBAERS (*Bull. Soc. chim. Belg.*, 1924, **33**, 232—245).—The system phthalic anhydride-sec.-butyl alcohol gives a normal freezing-point curve provided that the system is not subjected to prolonged heating at temperatures above 110°; under the latter conditions, the phthalate is formed in equilibrium with its components. This reaction is considered to be reversible, since the products of dissociation can be extracted from the fused phthalate. The equilibrium conditions between the phthalate and each of its components in excess were studied separately. With the anhydride, a normal curve indicating a eutectic at 53·6° (95 mols. anhydride, 5 mols. phthalate) was observed; with the alcohol, the eutectic could not be detected, and no evidence of the formation of a neutral phthalate was obtained. The freezing-point curves of mixtures of the racemic and active forms of the phthalate are of a type not hitherto observed.

F. B.

**Potassium Salts of Phenolphthalein.** H. BASSETT and D. J. T. BAGNALL (*J. Chem. Soc.*, 1924, **125**, 1366—1373).—The system phenolphthalein-potassium hydroxide-water at 25° gives results rather less definite than those obtained with the sodium

compounds (T., 1923, **123**, 1291), the curves corresponding with the hydrates of the mono-, di-, and tri-potassium salts being practically continuous. The mono-potassium salt gave hydrates with 5, 4, and 3 mols. of water; the di-salt with 10, 9, and 8 mols., and the tri-salt with 9, 8, 7, 6, 5, and 4 mols. of water. The tri-potassium salt as tetrahydrate can exist in contact with a range of solutions in which the ratio potash : phenolphthalein is less than that for the tri-salt and also with solutions supersaturated with respect to  $\text{KOH}\cdot 2\text{H}_2\text{O}$  (cf. Pickering, T., 1893, **63**, 890). No red salt was obtained as a solid phase, but dehydration experiments indicated that a red salt of phenolphthalein can exist in the solid state. By heating the dry tripotassium salt to constant weight at  $150^\circ$  a deep red product was obtained corresponding in composition with a dihydrate of the tripotassium salt. It is probably either the dipotassium salt,  $\text{CO}_2\text{K}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OK})\cdot\text{C}_6\text{H}_4\cdot\text{O}$  (formed by elimination of potassium hydroxide) or an equimolecular mixture of the mono-salt,  $\text{CO}_2\text{K}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{O}$ , and a hydrate,  $2\text{KOH}\cdot\text{H}_2\text{O}$ . The colour of the red dehydration product is unaltered on heating at  $100^\circ$  in a current of dry carbon dioxide, but in contact with the mother-liquors from the tripotassium salt the red colour disappears. The dry, colourless monopotassium salt partly melts in its water of crystallisation at  $100^\circ$ , giving a deep red, viscous mass, whilst on treatment with water it gives a red solution and a precipitate of phenolphthalein.

R. B.

#### Bile Acids. XX. Conversion to a Tricarboxylic Acid.

H. WIELAND and O. SCHLICHTING (*Z. physiol. Chem.*, 1924, **134**, 276—289; cf. A., 1921, i, 346; 1922, i, 41).—The second reaction product already described as resulting, together with norsolanellonic acid, from the oxidation of pyrodeoxybilianic acid with fuming nitric acid proves to be a *tetracarboxylic acid*,  $\text{C}_{16}\text{H}_{24}\text{O}_8$ . It is prepared more conveniently by the action of fuming nitric and sulphuric acids on the diketo acid,  $\text{C}_{23}\text{H}_{34}\text{O}_6$ , obtained from pyrodeoxybilianic acid by oxidation with permanganate. It has m. p.  $218^\circ$  (decomp.). Its *methyl* ester, formed by the action of diazomethane, has b. p.  $200\text{--}207^\circ/0.3$  mm. The acid on heating gives a monoketodicarboxylic *pyro acid*,  $\text{C}_{15}\text{H}_{22}\text{O}_5$ , m. p.  $187^\circ$ ; this is oxidised by nitric acid to an optically active *tricarboxylic acid*,  $\text{C}_{13}\text{H}_{20}\text{O}_6$ , m. p.  $187^\circ$ , with slight sintering; on heating, it gives an *anhydride*,  $\text{C}_{13}\text{H}_{18}\text{O}_5$ , m. p.  $147\text{--}148^\circ$ . For the interpretation of these results in relation to the structure of the bile acid molecule, the original paper must be consulted.

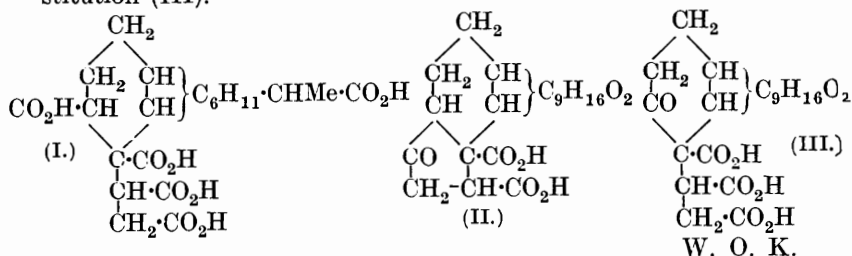
C. R. H.

#### Bile Acids. XVIII. Chollepidanic Acid. H. WIELAND

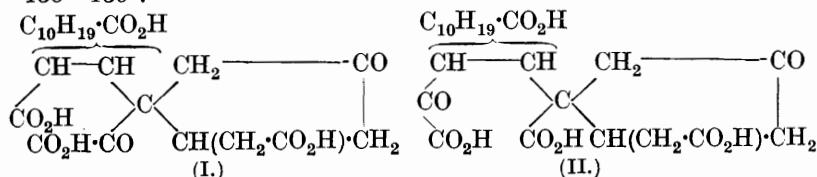
[with B. FLASCHENTRÄGER and A. REWOLLE] (*Z. physiol. Chem.*, 1924, **134**, 140—148).—When deoxybilianic acid (20 g.) is heated for 2 hours with 100 c.c. of fuming nitric acid (*d* 1.52), there is formed, along with cholidanic acid and two other acids, chollepidanic acid,  $\text{C}_{21}\text{H}_{30}\text{O}_{10}$  (cf. Wieland, A., 1921, i, 113). The yield of the purified acid is about 25% of the deoxybilianic acid used. It blackens and decomposes but does not melt at  $280^\circ$ . To this



acid formula (I) is assigned. The *pentamethyl* ester,  $C_{21}H_{25}O_5(OMe)_5$ , glistening needles arranged in rosettes, m. p.  $102^\circ$ , is formed from the silver salt and methyl iodide. The *monomethyl* ester, m. p.  $275^\circ$ , is formed when hydrogen chloride is passed into a boiling alcoholic solution of the acid. When chollepidanic acid is heated in a vacuum, the tribasic *pyrochollepidanic acid*,  $C_{20}H_{28}O_7$ , m. p.  $266^\circ$ , is obtained, and to it is assigned formula (II). This acid may be oxidised by potassium permanganate in alkaline solution to a tetrabasic acid,  $C_{19}H_{28}O_9$ , m. p.  $234^\circ$ , with the probable constitution (III).



**Bile Acids. XIX. Further Oxidation of Pyrodeoxybiliaric Acid.** H. WIELAND and W. MOTHES (*Z. physiol. Chem.*, 1924, **134**, 149—157).—When the diketotetracarboxylic acid,  $C_{23}H_{34}O_6$ , obtained from pyrodeoxybiliaric acid by oxidation (A., 1921, i, 112) is further oxidised at  $66^\circ$  with potassium permanganate, *norcilianic acid*,  $C_{23}H_{32}O_{10}$ , a tetrabasic acid, m. p.  $122^\circ$  (decomp.), and *isonorcilianic acid*, isolated as the sodium salt,  $C_{23}H_{31}O_{10}Na$ , are obtained. To these acids are assigned formulæ (I) and (II), respectively. On further oxidation with chromic acid, both yield biloidanic acid. Norcilianic acid forms a *semicarbazide* of the *semicarbazone*,  $C_{25}H_{38}O_{10}N_6$ , and when methylated with diazomethane yields a *pentamethyl* ester, m. p.  $138$ — $139^\circ$ .



W. O. K.

**Mechanism of Phenylhydrazone Formation.** S. BODFORSS (*Z. physikal. Chem.*, 1924, **109**, 223—259).—The reactions between phenylhydrazine and ketones and aldehydes have been studied kinetically. The conductivity method proving unsuitable, the reaction was followed by titrating the phenylhydrazine with silver nitrate. It is found that the velocity of the reactions with *m*-nitrobenzaldehyde and other aromatic aldehydes is determined by the rate of decomposition of an intermediate compound. With aldehyde in excess, the reaction gives a unimolecular constant. With hydrazine in excess, the results are complex. The reaction with

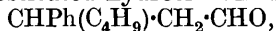
acetophenone is bimolecular in presence of excess of ketone, and probably unimolecular with excess of phenylhydrazine. S. B.

**Polymorphic Nitrobenzaldehydhydrazones.** F. D. CHATT-  
AWAY and A. J. WALKER (*J. Chem. Soc.*, 1924, **125**, 1207—1215).  
—*o*-Nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone, *p*-nitro-  
benzaldehyde-2:4-dichlorophenylhydrazone, and *p*-nitrobenzalde-  
hyde-4-chloro-2-bromophenylhydrazone exist in two well-defined  
forms, a yellow or orange, labile form, separating first, and a dark  
red, stable form into which the labile is transformed in contact  
with a solvent. *p*-Nitrobenzaldehyde-2-chloro-4-bromophenyl-  
hydrazone is trimorphic, the least stable, yellow, hair-like, non-  
pleochroic needles changing into orange, monoclinic needles and  
these into dark red, orthorhombic crystals, the transition tem-  
perature of the latter change being about 154°. The solubility  
curves of the labile and stable forms of these hydrazones in alcohol  
are practically parallel and the solubility ratios, labile : stable, are  
exceptionally large. The rates of transformation of the labile  
forms in contact with different solvents were determined approxi-  
mately and crystallographic measurements of the stable forms were  
made. The stable forms of the three *p*-nitrobenzaldehyde-2:4-  
dihalogenophenylhydrazones crystallise in the orthorhombic  
system, and those of *o*-nitrobenzaldehyde-2-chloro-4-bromophenyl-  
hydrazone and *p*-nitrobenzaldehyde-2:4-dibromophenylhydrazone  
(of which only one form was observed) in the monoclinic system.

R. B.

### Compounds of Magnesium Alkyl Halides with Carbonyl Compounds and the Reducing Action of Grignard Reagents.

**II.** K. HESS and W. WUSTROW (*Annalen*, 1924, **437**, 256—273; cf.  
A., 1921, i, 777).—The reducing action of magnesium alkyl halides  
previously observed in the case of benzaldehyde (cf. also Leroid,  
A., 1922, i, 215) has now been studied with the unsaturated alde-  
hydes crotonaldehyde and cinnamaldehyde, and in both cases the  
unsaturated alcohol was obtained. Cinnamaldehyde and magnesium  
*isobutyl* halides form at low temperatures bright yellow, stable  
additive compounds of 1 mol. of aldehyde and 1 mol. of Grignard  
reagent, which on decomposition with water yield  $\alpha$ -phenyl- $\epsilon$ -methyl-  
 $\Delta^a$ -hexen- $\gamma$ -ol. On warming, the additive compound decomposes,  
giving *isobutylene* and a colourless compound, which on decom-  
position with water yields cinnamaldehyde. These changes are  
represented by co-ordination formulæ of the type previously  
suggested. If the co-ordination number 4 is assumed for magnesium  
(cf. Meisenheimer and Casper, A., 1921, i, 654), the first yellow  
compound (I) must be represented by  $\text{CH} \begin{smallmatrix} \text{CHO} \\ \text{CHPh} \end{smallmatrix} \text{Mg} \begin{smallmatrix} \text{Br} \\ \text{C}_4\text{H}_9 \end{smallmatrix}$  but  
the corresponding substituted hydrocinnamaldehyde,



has not been obtained on decomposition with water. An isomeric  
compound,  $\text{CHPh} \cdot \text{CH} \cdot \text{CH} \begin{smallmatrix} \text{OMgBr} \\ \text{C}_4\text{H}_9 \end{smallmatrix}$  (III), has been obtained by

the action of magnesium ethyl bromide on  $\alpha$ -phenyl- $\epsilon$ -methyl- $\Delta^{\alpha}$ -hexen- $\gamma$ -ol; on warming, this yields no butylene, but reacts with water, forming the secondary alcohol,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{OH}$ , or its anhydro product,  $\alpha$ -phenyl- $\epsilon$ -methyl- $\Delta^{\alpha\gamma}$ -hexadiene. The two isomerides are also distinguished by their behaviour with acetyl chloride, the first leading to cinnamaldehyde and the second to  $\alpha$ -phenyl- $\epsilon$ -methyl- $\Delta^{\alpha}$ -hexen- $\gamma$ -yl acetate. The colourless compound,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{MgBr}$  (II), on treatment with acetyl chloride, yields cinnamyl acetate, but no cinnamaldehyde.

The action of magnesium ethyl bromide on crotonaldehyde yields only  $\Delta^{\beta}$ -hexen- $\delta$ -ol (Rief, A., 1906, i, 394). Magnesium sec.-*n*-butyl bromide yields chiefly  $\epsilon$ -methyl- $\Delta^{\beta}$ -hepten- $\delta$ -ol, a mobile oil, b. p. 69—70°/18 mm.,  $\alpha_D^{20}$  0.8473,  $n_D^{20}$  1.44113, besides a little crotyl alcohol ( $\alpha$ -naphthylurethane, long needles, m. p. 89°) and a little dicrotyl ether. Better yields of crotyl alcohol were obtained with magnesium isobutyl bromide and using phenetole in place of ether, isobutylene being also formed. The following constants of crotyl alcohol are given: b. p. 118°/764 mm.,  $d_4^{20}$  0.8539,  $n_D^{20}$  1.41898,  $n_D^{20}$  1.42403,  $n_D^{20}$  1.43156,  $n_D^{20}$  1.43705. Magnesium cyclohexyl chloride gives only  $\alpha$ -cyclohexylbuten- $\alpha$ -ol, a colourless oil of aromatic odour, b. p. 98—100°/13 mm.,  $d_4^{20}$  0.9225,  $n_D^{20}$  1.47623,  $n_D^{20}$  1.47987,  $n_D^{20}$  1.48635,  $n_D^{20}$  1.49245.

Magnesium ethyl bromide and cinnamaldehyde yield the bright yellow additive compound,  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}\cdot\text{MgBrEt}$ , which with water yields  $\alpha$ -phenyl- $\Delta^{\alpha}$ -penten- $\gamma$ -ol (Klages, A., 1906, i, 661) for which constants are given, and on heating with methyl alcohol loses ethylene, giving a compound,  $\text{C}_9\text{H}_9\text{OBrMg}$ , from which only resinous products were obtained. The analogous additive compound,  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}\cdot\text{MgBrC}_4\text{H}_9$ , obtained from magnesium isobutyl bromide or chloride at -10°, contains 1 mol. of ether which is only partly lost on drying. With ammonium chloride solution in the cold, it yields  $\alpha$ -phenyl- $\epsilon$ -methyl- $\Delta^{\alpha}$ -hexen- $\gamma$ -ol, thin needles, m. p. 37°, b. p. 160—162°/15 mm. (benzoate, m. p. 59—60°). On boiling with methyl alcohol, the additive compound loses butylene, yielding a compound,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OMgBr}$ , from which only resinous products could be obtained. If, however, the decomposition takes place in boiling ether, the product obtained has the same composition, but yields cinnamyl alcohol (*p*-nitrobenzoate, m. p. 74—75°), on treatment with water, and on treatment with acetyl chloride cinnamyl acetate, b. p. 140—141°/18 mm.,  $d_4^{12}$  1.0567,  $n_D^{12}$  1.5369,  $n_D^{12}$  1.54415,  $n_D^{12}$  1.55915,  $n_D^{12}$  1.57267, and  $\alpha$ -phenyl- $\epsilon$ -methyl- $\Delta^{\alpha\gamma}$ -hexadiene. The additive compound,  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}\cdot\text{MgClC}_4\text{H}_9$ , from magnesium isobutyl chloride and cinnamaldehyde on treatment with acetyl chloride, yields cinnamyl acetate and  $\alpha$ -phenyl- $\epsilon$ -methyl- $\Delta^{\alpha\gamma}$ -hexadiene, whilst the compound obtained from magnesium ethyl bromide and  $\alpha$ -phenyl- $\epsilon$ -methyl- $\Delta^{\alpha}$ -hexen- $\gamma$ -ol yields only the corresponding acetate and  $\alpha$ -phenyl- $\epsilon$ -methyl- $\Delta^{\alpha\gamma}$ -hexadiene. R. B.

**Simplification of the Gattermann Synthesis of Aromatic Aldehydes. II.** R. ADAMS and E. MONTGOMERY (*J. Amer. Chem. Soc.*, 1924, 46, 1518—1521; cf. this vol., i, 51).—Aldehydo

derivatives of phenols and phenol ethers may be prepared in good yields by saturating a cooled mixture of the phenol or phenol ether (1 mol.), powdered zinc cyanide (2 mols.), and benzene, with hydrogen chloride, adding powdered anhydrous aluminium chloride, and then passing in a slow stream of hydrogen chloride at 40–45° for 3–4 hours. The imine hydrochloride is precipitated by addition of excess of 10% hydrochloric acid, and hydrolysed to the aldehyde by refluxing. F. G. W.

**Mobility of Organically Combined Chlorine in the Friedel-Crafts Reaction. Influence of the Solvent.** CHOPIN (*Bull. Soc. chim.*, 1924, [iv], **35**, 610–614).—The rates of reaction between acetyl chloride and benzene in the following solvents decrease in the order benzene, light petroleum, chlorobenzene, bromobenzene, carbon disulphide, nitrobenzene, the reaction being carried out at 4° under reduced pressure, and its progress followed by determination of the hydrogen chloride liberated. In nitrobenzene, the reaction is much slower if the aluminium chloride is dissolved prior to the addition of the other reactants. Chromium chloride in chlorobenzene gave practically no reaction, whilst with ferric chloride the above temperature is too low. Naphthalene reacts more slowly, toluene more rapidly, than benzene. In the reaction between acetyl chloride and naphthalene, the product in light petroleum solution is a mixture of about equal parts of  $\alpha$ - and  $\beta$ -naphthyl methyl ketones. In nitrobenzene, the  $\beta$ - predominates; in bromobenzene, the  $\alpha$ - predominates, and is formed exclusively in chlorobenzene and carbon disulphide. F. G. W.

**The Beckmann Rearrangement.** A. LACHMAN (*J. Amer. Chem. Soc.*, 1924, **46**, 1477–1483).—Benzophenoneoxime decomposes when heated at 185°, either alone or in presence of sodium or potassium chloride (cf. Hantzsch and Kraft, A., 1892, 338) with formation of benzophenone and benzophenoneimine in approximately equimolecular proportions, nitrogen, oxides of nitrogen, and water. The latter hydrolyses some of the benzophenoneimine, yielding ammonia in amount corresponding exactly with the excess of benzophenone found in the reaction product. No benzanilide is formed, and the reaction forms a convenient method of preparing benzophenoneimine. Lehmann's observations (*Z. angew. Chem.*, 1923, **36**, 360) on the decomposition of benzophenoneoxime in presence of hydrogen chloride were verified, but the formation of benzanilide by less than one equivalent of hydrogen chloride at slightly higher temperatures, and even in presence of water, was demonstrated. It is concluded that the Beckmann rearrangement is the direct conversion of the oxime salt into the acid amide and free acid, according to the equation  $\text{CPh}_2\text{:NOH}\cdot\text{HCl} = \text{COPh}\cdot\text{NHPh} + \text{HCl}$ . Pure benzophenoneoxime, of which a convenient method of preparation is described, has m. p. 143°. F. G. W.

**Preparation of Anthraquinone Derivatives.** H. A. E. DRESCHER, J. THOMAS, and SCOTTISH DYES, LTD. (Brit. Pat. 214765).—Imidoanthraquinones are obtained by treating a halogen deriv-  
g g\*

ative of anthraquinone with the imide of a dibasic acid (*e.g.*, phthalimide) or a metallic salt of the imide in the presence of metallic copper (*e.g.*, copper bronze) or a copper salt. The imido-anthraquinones are converted into aminoanthraquinones by hydrolysis, *e.g.*, with concentrated sulphuric acid. Substituted benzoylamidoanthraquinones are prepared by partial hydrolysis of phthalimidoanthraquinones, *e.g.*, with boiling, dilute sodium hydroxide.

Details are given of the preparation of 1-phthalimido-, 2-phthalimido-, 1:5-diphthalimido-, 1-chloro-5-phthalimido-, 2-nitro-1-phthalimido-, 1-amino-4-phthalimido-2-methyl-, 1-methylamino-4-phthalimido-, and 2-amino-1-phthalimido-anthraquinones, and of their conversion into the corresponding aminoanthraquinones; also of the preparation of 2-benzoylamidoanthraquinone-2'-carboxylic acid by partial hydrolysis of 2-phthalimidoanthraquinone.

W. T. K. B.

**Terpenes and Ethereal Oils. CXXVII. Diosphenol (Buchu-camphor) and Homologous Compounds.** O. WALLACH and A. WEISSENBORN (*Annalen*, 1924, **437**, 148—186; cf. A., 1916, i, 487; 1918, i, 440, 442).—Both dibromomenthone and dibromocarvomenthone yield, on treatment with alkali, the same product, diosphenol (buchu-camphor), and on treatment with ammonia in methyl-alcoholic solution give two isomeric monobrominated amines, which are stable in acid solution but in the presence of sodium hydroxide are both converted into diosphenol, with evolution of ammonia. If the ammonia is replaced by piperidine or other amines, stable, well-crystallised monobrominated bases can be isolated. In both cases, the tertiary bromine atom is the more mobile and the first step in the reaction is replacement of the bromine atom by an amine residue and not splitting off of hydrogen bromide. A mechanism is suggested to explain the conversion of both menthone and carvomenthone derivatives into diosphenol.

The structure of diosphenol has been established as 2-hydroxy- $\Delta^1$ -menthen-3-one (I), by its synthesis by oxidation of  $\Delta^1$ -menthen-



3-one through the 1:2-dihydroxyketone; carvenone ( $\Delta^3$ -menthen-2-one) under similar conditions yields the isomeric form (II). The *o*-cyclohexandiones do not appear to be capable of existence except under special conditions. The general name, diosphenols, is proposed for the homologous series of 1:2-hydroxycyclohexenones. They possess reducing properties, and give well crystallised dioximes derived from the *o*-diketones. These dioximes give complex compounds with the metals of the eighth group; the nickel compounds are characterised by their insolubility and intense

red or orange colour, and can be applied in the detection or determination of nickel. A dicyclic diosphenol obtained from  $\beta$ -keto-decahydronaphthalene by analogous methods possesses similar properties to the monocyclic diosphenols. On heating with potassium hydroxide the bicyclic diosphenol is converted into an  $\alpha$ -hydroxy acid which on oxidation yields hydrindone, the six-membered ring being converted into a five-membered, as previously observed in the cyclohexanone series (A., 1918, i, 442; 1919, i, 267).

The conversion of 2:4-dibromomenthone into diosphenol is most easily accomplished by treatment with ammonia in alcoholic solution, the brominated amine (syrupy hydrochloride) being more easily decomposed with sodium hydroxide than the *piperidide*,  $C_{15}H_{26}ONBr$ , needles or prisms, m. p. 127—128°, or *anilide*,  $C_{16}H_{22}ONBr$ , needles, (decomp.) 180°. Similarly, dibromocarvo-menthone (1:3-dibromomenthan-2-one) yields a *bromopiperidide*,  $C_{15}H_{26}ONBr$ , m. p. 115—116°. Both the active and inactive preparations yield inactive diosphenol. With sodium methoxide, inactive 1:3-dibromomenthan-2-one is converted into 3-bromo-1-hydroxymenthane-2-one, m. p. 92° (acetyl derivative, m. p. 155°), which is converted into diosphenol by treatment with alkali.

Oxidation of  $\Delta^1$ -menthen-3-one with cold dilute potassium permanganate in acetone solution yields diosphenol, m. p. 83° (phenylurethane, m. p. 113—114°; cf. Asahina and Mituhori, A., 1922, i, 667). Carvenone under similar conditions gives an oil yielding the diosphenol reaction with ferric chloride. It dissolves in sodium hydroxide and, on acidifying, the diosphenol, m. p. 83°, separates. Both diosphenols yield the same dioxime, but the liquid diosphenol yields a *phenylurethane*,  $C_{17}H_{21}O_3 + H_2O$ , m. p. 165—166°.

$\beta$ -Ketodecahydronaphthalene (dibenzylidene derivative, m. p. 119—120°;  $\alpha$ -ketotetrahydronaphthalene gives a *monobenzylidene* derivative, m. p. 206—207°) on bromination in acetic acid yields a viscous fluid which on shaking with 20% potassium hydroxide yields a dibasic acid,  $C_{10}H_{16}O_4$ , m. p. 165° (together with a lower melting acid, cf. Hückel, this vol., i, 31), and the *diosphenol*,  $C_{10}H_{14}O_2$  (annexed formula), colourless, rhombic crystals,

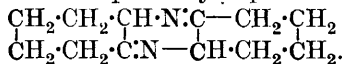


m. p. 88—89°. The *dioxime*, m. p. 196—197°, gives an intense bright orange precipitate with nickel salts. Besides the diosphenol, a small quantity of an isomeric substance, m. p. 99—100°, is formed, yielding a very insoluble deep red *dioxime*. On heating with potassium hydroxide at 120—130°, the diosphenol, m. p. 88—89°, yields a mixture of two acids difficult to separate. The more readily purified product is an  $\alpha$ -hydroxy acid,  $C_{10}H_{16}O_3$ , m. p. 128—129°, which on oxidation with lead peroxide and sulphuric acid yields hexahydro-2-hydrindone,  $C_9H_{14}O$  (semicarbazone, m. p. 240°; cf. Borsche and Lange, this vol., i, 33; *oxime*, m. p. 160—161°), a result which points to a  $\beta\beta$ -structure for the diosphenol of m. p. 88—89°. The second acid,  $C_{10}H_{16}O_3$ , m. p. about 100°, on oxidation yields a mixture of ketones which give a semicarbazone with melting point

approximating to that of the semicarbazone of hexahydro-1-hydrindone.

The *monoxime* of buchu-camphor, m. p. 124° (cf. Kondakov, A., 1897, i, 227; Semmler, A., 1906, i, 373), gives a yellow solution in alkali, whereas the *dioxime*, m. p. 197°, gives a nearly colourless solution. The monoxime is stable in acid solution, but when the dioxime is boiled with dilute acid, diosphenol is partly regenerated. The dioxime gives a very insoluble orange *nickel* compound.

The simplest diosphenol, 2-hydroxy- $\Delta^1$ -cyclohexen-3-one, m. p. 38—40°, b. p. 193—195° (*phenylurethane*, m. p. 124°), was obtained from dibromocyclohexanone, m. p. 106—107°, by the action of potassium hydroxide. Concentrated potassium hydroxide converts it into 1-hydroxycyclopentane-1-carboxylic acid. With phenylhydrazine, it yields an osazone, golden-yellow needles, m. p. 152—153°, identical with that obtained from 1-hydroxycyclohexan-2-one; the *dioxime* has m. p. 189—190°, yields a *dibenzoyl* compound, m. p. about 170° (decomp.), and an intense red *nickel* compound,  $C_{12}H_{18}O_4N_4Ni$ , which can be used for the determination of nickel. On reduction with zinc dust and potassium hydroxide, the dioxime yields a colourless *base*,  $(C_6H_9N)_2$ , m. p. 108—109° (insoluble *picrate*), which is probably a phenazine of the structure



2-Hydroxy- $\Delta^1$ -cyclohexen-3-one can also be obtained by converting  $\Delta^1$ -cyclohexenone into the ketoglycol,  $C_6H_8(OH)_2O$ , and treating this with dilute sulphuric acid or by careful oxidation of 1-hydroxycyclohexan-2-one, whilst the formation of its dioxime can be easily detected when hydroxylamine acts on the product obtained by the action of nitrous acid on cyclohexanone (cf. Borsche, A., 1910, i, 178).

1 : 3-Dibromo-1-methylcyclohexan-2-one is converted by potassium hydroxide into 2-hydroxy-1-methyl- $\Delta^1$ -cyclohexen-3-one, m. p. 63° (diphenylhydrazone, m. p. 150—151°, *dioxime*, m. p. 165—166°, yielding an orange *nickel* compound), which yields two semicarbazones, one, needles, m. p. 174—175°, and a more insoluble isomeride, m. p. 240°. The diosphenol is identical with the product obtained by Harries from 1-methyl- $\Delta^1$ -cyclohexen-3-one (A., 1902, i, 378). The *bromopiperidide*,  $C_{12}H_{20}ONBr$ , has m. p. 110—111°. Similarly, the dibromo-derivative of 4-methylcyclohexanone yields an oily diosphenol which with hydroxylamine gives 1-methylcyclohexan-3 : 4-dione *dioxime*, needles, m. p. 180—181° (decomp.) [*dibenzoyl* derivative, m. p. about 170° (decomp.), deep red *nickel* compound, very insoluble]. The same diosphenol and dioxime were obtained similarly from 3-methylcyclohexanone, a small quantity of 1-methylcyclohexan-2 : 3-dione dioxime being also isolated, indicating the formation of the 2 : 3-dione as a by-product. The diosphenol,  $C_8H_{12}O_3$ , m. p. 71—72°, obtained previously (A., 1918, i, 442) from 1 : 3-dimethylcyclohexan-5-one is identical with the product prepared from 1 : 5-dimethyl- $\Delta^1$ -cyclohexen-3-one and must be regarded as 2-hydroxy-1 : 5-dimethylcyclohexen-3-one

(*dioxime*, m. p. 163—164°, orange *nickel* compound). The diosphenol,  $C_9H_{14}O_2$ , m. p. 90°, prepared from dibromodihydroisophorone (A., 1916, i, 487) is identical with the product obtained by oxidation of isophorone (1 : 5 : 5-trimethyl- $\Delta^1$ -cyclohexen-3-one) and must therefore be 2-hydroxy-1 : 5 : 5-trimethylcyclohexan-3-one (*dioxime*, m. p. 177—178°, orange-yellow *nickel* compound). R. B.

**New Form of Fenchoneoxime. Characterisation of Fenchone in presence of Camphor.** M. DELÉPINE (*Compt. rend.*, 1924, 178, 1721—1723).—When *d*-fenchone was treated with hydroxylamine in alkaline solution according to Rimini's method (A., 1896, i, 359), it gave, not the expected  $\alpha$ -oxime (m. p. 165°,  $[\alpha]_D + 47^\circ$ ), but a much more soluble compound,  $\beta$ -fenchoneoxime; m. p. 123°,  $[\alpha]_D + 129.3^\circ$ . This is converted into the usual  $\alpha$ -form by being heated alone at 170—180°, or by evaporating its alcoholic solution to dryness, or by boiling an acidified alcoholic solution, or even if the solution is kept for some time. The reverse change,  $\alpha$  into  $\beta$ , was not effected; although the formation of the  $\beta$ -variety evidently depended on the alkalinity of the mother-liquor, yet treatment of the  $\alpha$ -form with alcoholic alkali hydroxide brought about no conversion. The two forms ( $[\alpha]_D - 96^\circ$ , and  $[\alpha]_D - 47^\circ$ , respectively) were also obtained from *l*-fenchone (cf. Wallach, A., 1893, i, 105).

A mixture of camphor and fenchone can be treated and so the proportion of fenchone determined. The oximes are separated by fractional crystallisation, taking advantage of the readier solubility of camphoroxime in alkaline media. W. A. S.

**Reduction of Glycidic Esters in the Terpene Series. Synthesis of Inactive Citronellol and Rhodinol.** A. VERLEY (*Bull. Soc. chim.*, 1924, [iv], 35, 608—610).—Inactive citronellol and inactive rhodinol are obtained, respectively, by the reduction, with sodium and amyl alcohol, of the glycidic esters of  $\alpha$ - and  $\beta$ -methylheptenones. Behal's failure to repeat the author's synthesis of nerol, and the action of ozone on methylheptenone are discussed. F. G. W.

**Formation and Catalytic Decomposition of Terpinolene.** A. MAILHE (*J. Usines Gaz*, 1923, 47, 370—373).—Terpin, when passed over alumina in glass at 310—320°, yields terpinolene; terpineol yields a liquid, presumably terpinolene. The catalyst remains active for several days, and is easily regenerated by heat. Terpinolene passed over copper turnings at 500—550° gave a gas containing 27%  $C_nH_{2n}$ , 15%  $C_nH_{2n+2}$ , 18%  $CH_4$ , 40%  $H_2$ , and a liquid containing benzene, cyclohexane, toluene, methylcyclohexane, *m*-xylene, and *m*-cymene. CHEMICAL ABSTRACTS.

**Abnormal Phenomena in the Terpene Group in the Light of an Extension of Thiele's Hypothesis.** K. SŁAWIŃSKI (*Roczniki Chemji*, 1923, 3, 200—204).—Pinene and camphene behave abnormally on oxidation and addition of halogen acids



in that some derivatives are formed by the addition, for example, of the elements of water and oxygen to the double bond (formation of corresponding glycols) whilst others are due to the fission of the bridge (formation of bornyl chloride, sobrerol, etc.). It is suggested that these phenomena can be accounted for by assuming that the system formed by a ring conjugated with a double linking, such as is present in vinyltrimethylene, camphene, and pinene, behaves like a pair of conjugated double linkings towards oxidising and other agents (cf. Eisenlohr, *Spectrochemie der organischen Verbindungen*, 1912). G. A. R. K.

**Essential Oil of *Pinus pinea*.** G. DUPONT and M. BARRAUD (*Bull. Soc. chim.*, 1924, [iv], 35, 625—631).—The essential oil of *Pinus pinea* consists of *l*-limonene (75.4%) of greater optical activity ( $[\alpha]_D -123.7^\circ$ ) than any natural limonene previously obtained, together with pinene (16.7%) and an inactive sesquiterpene,  $d^{15}_D 0.9157$ ,  $n^{20}_D 1.4983$  (6.6%). [Cf. *B.*, 1924, 615.] F. G. W.

**New Synthetic Nitrophenol Glucosides and the Disinfectant Action and Toxicity of the Nitrophenols.** E. GLASER and W. WULWEK.—(See i, 797.)

**The Properties of Loroglossin and its Products of Hydrolysis, Dextrose and Loroglossigenin.** M. BRIDEL and P. DELAUNEY (*J. Pharm. Chim.*, 1924, [vii], 29, 393—402; cf. *A.*, 1919, i, 243).—Loroglossin,  $C_{30}H_{42}O_{18}$ , is an odourless and bitter glucoside which has been extracted from sixteen species of the order *Orchidaceae* in the form of long, colourless needles, having no sharp m. p. (about 140—150°). The anhydrous substance gives  $[\alpha]_D -45.65^\circ$  in water, and  $-36.28^\circ$  in 50% methyl-alcoholic solution. Its aqueous solution froths strongly when shaken. It gives a red colour with cold, concentrated sulphuric acid, but no coloration with cold nitric acid, hydrochloric acid, or ferric chloride. It is hydrolysed by sulphuric acid, giving 51.41% of dextrose and a substance, *loroglossigenin*, crystals, m. p. 77°, having an odour of mown hay. The substance is best obtained by the hydrolysis of loroglossin with emulsin, although the reaction proceeds slowly. It behaves like loroglossin towards sulphuric acid, but gives with ferric chloride a faint violet coloration, which disappears on shaking with ether or on warming. It has no reducing properties.

W. T. K. B.

**Synthesis of Amygdalin.** R. CAMPBELL and W. N. HAWORTH (*J. Chem. Soc.*, 1924, 125, 1337—1343; cf. Haworth and Wylam, *T.*, 1923, 123, 3120).—Ethyl *dl*-mandelate condenses with  $\beta$ -bromohepta-acetylgentiobiose in the presence of silver oxide, giving ethyl *dl*-hepta-acetylamygdalinate, m. p. 205°,  $[\alpha]_D -62.0^\circ$  (cf. Zemplén, this vol., i, 617). The same product was obtained by acetylation of *dl*-amygdalinic acid and crystallisation of the hepta-acetylamygdalinic acid from alcohol, when direct esterification takes

place, and by methylation of silver amygdalinate with methyl iodide followed by acetylation of the ester with acetic anhydride and sodium acetate, a by-product, m. p. 184—186°,  $[\alpha]_D -28.6^\circ$ , being obtained on one occasion. On treatment with ammonia in dry methyl alcohol, ethyl *dl*-hepta-acetylamygdalinate is converted into *dl*-amygdalinamide, a colourless, brittle solid,  $[\alpha]_D -77.0^\circ$ , which on acetylation in the presence of pyridine yielded *hepta-acetylamygdalinamide* in two isomeric forms, m. p. 166—167° and 152—153°, and  $[\alpha]_D -68.6^\circ$  and  $-49.7^\circ$ , each containing 1 mol. of combined pyridine, which were separated by crystallisation from alcohol. The acetylated amide, m. p. 166—167°, on digestion with phosphoric oxide in xylene solution, yielded *d*-hepta-acetyl-amygdalin,  $[\alpha]_D -36.2^\circ$  (Caldwell and Courtauld, T., 1907, **91**, 671), the de-acetylation of which has already been effected by Fischer and Bergmann (A., 1917, i, 657).  
R. B.

**Strophanthin. IV. Anhydrostrophanthidin and Dianhydrostrophanthidin.** W. A. JACOBS and A. M. COLLINS (J. Biol. Chem., 1924, **59**, 713—730; cf. A., 1923, i, 123; this vol., i, 65). —The action of 10% absolute alcoholic hydrochloric acid on strophanthidin at room temperature gives a product,  $C_{25}H_{34}O_5$ , which is characterised as the *ethylal* of *oxidoanhydrostrophanthidin*, needles, m. p. 223—230°;  $[\alpha]_D -50^\circ$ . On alkaline hydrolysis this gives an *acid*,  $C_{25}H_{36}O_6$ , rhombic plates, m. p. 120—125° (decomp.); *methyl ester*, m. p. 182—186°;  $[\alpha]_D^{25} -81.7^\circ$  in chloroform; on acid hydrolysis it gives anhydrostrophanthidin. If strophanthidin be boiled with 5% alcoholic hydrogen chloride 2 mols. of water are eliminated and the *ethylal* of *oxidodianhydrostrophanthidin* is formed, which, in turn, on acid hydrolysis gives dianhydrostrophanthidin,  $C_{23}H_{28}O_4$ . Both anhydro- and dianhydro-strophanthidin form an oxime, a phenylhydrazone, a monoacetate, and a mono-benzoate. The substance,  $C_{24}H_{30}O_4$ , previously described by Windaus and Hermanns (A., 1915, i, 704) as anhydrostrophanthidin, has been identified as the *methylal* of *oxidodianhydrostrophanthidin*. A similar series of reactions has been carried through with dihydrostrophanthidin. The dianhydro derivatives both of strophanthidin and of dihydrostrophanthidin exhibit mutarotation.

It is concluded that the molecule of strophanthidin contains three hydroxyl groups, a carbonyl group and a lactone group. The formula of the basic hydrocarbon skeleton of strophanthidin becomes  $C_{23}H_{40}$  and indicates the probable relationship of this substance to cholesterol and the bile acids.

*Anhydrostrophanthidin*,  $C_{23}H_{30}O_5$ , forms needles with  $2H_2O$  from 50% alcohol; m. p. (air-dried) 223—226°, with slight sintering;  $[\alpha]_D^{25} -145^\circ$  in 95% alcohol; *oxime*, small prisms with  $1H_2O$  from 95% alcohol; m. p. 260—265°; *phenylhydrazone*, needles containing  $2H_2O$ , m. p. (air-dry) 260—264°. The *acetate*, clusters of needles, sinters at 280° and melts at 292—294°. The *benzoate*, flat needles and platelets, sinters at 270° and melts at 287—289°.

The *ethylal* of *dianhydrostrophanthidin*,  $C_{25}H_{32}O_4$ , forms colourless

needles which on rapid heating sinter at  $238^{\circ}$  and melt at  $249-251^{\circ}$ ;  $[\alpha]_D^{25} -142^{\circ}$  in chloroform. The *acid*,  $C_{25}H_{34}O_5$ , obtained by alkaline hydrolysis of the above, forms needles, m. p.  $198-200^{\circ}$  (decomp.),  $[\alpha]_D^{25} -85.5^{\circ}$  in chloroform; *methyl ester*, colourless needles, m. p.  $152-156^{\circ}$ . The *methylal* of *dianhydrostrophanthidin*,  $C_{24}H_{30}O_4$ , forms long needles sintering at  $245^{\circ}$ , m. p.  $252-254^{\circ}$ ;  $[\alpha]_D^{24} -131^{\circ}$  in chloroform.

*Dianhydrostrophanthidin*,  $C_{23}H_{28}O_4$ , forms needles, m. p.  $233-236^{\circ}$ ;  $[\alpha]_D^{25} -222^{\circ}$  in chloroform; *oxime*, stout prisms, m. p.  $279-281^{\circ}$  with effervescence,  $[\alpha]_D^{25} -174^{\circ}$  in pyridine; *phenylhydrazone*, needles or platelets containing  $1.5H_2O$ , m. p. (air-dry)  $219-227^{\circ}$ ,  $[\alpha]_D^{25} -245^{\circ}$  in chloroform. The *acetate*, stout prisms with  $0.5H_2O$ , softens at  $180^{\circ}$  to a resin which melts at  $203-206^{\circ}$ ,  $[\alpha]_D^{25} -222^{\circ}$  in chloroform. The *oxime* of the acetate forms platelets, m. p.  $224-226^{\circ}$ ; the *oxime* of the benzoate, prisms, m. p.  $283-285^{\circ}$ .

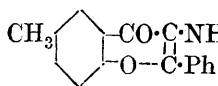
The *ethylal* of *oxidodianhydrodihydrostrophanthidin*,  $C_{25}H_{34}O_4$ , forms needles which sinter above  $210^{\circ}$ , m. p.  $216-218^{\circ}$ ,  $[\alpha]_D^{25} -101.3^{\circ}$  in chloroform. *Dianhydrodihydrostrophanthidin* forms needles sintering at  $190^{\circ}$ , m. p.  $193-199^{\circ}$ ,  $[\alpha]_D^{24} -184^{\circ}$  in chloroform. The *oxime* forms prisms, m. p.  $291-292^{\circ}$ . C. R. H.

**Tannins and Similar Substances. XVI. Stereoisomeric Catechins. IV.** K. FREUDENBERG and L. PURRMANN (*Annalen*, 1924, **437**, 274—285; cf. A., 1923, i, 697).—The previously studied relations of the stereoisomeric catechins and epicatechin have been further investigated with larger quantities of material, a good yield of *l*-epicatechin, together with a little *dl*-catechin, being obtained from the heartwood of *Acacia catechu*. The transformation of *d*-catechin and of *l*-epicatechin to *l*-catechin and *dl*-catechin is promoted considerably by the presence of a trace of potassium hydrogen carbonate. The epicatechins are rather less stable than the corresponding catechins, and *dl*-epicatechin is only obtained pure by mixing the *d*- and *l*-forms. The active forms are easily separated from the racemates and are recognised by their rotatory powers in alcohol, in the case of the epicatechins, and in aqueous acetone, disappearing in alcohol, in the case of the catechins. The data now available lead to the conclusion that the acacatechin examined by Perkin (T., 1905, **87**, 398) consisted largely of *dl*-catechin admixed with some *l*-epicatechin, a conclusion which has been confirmed by a series of mixed melting points of Perkin's derivatives with those of *dl*-catechin, and by the observation that *dl*-catechin always sinters  $60-70^{\circ}$  below its m. p. ( $205-210^{\circ}$ ) when epicatechin is present. The "catechin C" of Perkin and Yoshitake (T., 1902, **81**, 1167) obtained from Gambier catechin, m. p.  $235-237^{\circ}$  [disazobenzene derivative, m. p.  $215-217^{\circ}$  (decomp.)] appears to be identical with *d*-epicatechin, m. p.  $245^{\circ}$  (decomp.) [disazobenzene derivative, m. p.  $216-218^{\circ}$  (decomp.)], and the authors have isolated a small quantity of *d*-epicatechin from Gambier catechin. Bromotetramethyl-*d*-catechin has m. p.  $172-173^{\circ}$ , without decomposition (cf. Kostanecki and Krembs,

A., 1902, i, 637), and the acetate, m. p. 174—175°. *dl-Catechin tetramethyl ether* melts at 142°, the *monoacetate* at 134—135°, and the *toluenesulphonate* at 156—157°. *dl-Catechin pentabenzoate* melts at 181—182°, and the *pentamethyl ether* at 110—111°. *d-Epi-catechin tetramethyl ether* melts at 93—94° and the *acetate* at 91—92°. The melting points and rotatory powers of the stereoisomeric catechins and epicatechins and their derivatives are tabulated.

R. B.

**Anilino-flavones.** K. VON AUWERS and O. JORDAN (*J. pr. Chem.*, 1924, [ii], 107, 330—357).—Auwers and Müller (A., 1909, i, 222) obtained by heating together in toluene solution aniline and 3-chloroacetyl-*p*-tolyl benzoate, *N*-benzoyl-3-phenylglycyl-*p*-cresol, and a by-product, m. p. 133—134°, now identified as 3-anilino-6-methylflavone (annexed formula). When the solvent



used is benzene scarcely any of this product is formed, whilst if it be xylene, 22% of the theoretical yield is obtained. The

authors discuss the mechanism of the reaction, and describe experiments on the stability of compounds of the type  $R \cdot CO \cdot CH_2 \cdot NH \cdot Ph$ , the results of which bear on the question. 3-Anilino-6-methylflavone yields an unstable *hydrochloride* and *acetyl* (m. p. 165—167°) and *benzoyl* (m. p. 154—155°) derivatives, but no alkyl derivatives; neither can the latter be obtained by condensing 3-chloroacetyl-*p*-tolyl benzoate with, *e.g.*, methyl-aniline. With bromine in carbon disulphide it gives an unstable *compound*, m. p. 80—85°, and when the reaction mixture is heated, the *p*-bromoanilino-flavone, m. p. 154°, is formed, identical with the product of interaction of *p*-bromoaniline and 3-chloroacetyl-*p*-tolyl benzoate. When the flavone is heated with alcoholic sodium ethoxide, it breaks up, giving aniline, benzoic acid, *p*-hydroxytoluic acid, and benzanilide, together with unidentified products, whilst with the cold reagent partial conversion to *N*-benzoyl-3-phenylglycyl-*p*-cresol takes place.

Analogous flavone derivatives were prepared. The yields were poor, being mostly about 20% of the theoretical. *o*-Chloroacetyl-*m*-methoxyphenyl benzoate failed to react satisfactorily. 3-Chloroacetyl-*p*-tolyl benzoate and *o*-toluidine gives 3-toluidino-6-methylflavone, yellow needles, m. p. 107—108°; the corresponding compound with *m*-toluidine has m. p. 118—119°; with *p*-toluidine, m. p. 149.5°. 3-Chloroacetyl-*p*-tolyl *p*-methoxybenzoate yields with aniline 3-anilino-4'-methoxy-6-methylflavone, yellow needles, m. p. 151—152°, and the *p*-anisidino-analogue has m. p. 165—166°.

*o*-Chloroacetyl-*p*-methoxyphenyl benzoate forms colourless needles, m. p. 96—97°, and reacts with aniline to yield normally a flavone, m. p. 133—134°, and analogous products with *o*-toluidine (yield exceptional, *viz.*, 45%, m. p. 162.5—163°), with *m*-xylylidine (m. p. 95—96.5°), and with *p*-anisidine (m. p. 120—121°). *o*-Chloroacetyl-*p*-methoxyphenyl anisate, colourless needles, has m. p. 109.5—110.5°, but yields scarcely any flavone. 3-Anilino-flavone, the

simplest representative of the group, was obtained from *o*-chloro-acetophenyl benzoate (colourless rods, m. p. 81—82°) and aniline. It forms yellow needles, m. p. 116°.

The following compounds are also described: *m*-acetyl-*p*-ethoxy-toluene, m. p. 44—45°; ethyl *o*-ethoxytoluate, b. p. 143—143.5°/10 mm.; *N*-methyl-3-phenylglycyl-*p*-cresol, m. p. 87—88°; and its benzoyl derivative, m. p. 120—121°; 3- $\alpha$ -bromopropionyl-*p*-tolyl anisate, m. p. 86.5—87.5°; 3- $\alpha$ -methylphenylglycyl-*p*-cresol, m. p. 96.5—97.5°; 2-chloroacetyl-5-methoxyphenyl anisate, m. p. 152.5—153°; *N*-acetyl-3-phenylglycyl-*p*-tolyl acetate, m. p. 123—124°; and *N*-acetyl-3-phenylglycyl-*p*-cresol, m. p. 152—153°. W. A. S.

**Preparation of Synthetic *d*- and *l*- $\psi$ -Cocaine.** E. MERCK (Brit. Pat. 210050).—Racemic  $\psi$ -ecgonine methyl ester (cf. Willstätter and others, A., 1921, i, 122, and this vol., i, 70) is resolved and the optically active esters obtained are benzoylated with benzoic anhydride. Specimen resolutions by means of *d*- $\alpha$ -bromocamphor- $\beta$ -sulphonic acid, *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonic acid, and malic acid are described. *d*- $\psi$ -Ecgonine methyl ester *d*- $\alpha$ -bromocamphor- $\beta$ -sulphonate forms crystals resembling a coffin-lid in shape and having m. p. 198° and  $[\alpha]_D^{20} + 71.5^\circ$  (in 5% aqueous solution); it yields *d*- $\psi$ -ecgonine methyl ester melting at 115° and identical with the natural product. Benzoylation of this ester with benzoic anhydride in benzene solution yields *d*- $\psi$ -cocaine, m. p. 45°. The hydrochloride of the latter is sparingly soluble in water and has m. p. 205° and  $[\alpha]_D^{20} + 43^\circ$  (in 5% solution). *l*- $\psi$ -Ecgonine methyl ester *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonate has m. p. 243° and  $[\alpha]_D^{20} + 43.7^\circ$  (in 5% aqueous solution). *l*- $\psi$ -Ecgonine methyl ester has  $[\alpha]_D^{20} - 14.8^\circ$  (in 10% methyl-alcoholic solution); it yields *l*- $\psi$ -cocaine on benzoylation and the *r*-ester, m. p. 128°, when mixed with *d*- $\psi$ -ecgonine methyl ester. *d*- $\psi$ -Ecgonine methyl ester *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonate is a readily soluble salt, m. p. 130°. *l*- $\psi$ -Ecgonine methyl ester *l*-malate is sparingly soluble and has m. p. 176° and  $[\alpha]_D^{20} - 18.2^\circ$  (in 5% aqueous solution). The corresponding *d*-ester *l*-malate is soluble and melts at 142°.

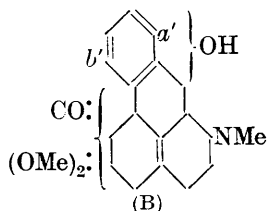
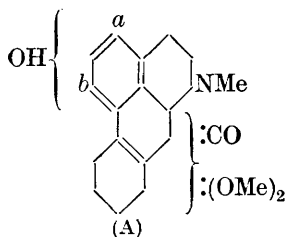
W. T. K. B.

**Preparation of Tropacocaine from Javanese Coca Leaves.** K. HARA and T. SAKAMOTO (*J. Pharm. Soc. Japan*, 1924, 503, 33—38).—Tropacocaine is soluble in dilute ammonia; its hydrobromide is insoluble in water. Utilising this property, the authors have prepared tropacocaine hydrochloride from petroleum extracts of coca leaves produced in Java (yield about 1% of the crude extract). The residue, from which tropacocaine has thus been prepared, is then used as material for preparing cocaine. [Cf. B., 1924, 653.] K. K.

**Alkaloids of *Datura alba*, Nees.** S. OSADA (*J. Pharm. Soc. Japan*, 1924, No. 504, 89—93).—The seeds of *Datura alba*, Nees, from the wild Formosa plant, on extraction with warm 96% alcohol, gave about 12% of brown oil, in which the following alkaloids were identified: *l*-scopolamine 0.24%, hyoscyamine 0.02%, and atropine

(as gold double salt) 0.0026%. A small amount of a *base* which gives a *chloroaurate*, m. p.  $220^{\circ}$ , was also obtained. K. K.

**Alkaloids of Sinomenium and Cocculus. II. Constitution of Sinomenine.** E. OCHIAI (*J. Pharm. Soc. Japan*, 1924, No. 503, 8—23; cf. Kondo, Ochiai, and Nakajima, A., 1923, i, 1222; K. Goto, *J. Chem. Soc. Japan*, 1923, 44, 795).—When treated in glacial acetic acid solution with bromine, sinomenine hydrochloride gives two *monobromides*; one, white needles, melts at  $205^{\circ}$  (decomp.), and the other, needles (obtained in larger amount), at  $138^{\circ}$  (decomp.). Both give a green coloration with ferric chloride. The iodine values (Wijs) of sinomenine and of its benzoyl derivative were found to be 143.9 and 53.89, respectively, whence sinomenine probably has the formula  $C_{19}H_{23}O_4N$ , and contains one ethylenic linking. When reduced by Skita's method, sinomenine affords *dihydrosinomenine*,  $C_{19}H_{25}O_4N$ , m. p.  $199^{\circ}$  (decomp.),  $[\alpha]_D^{16} +170.5^{\circ}$ . Sinomenine gives an *oxime*, m. p.  $254^{\circ}$ , and a *semicarbazone*, m. p.  $264^{\circ}$ , both of which give a green coloration with ferric chloride. Methyl- and dihydrosinomenine also give *semicarbazones*, the former of m. p.  $252^{\circ}$ , the latter of m. p.  $207^{\circ}$ . Thus, one oxygen atom in sinomenine is present in a carbonyl radical, the others in two methoxyl radicals and one phenolic hydroxyl radical. When sinomenine is heated with excess of benzoic anhydride in a sealed tube at  $150$ — $160^{\circ}$  for 6 hours, a colourless, optically inactive *substance*,  $C_{25}H_{22}O_5$  (m. p.  $206^{\circ}$ ), is produced, which is insoluble in acids and alkalis and contains one ethylenic linking, probably produced by the breaking of a nucleus. When treated with ethyl chloroformate in alkaline solution, sinomenine gives a light non-crystallisable *substance*,  $C_{25}H_{32}O_8NCl$ , decomp. at  $183^{\circ}$ ,  $[\alpha]_D^{17} -108.4^{\circ}$ . When distilled with excess of zinc dust, sinomenine affords considerable quantities of phenanthrene, and also of trimethylamine, and a small amount of an oily *substance* having an odour of quinoline. From these facts the author proposes one of the two following formulæ for sinomenine:



K. K.

**Formation of Quaternary Ammonium Salts. II.** E. DE B. BARNETT, J. W. COOK, and W. C. PECK (*J. Chem. Soc.*, 1924, 125, 1035—1040).—The formation of quinolpyridinium salts, which had previously been shown to occur when *p*-benzoquinone was heated with the pyridine salts of inorganic acids, has now been

extended to salts of organic acids. Reaction takes place with difficulty, and the products can only be purified via the picrates. *Dihydroxyphenylpyridinium phenylacetate*, brown leaflets, m. p. 160°, was obtained by interaction of *p*-benzoquinone, pyridine, and phenylacetic acid.

The interaction of ethylenic compounds and pyridine-bromine mixtures has also been investigated. Well-defined *vic*-bromopyridinium salts were obtained from anethole, *isosafole*, *cyclohexane*, and *stilbene*, the respective compounds formed being:  $\beta$ (or  $\alpha$ )-*bromodihydroanethole*- $\alpha$ (or  $\beta$ )-*pyridinium bromide*, m. p. 170—172° (decomp.);  $\beta$ (or  $\alpha$ )-*bromodihydrosafrole*- $\alpha$ (or  $\beta$ )-*pyridinium bromide*, m. p. 193° (decomp.); 1-*bromocyclohexane*-2-*pyridinium bromide*, m. p. 165—170°;  $\beta$ -*bromo*- $\alpha\beta$ -*diphenylethylpyridinium bromide*, m. p. 190—193°, which after boiling with water and precipitated calcium carbonate gave  $\beta$ -*dihydroxy*- $\alpha\beta$ -*diphenylethylpyridinium bromide*, m. p. 238—240°. Cinnamic acid yielded  $\alpha$ -*bromo*- $\beta$ -*phenylpropionic acid*- $\beta$ -*pyridinium bromide*, m. p. 193—198° (decomp.), which on boiling with water or alcohol was converted into a *betaine*, m. p. 178—180°. *Methyl*  $\alpha$ -*bromo*- $\beta$ -*phenylpropionate*- $\beta$ -*pyridinium bromide*, m. p. 178° (decomp.), and the corresponding *ethyl* ester, m. p. 157—158° (decomp.), were obtained from methyl and ethyl cinnamate respectively. Both of these esters when treated with ammonia gave methyl and ethyl  $\alpha$ -*bromocinnamates* in 80—90% yield. The product obtained from safole was too soluble to be isolated and probably consists of a dipyridinium salt.

C. J. S.

**Synthesis of Pyridine-ketones from Hydroxymethyleneacetone and -acetophenone.** E. BENARY and H. PSILLE (*Ber.*, 1924, 57, [B], 828—834).—An ethereal solution of  $\omega$ -formylacetophenone was added to a saturated solution of ammonium acetate in glacial acetic acid and allowed to stand. Di- $\beta$ -benzoylvinylamine,  $(\text{CHBz}:\text{CH})_2\text{NH}$ , separated (Claisen's "ammonia compound of benzoylacetaldehyde," A., 1888, 690) which gave 1:3-diphenylpyrazole with phenylhydrazine (cf. Knorr, A., 1893, i, 230). From the acetic acid mother-liquor a base,  $\text{C}_{18}\text{H}_{13}\text{ON}$ , was recovered, colourless crystals, m. p. 89.5°; its *oxime* (m. p. 183—184°) with phosphorus pentachloride gave an *anilide*,  $\text{C}_{18}\text{H}_{14}\text{ON}_2$ , leaflets, m. p. 199°, which hydrolysed to an acid,  $\text{C}_{12}\text{H}_9\text{O}_2\text{N}$ , colourless needles, m. p. 220—229°, yielding 2-phenylpyridine (picrate, m. p. 175°) on heating with lime. The acid was therefore 2-*phenylpyridine*-5-*carboxylic acid*, and the original base 3-*benzoyl*-6-*phenylpyridine*. The latter is slowly attacked by permanganate and is unaffected by fused potassium hydroxide; it forms a yellow *picrate*, m. p. 175°; a colourless *hydrochloride*, m. p. 202°; a *nitrate*, m. p. 135—136°, and a *sulphate*, m. p. 137—138°. 3-Benzoyl-6-phenylpyridine with alcohol and zinc dust afforded 2-*phenyl*-5- $\alpha$ -*hydroxybenzylpyridine*,  $\text{OH}\cdot\text{CHPh}\cdot\text{C}_5\text{H}_3\text{NPh}$ , rhombohedra, m. p. 115—116° (*picrate*, m. p. 175—176°; *hydrochloride*, m. p. 173—174°). With phosphorus pentachloride the carbinol yielded 2-*phenyl*-5- $\alpha$ -*chlorobenzylpyridine*, m. p. 79°, reduced by acetic

acid and zinc dust to 2-phenyl-5-benzylpyridine, as leaflets, m. p. 63—63.5° (*picrate*, m. p. 145—146°; *hydrochloride*, m. p. 170°).

Treatment of sodium formyl-acetone with ammonium acetate and glacial acetic acid gave 3-acetyl-6-methylpyridine, b. p. 231—232° (cf. Knudson, A., 1895, i, 564), oxime, m. p. 182°. *Hydrochloride*, hygroscopic; *picrate*, m. p. 190°; *chloromercurate*,  $C_8H_9ON \cdot HgCl_2$ , m. p. 128°, and *methiodide*, m. p. 156.5°. On warming with nitric acid (1.42) 5-acetyl-2-methyl pyridine yielded 2-methylpyridine-5-carboxylic acid nitrate, m. p. 170—171°, which on distillation with lime yielded pyridine but no  $\alpha$ -picoline; the nitrate yielded a dark green copper salt,  $(C_5H_3NMe \cdot CO_2)_2Cu$ ,  $(AcO)_2Cu$ , from which the free acid was obtained, m. p. 207° (cf. Ladenberg, *Ann.*, 1888, 247, 43). 3-Acetyl-6-methylpyridine, when condensed with formic ester by means of sodium ethoxide, gave the orange sodium salt of 5-hydroxyacryl-2-methylpyridine,  $C_5H_3NMe \cdot CO \cdot CH : CH \cdot OH$  (copper salt, light olive-green). 5-Hydroxyacryl-2-methylpyridine was obtained as an unstable yellow oil by the action of sulphuric acid on the copper salt; it gave no precipitate with picric acid or with mercuric chloride. The sodium salt reacted with aniline to form 5-hydroxyacryl-2-methylpyridine-anil,  $C_5H_3NMe \cdot CO \cdot CH : CH \cdot NHPH$ , as pale yellow needles, m. p. 154—155°.

F. A. M.

**New Method in the isoQuinoline and its Ring Homologous Series.** J. VON BRAUN, G. BLESSING, and R. S. CAHN (*Ber.*, 1924, 57, [B], 908—912).—Ring closure with the formation of tetrahydroisoquinolines and *as*-homotetrahydroisoquinolines is readily effected by the successive action of phosphorus pentachloride and aluminium chloride on acylated derivatives of  $\beta$ -phenylethyl- and  $\gamma$ -phenylpropyl-glycine.

The benzenesulphonyl derivative of  $\beta$ -phenylethylglycine,  $CH_2Ph \cdot CH_2 \cdot N(SO_2Ph) \cdot CH_2 \cdot CO_2H$ , m. p. 122°, is dissolved in nitrobenzene and treated successively with phosphorus pentachloride and aluminium chloride, thus giving 2-benzenesulphonyltetrahydroisoquinoline, m. p. 154° (yield 80%), from which tetrahydroisoquinoline is readily obtained, the over-all yield being about 50% of that theoretically possible.  $\beta$ -m-Tolylethylamine is converted by ethyl bromoacetate in ethereal solution into ethyl  $\beta$ -m-tolylethylaminoacetate, b. p. 165—167°/11 mm., which is transformed by concentrated hydrochloric acid into  $\beta$ -m-tolylethylglycine hydrochloride, m. p. 212—214°. The latter compound is converted into  $\beta$ -m-tolylethylbenzenesulphonylglycine, m. p. 105—106°, from which 2-benzenesulphonyl-6-methyltetrahydroisoquinoline, m. p. 102°, is derived. 6-Methyltetrahydroisoquinoline has b. p. 110°/11 mm., 255—256°/758 mm.,  $d_4^{20}$  1.0235; the hydrochloride, m. p. 195—197°, *picrate*, m. p. 205°, nitroso derivative, m. p. 98°, and quaternary methiodide, m. p. 144—145°, are described.

Ethyl  $\gamma$ -phenylpropylaminoacetate, b. p. 167—170°/11 mm., is transformed into  $\gamma$ -phenylpropylglycine hydrochloride, decomp. 201°. The non-crystalline benzenesulphonyl derivative of  $\gamma$ -phenylpropylglycine and the corresponding toluene-p-sulphonyl compound, m. p.



98—100°, are described. The latter substance is readily transformed in the usual manner into *toluene-p-sulphonyl-as-homotetrahydroisquinoline*, m. p. 135°, from which the free base,  $C_6H_4 \begin{smallmatrix} \text{[CH}_2\text{]}_3 \\ \text{CH}_2 \end{smallmatrix} \text{NH}$ , is obtained by hydrolysis. H. W.

**Preparation of Compounds Related to the Acridines.** BRITISH DYESTUFFS CORPORATION, W. H. PERKIN, and G. R. CLEMO (Brit. Pat. 214756).—Dihydroacridines are obtained by reducing the corresponding acridones with sodium amalgam in hot alcoholic solution in presence of sodium hydrogen carbonate, carbon dioxide being passed through the reacting mixture. After removal of the alcohol, the dihydroacridine is precipitated by adding water. The dihydroacridines yield the corresponding acridines when oxidised (e.g., with nitrous acid or chromic acid).

9-Aminodihydroacridine (almost colourless hairs, m. p. 114°), obtained by reducing 9-nitroacridone with sodium amalgam, is converted into 9-aminoacridine by acylating (to protect the amino group), oxidising as above, and hydrolysing the product.

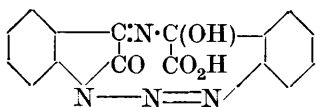
W. T. K. B.

**Products of the Action of Ammonia on Isatin.** A. REISSERT and H. HOPPMANN (Ber., 1924, **57**, [B], 972—981).—The constitution of many of the compounds isolated by Laurent in the years 1842 and 1845 has been elucidated.

*Isatin ammonia* [3-amino-3-hydroxy-2-ketodihydroindole], the primary product of the action of isatin and ammonia, is obtained when ammonia is passed into an ice-cold, alcoholic suspension of isatin until further separation of crystals does not occur; it readily loses ammonia when exposed to the air. If the stream of ammonia is interrupted as soon as the isatin is completely dissolved and the solution is then preserved, isatin-3-imide (Laurent's imesatin) is obtained in dark yellow, rectangular prisms, m. p. 175—176°, which is considerably more stable than the corresponding 2-compound. If the action of alcoholic ammonia on isatin is very protracted or if concentrated aqueous ammonia is used, 3-isatinimidyl-

*o*-aminomandelic acid,  $NH_2 \cdot C_6H_4 \cdot C(OH)(CO_2H) \cdot N:C \begin{smallmatrix} \text{CO} \\ \text{C}_6H_4 \end{smallmatrix} \text{NH}$  (Laurent's imasatic or isamic acid), is produced, which is more conveniently prepared by boiling isatin with ammonium acetate solution. It forms red, prismatic crystals, m. p. 164—165° (decomp.). The *ammonium* and *aniline* salt, m. p. 198°, and the *o*-benzoyl derivative, m. p. 188°, are described. The constitution of the acid is established by its synthesis from isatin-3-imine and ammonium isatate. The acid could not be converted into its cyclic anhydride, but when esterified, yields derivatives thereof of the type  $NH \begin{smallmatrix} \text{C}_6H_4 \\ \text{CO} \end{smallmatrix} > C:N \cdot C(OH) \begin{smallmatrix} \text{C}_6H_4 \\ \text{C(OR)} \end{smallmatrix} > N$ , of which the *methyl*, m. p. 186—187°, *ethyl*, m. p. 197°, and *propyl*, m. p. 181°, compounds are described; they are reconverted by sodium hydr-

oxide into the acid. Diazotisation of the latter substance in aqueous solution leads to the production of 3-isatinimidyl-o-N-azomandelic



acid (annexed formula), m. p. about 140° (decomp.). If, however, ethyl nitrate is used, both hydroxy groups are esterified with formation of ethyl 3-isatinimidyl-o-N-azophenylethoxyacetate, m. p. 214—

215°, which is hydrolysed to the corresponding acid, m. p. 195°. Ethyl 3-isatinimido-o-N-azomandellate has m. p. 214—215°.

When isatin is subjected to the prolonged action of aqueous ammonia, a phenolic substance (Laurent's imasatin), m. p. 230° after softening at 200°, is produced in addition to 3-isatinimidyl-o-aminomandelic acid. Since it can be synthesised by warming isatin and isatinimine in alcoholic solution, it is regarded as 3-isatinimidyl-3-dioxindole, although its genetic relationship to 3-isatinimidyl-o-aminomandelic acid could not be established. The *monobenzoyl* derivative decomposes above 240°.

Laurent's amasatin or isamide can be prepared by heating ammonium 3-isatinamidyl-o-aminomandellate, and is therefore 3-isatinimidyl-o-aminomandelamide; the corresponding *anilide* has m. p. 168°.

When isatin is treated with ammonia under pressure at the atmospheric temperature, Sommaruga's "di-iminoisatin or isatin-diamine" is produced, which appears to be a polymeric isatinimine. At 100°, "hydroxydiaminodi-iminoisatin,"  $C_{16}H_{14}O_3N_6$ , is also formed.

H. W.

### Preparation of a Monochloro Derivative of Antipyrine.

A. LEULIER (*J. Pharm. Chim.*, 1924, [vii], 29, 447—449).—A *monochloroantipyrine*,  $C_{11}H_{11}ON_2Cl$ , faintly yellow needles, m. p. 123—124°, is obtained by dissolving antipyrine in a 20% solution of chlorine and keeping the mixture for  $\frac{1}{4}$  hour. The yield is smaller if sodium hypochlorite is used. Its aqueous solution gives a red coloration with ferric chloride.

W. T. K. B.

### Synthesis of Pyrazolealdehydes. II. C. A. ROJAHN and

A. SEITZ (*Annalen*, 1924, 437, 297—308; cf. this vol., i, 91).—The methods previously found successful in the preparation of pyrazole-4-aldehydes have been used in the synthesis of the 3(5)-aldehydes. The reduction of the acid chlorides affords, besides the aldehyde, oily by-products, which were found to be pyrazoles containing a methyl group less than was expected, carbon monoxide being lost in the reaction. It remains uncertain whether the decomposition is  $R \cdot COCl \rightarrow RH + CO + HCl$  or  $R \cdot COH \rightarrow RH + CO$ . The 3- and 5-pyrazolealdehydes are for the most part oils with the general reactions of aromatic aldehydes. They do not undergo the benzoin or Cannizzaro reaction, the latter only affording traces of the carboxylic acid and resinous products (cf. Fischer and Zerweck, A., 1923, i, 364). 1-Phenyl-5-methylpyrazole-3-carboxylic acid with thionyl chloride yields 1-phenyl-5-methyl-

*pyrazole-3-carboxyl chloride*, m. p.  $85^{\circ}$  (*anilide*, m. p.  $138^{\circ}$ ), which on reduction in xylene with palladium-barium sulphate catalyst, either with or without "sulphured" quinoline, gives 60—70% of the theoretical yield of 1-phenyl-5-methylpyrazole-3-aldehyde,  $d^{15}_4 = 1.155$  (*phenylhydrazone*, m. p.  $173^{\circ}$ ; *semicarbazone*, m. p.  $183^{\circ}$ ; *oxime*, m. p.  $166^{\circ}$ ; *aminoguanidine nitrate derivative* ( $+1\text{H}_2\text{O}$ ),  $\text{C}_{12}\text{H}_{17}\text{O}_4\text{N}_7$ , m. p.  $155^{\circ}$ ). On shaking the bisulphite compound with aqueous potassium cyanide, the *hydroxymitrile* is formed, yellow needles, m. p.  $121^{\circ}$ . 1-Phenylpyrazole-5-carboxylic acid similarly yields 1-phenylpyrazole-5-carboxyl chloride, long needles, m. p.  $53^{\circ}$ , which on reduction with the catalyst and in the presence of a glowing copper spiral yields 1-phenylpyrazole-5-aldehyde (*semicarbazone*, m. p.  $168^{\circ}$ ; *oxime*, m. p.  $177^{\circ}$ , *aminoguanidine nitrate derivative*,  $\text{C}_{11}\text{H}_{12}\text{N}_6\text{HNO}_3$ , m. p.  $192^{\circ}$ ), and a little 1-phenylpyrazole. By the condensation of ethyl acetylpyruvate with phenylhydrazine (cf. Claisen, A., 1894, i, 346) besides the 1-phenyl-5-methylpyrazole-3-carboxylic acid a higher melting product was obtained which with thionyl chloride yields 1-phenyl-3-methylpyrazole-5-carboxyl chloride, m. p.  $39\text{--}41^{\circ}$ , identified by conversion to the corresponding acid and amide. On reduction in the presence of a glowing copper spiral, 1-phenyl-3-methylpyrazole was obtained together with 1-phenyl-3-methylpyrazole-5-aldehyde (*aminoguanidine nitrate derivative*, m. p.  $196^{\circ}$ ), which yields two *semicarbazones*, m. p.  $166^{\circ}$  and  $195^{\circ}$ , and two *oximes*, m. p.  $146^{\circ}$  and  $179^{\circ}$ , partial transformation of the lower-melting isomeride taking place in each case on seeding. 1-Phenyl-5-methylpyrazole-3-carboxylic acid on bromination in acetic acid solution yields 4-bromo-1-phenyl-5-methylpyrazole-3-carboxylic acid, white needles, m. p.  $184^{\circ}$ , converted to 4-bromo-1-phenyl-5-methylpyrazole-3-carboxyl chloride, long, lustrous needles, m. p.  $78^{\circ}$ , by thionyl chloride; the chloride on reduction yields 4-bromo-1-phenyl-5-methylpyrazole, b. p.  $130^{\circ}$  (*methiodide*, m. p.  $206^{\circ}$ ), which was also obtained by brominating 1-phenyl-5-methylpyrazole, and 4-bromo-1-phenyl-5-methylpyrazolealdehyde, m. p.  $71^{\circ}$  (*oxime*, m. p.  $194^{\circ}$ ; *semicarbazone*, m. p.  $217^{\circ}$ ; *aminoguanidine nitrate derivative*,  $+1\text{H}_2\text{O}$ , m. p.  $193^{\circ}$ ), the bisulphite liquor used in the separation yielding also some 4-bromo-1-phenyl-5-methyl-3-hydroxymethylpyrazole, m. p.  $166\text{--}167^{\circ}$  (*acetate*, m. p.  $108^{\circ}$ ). 4-Chloro-1-phenyl-5-methylpyrazole-3-carboxylic acid, m. p.  $221^{\circ}$ , was obtained by the action of chlorine on a cold chloroform solution of 1-phenyl-5-methylpyrazole-3-carboxylic acid. R. B.

**Conversion of Diketopiperazines into the corresponding Piperazines.** E. ABDERHALDEN, E. KLARMANN, and E. SCHWAB (*Z. physiol. Chem.*, 1924, 135, 180—187).—Piperazine hydrochloride was prepared from glycine anhydride by reduction with sodium, amyl alcohol, etc. *iso*Butylpiperazine dihydrochloride was similarly prepared from leucylglycine anhydride using sodium and ethyl alcohol. *Dibenzoylisobutylpiperazine* does not melt at  $300^{\circ}$ . The yields throughout were not good. The authors discuss the possibilities of the addition of amino-acids occurring through the imino

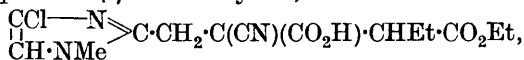
group or through the hydroxyl group of the tautomeric form of diketopiperazines.

E. M. C.

**Preparation of Compounds of Diketopiperazines with Amino-acids or Polypeptides. II.** E. ABDERHALDEN and E. KLARMANN (*Z. physiol. Chem.*, 1924, **135**, 199—202).—Neither alanylglycine anhydride nor leucylglycine anhydride reacts with chloroacetyl chloride (cf. A., 1923, i, 1025). Glycine anhydride and  $\alpha$ -bromo- $\gamma$ -methylvaleryl chloride gave 1:4-di( $\alpha$ -bromo- $\gamma$ -methylvaleryl)-2:5-diketopiperazine, m. p. 145°, which with ammonia gave glycine anhydride and leucinamide.

E. M. C.

**Synthetic Experiments in the Glyoxaline Group.** A. SONN, E. HOTES, and H. SIEG (*Ber.*, 1924, **57**, [B], 953—959).—4-Chloro-1-methylglyoxaline is converted by formaldehyde at 130—140° into 4-chloro-1-methyl-2-hydroxymethylglyoxaline, m. p. 120° (cf. Sarasin, A., 1923, i, 711); the picrate, m. p. 150—151°, hydrochloride, m. p. 162°, additive compound with mercuric chloride, m. p. 161—162°, the benzoate, m. p. 75°, and its picrate, m. p. 167°, are described. The base is transformed by thionyl chloride into 4-chloro-1-methyl-2-chloromethylglyoxaline hydrochloride, m. p. 167—168° (corresponding picrate, m. p. 156—157°), which is reduced by zinc dust and glacial acetic acid to 4-chloro-1:2-dimethylglyoxaline, a yellow liquid (picrate, m. p. 175—176°), and by phosphorus and hydriodic acid to 1:2-dimethylglyoxaline. The catalytic reduction of 4-chloro-1-methyl-2-hydroxymethylglyoxaline yields 1-methyl-2-hydroxymethylglyoxaline, which is identified as the picrate, m. p. 136—137°. The following compounds are obtained from 4-chloro-1-methyl-2-chloromethylglyoxaline: 4-chloro-1-methyl-2-ethoxymethylglyoxaline, a pale yellow, mobile liquid, and its picrate, m. p. 101—102°; 4-chloro-1-methyl-2-methylamino-methylglyoxaline picrate, m. p. 178°; 4-chloro-1-methyl-2-dimethylaminomethylglyoxaline hydrochloride, m. p. 198° (decomp.); 4-chloro-1-methyl-2-anilinomethylglyoxaline, m. p. 125—126°, and its picrate, m. p. 170—171°; 4-chloro-2-p-ethoxyanilino-1-methylglyoxaline, m. p. 114—115°. 4-Chloro-1-methyl-2-cyanomethylglyoxaline, m. p. 128° after softening at 110° (picrate, m. p. 177—178°) is reduced by sodium and alcohol to 4-chloro-1-methyl-2-aminoethylglyoxaline, which is analysed as the picrate, m. p. 176° after previous softening. The action of 4-chloro-1-methyl-2-chloromethylglyoxaline on the sodium derivative of ethyl  $\alpha$ -cyano- $\beta$ -ethylsuccinate and subsequent hydrolysis of the product with boiling concentrated hydrochloric acid leads to the isolation of 4-chloro-1-methyl-2- $\beta$ -cyano- $\gamma$ -carboxy-n-amyglyoxaline hydrochloride, plates, decomp. 250° after darkening at 242° and (?) ( $\gamma$ )ethyl hydrogen  $\beta$ -cyano- $\alpha$ -4-chloro-1-methyl-2-glyoxalinylpentane- $\beta\gamma$ -dicarboxylate,



m. p. 128° (picrate, m. p. 163—164° after slight previous softening). 4-Chloro-1-methyl-2-chloromethylglyoxaline gives a non-crystalline condensation product with ethyl sodiomalonate which is trans-

formed by successive bromination, hydrolysis, and elimination of carbon dioxide into a non-homogeneous, brominated monocarboxylic acid; the latter is converted by saturated aqueous ammonia at 50—60° into *ammonium α-amino-β-4-chloro-5-bromo-1-methylglyoxalinypropionate*, m. p. 205—206° after previous softening (picrate of amino-acid, m. p. 231°).

Dimethyloxamide is converted by phosphorus pentabromide into *dibromo-1-methylglyoxaline*, colourless needles, m. p. 78—79° (picrate, m. p. 146°).

H. W.

### Stable and Labile Acyl Derivatives of the Indazoles.

K. VON AUWERS and H. G. ALLARDT (*Annalen*, 1924, **438**, 1—33). —The 2-acyl derivatives of indazole and substituted indazoles have been examined, especially with regard to the stabilities of the labile forms (cf. A., 1919, i, 455; 1920, i, 638, 640; 1921, i, 806). The general method of the preparation of the labile forms is by the action of the silver salt of the indazole on the corresponding indazole in dry ether at 0° or by the interaction of the indazole and the acid chloride in dry pyridine or ether at 0°. The stable form is produced by the interaction of the sodium salt and the acid chloride under similar conditions. Many acyl indazoles are rather easily hydrolysed, especially the labile form; with hydrogen chloride in dry ether, the latter give indazole hydrochloride, whereas the stable form is unchanged after some hours. The effect of the acyl group on the stability of the labile acylindazoles has been examined. Preliminary experiments were carried out in sealed tubes, and the relative stabilities of some of the compounds are given as follows: *o*-nitrobenzoyl-, *o*-nitrocinnamoyl-, 2-nitro-5-bromobenzoyl- (stable after 1 year); *p*-nitrobenzoyl-, phenylacetyl-, carbonyl-, succinyl- (partly converted), isobutyryl- (converted in a few days), crotonyl- (1 day), *n*-butyryl- (somewhat more stable), propionyl- and acetyl- (unstable).

The following stable and labile 2-acyl derivatives have been examined, and the following values, amongst others, are given (*s*=stable; *l*=labile; rotatory dispersions are also given when refractive indices are given).

(*s*)-2-Acetylindazole,  $d_4^{16.5}$  1.1886,  $n_{He}^{16.8}$  1.58955; (*l*)-2-acetyl indazole,  $d_4^{18.7}$  1.1007,  $n_{He}^{18.7}$  1.62682; (*s*)-2-chloroacetylindazole, monoclinic prisms, m. p. 82—83°, b. p. 162°/10 mm.,  $d_4^{20.6}$  1.2636,  $n_{He}^{20.6}$  1.57393; (*s*)-2-dichloroacetylindazole, stout white needles, m. p. 80—82°, b. p. 168—170°/13 mm.; (*s*)-2-trichloroacetylindazole, small prisms, m. p. 116—117°, hydrolysed by ethyl alcohol; (*s*)-2-cyanoacetylindazole, colourless crystals, m. p. 164—165°; (*s*)-2-bromoacetylindazole, fine needles, m. p. 73—74°; (*s*)-2- $\alpha$ -bromopropionylindazole, needles, m. p. 65—66°; (*s*)-2-*n*-butyrylindazole, colourless prisms, m. p. 61°, b. p. 150°/15 mm.,  $d_4^{23.5}$  1.1090,  $n_{He}^{23.5}$  1.55854; (*l*)-2-*n*-butyrylindazole, small, glassy prisms, m. p. 86—87°, easily converted to stable form,  $n_{He}^{22.5}$  1.62593 (in quinoline); (*s*)-2-isobutyrylindazole, oil, b. p. 132°/11 mm.,  $d_4^{2.8}$  1.1136,  $n_{He}^{2.8}$  1.56534; (*l*)-2-isobutyrylindazole, oil, easily converted to  $\alpha$ -form by ethereal hydrogen chloride,  $d_4^{3.0}$  1.1159,  $n_{He}^{3.0}$  1.57671; (*s*)-2-isovalerylindazole, b. p. 148—150°/11 mm.,  $d_4^{6.3}$  1.0879,  $n_{He}^{6.3}$

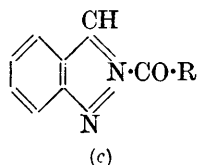
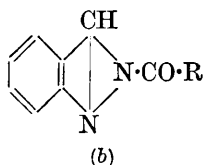
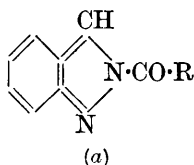
1.55466; (*l*)-2-*isovalerylindazole*, needles, m. p. 64° (approx.), unstable; (*s*)-2-*crotonylindazole* can only be prepared from the labile isomeride by standing over sulphuric acid, m. p. 78—80°; (*l*)-2-*crotonylindazole*, white, very hygroscopic crystals, m. p. 102°, resinifying on warming at 100°; (*s*)-2- $\Delta^7$ -*pentenoylindazole*, b. p. 168—170°/16 mm.,  $d_4^{25}$  1.1172,  $n_D^{25}$  1.57070; (*s*)-2-*nitrobenzoylindazole*, fine needles, m. p. 186—187°; (*l*)-2-*nitrobenzoylindazole*, fine, yellowish-green needles, m. p. 141—142°, stable, but by boiling in xylene, the (*s*)-isomeride produced, and by distillation under reduced pressure (13 mm.) this is also produced (b. p. 253—254°/13 mm.); (*s*)-2-*m-nitrobenzoylindazole*, stout, white crystals (benzene), needles (ether), m. p. 134°; (*l*)-2-*m-nitrobenzoylindazole*, very unstable; crystallisation from methyl alcohol hydrolyses the product; pale green, m. p. 142—144° (impure); (*s*)-2-*p-nitrobenzoylindazole*, fine needles, m. p. 164—165°; (*l*)-2-*p-nitrobenzoylindazole*, greenish-yellow, m. p. 137—138°, long heating giving the (*s*)-form; (*s*)-5-*bromo-2-o-nitrobenzoylindazole*, prisms, m. p. 186—187°; (*l*)-5-*bromo-2-o-nitrobenzoylindazole*, greenish-yellow needles, m. p. 189°, fairly stable, but slowly changed to the (*s*)-isomeride by heat; (*s*)-2-*o-chlorobenzoylindazole*, small prisms, m. p. 99°; (*l*)-2-*o-chlorobenzoylindazole*, fine, pale yellow needles, m. p. 76—77°, fairly stable; (*s*)-2-*phenylacetylindazole*, flat needles, m. p. 67—68°; (*l*)-2-*phenylacetylindazole*, m. p. 106—107°; (*s*)-2-*o-nitrophenylacetylindazole*, needles, m. p. 124—125°; (*l*)-2-*o-nitrophenylacetylindazole*, small needles, m. p. 107—108°, easily converted to the (*s*)-isomeride; (*s*)-2-*cinnamoylindazole*, fine needles, m. p. 120—121°; (*l*)-2-*cinnamoylindazole*, needles, m. p. 152—156°, not very stable; (*s*)-2-*o-nitrocinnamoylindazole*, fine needles, m. p. 185—187°; (*l*)-2-*o-nitrocinnamoylindazole*, fine, greenish-yellow needles, m. p. 156—157.5°, on heating giving the colourless stable isomeride; 2-*indazolecarboxyl chloride*, from indazole and carbonyl chloride in dry ether at -10° (produced together with di-indazyl carbonate) forms fine needles, m. p. 73—74°. It is decomposed to indazole by warm water, and with methyl alcohol gives *methyl indazole-2-carboxylate*. The *amide*, from ammonia and the above chloride, in ether forms needles, m. p. 167°. The labile form of the acid chloride could not be prepared. The following are also described: (*s*)-2:2'-*di-indazyl carbonate*, glassy needles, m. p. 137—138°, is prepared as a by-product of the above reaction and as main product on warming the acid chloride with indazole; (*l*)-2:2'-*di-indazyl carbonate*, from silver indazole and the above chloride in dry ether at -10°, is very unstable and has m. p. 149—151°; (*s*)-2-*indazole-carbanilide*, from indazole and phenylcarbimide or from the chloride and aniline, stout crystals, m. p. 104—105°; (*l*)-2-*indazole-carbanilide*, from indazole and phenylcarbimide in dry ether at -15°, crystals, m. p. 105—106°, is converted to the stable isomeride after heating for 2 hours; (*s*)-2:2'-*di-indazyl succinate*, small needles, m. p. 159°; (*l*)-2:2'-*di-indazyl succinate*, greenish-yellow needles, m. p. 140°, easily converted to the stable isomeride; 2-*indazyl hydrogen succinate*, needles, m. p. 146—147°, is prepared from silver indazole and succinyl chloride in dry ether and hydro-

lysing the *chloride* so obtained; (*s*)-2-indazole-*p*-toluenesulphonate, small, stout crystals; (*l*)-2-indazole-*p*-toluenesulphonate, small, six-sided crystals, easily changed to the (*s*)-isomeride; 2-indazyl phenyl carbonate, from 2-indazolecarboxyl chloride and sodium phenoxide in dry ether, m. p. 91°; 2-indazyl *o*-nitrophenyl carbonate, waxy needles, m. p. 97—98°, on distillation giving nitrophenyl-indazole (m. p. 153—154°, b. p. 245°/27 mm.); 2-indazyl *p*-tolyl thiocarbonate, long needles, m. p. 123°, decomposed on distillation under diminished pressure, giving a *compound*, m. p. 197—199°. 2-Picrylindazole from picryl chloride and indazole, golden, rhombic plates, m. p. 208—210°, possesses no basic properties. The refractive indices, rotatory dispersions, and densities are given of the following: (*s*)-2-acetyl-3-ethylindazole,  $d_4^{25}$  1.0951,  $n_D^{25}$  1.55639; (*s*)-2-acetyl-6-methylindazole,  $d_4^{25}$  1.1623,  $n_D^{25}$  1.58676; (*s*)-2-propionyl-5-methylindazole,  $d_4^{25}$  1.0544,  $n_D^{25}$  1.53682; (*l*)-2-propionyl-5-methylindazole,  $d_4^{25}$  1.0505,  $n_D^{25}$  1.55099.

The authors have shown that the presence of negative groups in aliphatic 2-acyl residues precludes the existence of the labile isomeride, but in aromatic acyl residues, with the negative group in the *o*- or *p*-position, the labile form has considerable stability, although if the negative group is in the *m*-position, the labile isomeride is less stable.

Attempts to prepare aminobenzoylindazoles by reduction of the corresponding nitro-compounds were unsuccessful. 2:2'-Diindazole derivatives of dibasic acids gave labile forms of varying stability.

Three possible formulæ are suggested for the acylindazoles:



of which (c) is not considered seriously.

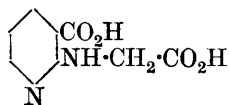
Spectrochemical experiments indicate (a) to be unlikely. The authors believe the isomerism to be steric in character and from measurements of the refractive index and rotatory dispersion it appears that formula (b) is the most likely for both isomerides. Against this, however, it is urged that the colour of certain of the labile isomerides suggests a quinonoid structure which would indicate (a) to be more likely; also that according to formula (b) the benzene ring and the 3-ring would not be co-planar, whereas for formula (a) the rings are co-planar; in the former case, isomerism would involve a large strain. Also if formula (a) be correct, hydrogen chloride should add on to the 1-nitrogen atom with difficulty in the case of one isomeride, owing to the proximity of the acyl group. This has been found to be true, the hydrogen chloride actually splitting off the acyl group. The question is left undecided.

A. E. C.

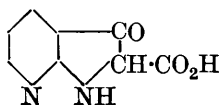
**Carbonyldiphenylhydrazine.** R. STOLLÉ (*Ber.*, 1924, **57**, [B], 1063—1066).—Carbonyldiphenylhydrazine was apparently obtained by Acree (*A.*, 1903, **i**, 861) from  $\alpha\alpha$ -diphenylhydrazine- $\beta$ -carbonyl chloride. Diphenylcarbamyl azide, m. p.  $85^\circ$  [decomp.  $+x\text{C}_6\text{H}_6$ , m. p.  $61^\circ$ ; Toschi (*A.*, 1914, **i**, 740), gives  $78\text{--}79^\circ$ ] on heating in tetrahydronaphthalene or xylene gives the unsaturated radical,  $\text{Ph}_2\text{N}\cdot\text{CO}\cdot\text{N}\cdot$ , but the carbonyl-diphenylhydrazine which is undoubtedly formed suffers rearrangement to 3-hydroxy-1-phenylbenzpyrazole,  $\text{C}_6\text{H}_4\langle\text{C}(\text{OH})\text{NPh}\rangle\text{N}$  (or the corresponding lactam) (cf. Curtius and Schmidt, *A.*, 1923, **i**, 1080). This substance, dense crystals, m. p.  $209^\circ$ , is converted by methyl sulphate into a mixture of the *N*- and *O*-ethers, the latter forming colourless plates, m. p.  $95^\circ$  (cf. König and Reissert, *A.*, 1899, **i**, 457). In moist tetrahydronaphthalene, diphenylcarbamyldiazide yields tetraphenylcarbazine,  $(\text{NPh}_2\cdot\text{NH})_2\text{CO}$ . Ethyl  $\beta\beta$ -diphenylhydrazinoformate, m. p.  $141^\circ$ , is obtained as a by-product when diphenylcarbamyldiazide is crystallised from alcohol. The action of carbonyl chloride on *o*-aminodiphenylamine yields *sym-di-o* : *o'*-anilinodiphenylcarbamide, m. p.  $204^\circ$ , and a small quantity of a substance, m. p.  $160^\circ$ , containing chlorine which with alkali or pyridine yields the above carbamide. The insensitiveness of diphenylcarbamyldiazide towards water, acids, and alkalis leads to the consideration of the phenylbenziminazolone formula,  $\text{C}_6\text{H}_4\langle\text{NH}\text{C}\rangle\text{CO}$ . The experiments to prepare carbonylhydrazines and benzpyrazolones are being continued. R. B.

**Condensation of 2-Aminonicotinic Acid with Chloroacetic Acid to Derivatives of 1:7-Benzdiazole.** E. SUCHARDA (*Roczniki Chemji*, 1923, **3**, 236—250).—So far no compounds analogous to indole or indigotin have been prepared containing pyridine in place of benzene rings. The synthesis of such compounds is now described.

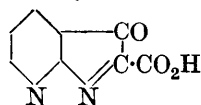
2-Aminonicotinic acid (Phillips, *A.*, 1894, **i**, 301) condenses with chloroacetic acid in the presence of potassium carbonate to give a good yield of *pyridylglycinecarboxylic acid* (I) crystallising with  $1\text{H}_2\text{O}$  and melting in the anhydrous condition at  $218\text{--}219^\circ$  (decomp.) with previous shrinking; the substance is strongly acid and forms a sodium salt, grey needles,  $\text{C}_8\text{H}_7\text{O}_4\text{N}_2\text{Na}\cdot 3\text{H}_2\text{O}$ . The action of mineral acids on the acid (I) leads to 3-keto-2 : 3-dihydro-1 : 7-benzdiazole-2-carboxylic acid (II) in quantitative yield.



(I.)



(II.)



(III.)

The new acid forms yellow crystals containing  $1\text{H}_2\text{O}$  which is lost at  $120^\circ$ , the anhydrous substance melting at  $220^\circ$  (decomp.) with previous darkening; it is amphoteric in nature, the basic character predominating. The *hydrochloride* forms yellow needles, m. p.  $284^\circ$  (decomp.); the *sulphate*,  $(\text{C}_8\text{H}_6\text{O}_3\text{N}_2)_2\cdot\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$ ,



forms yellow crystals, m. p.  $225^{\circ}$  (decomp.). By the action of sodium nitrate on the above sulphate the 1-nitroso derivative of the acid is produced; it is a microcrystalline, flesh-coloured substance decomposing violently at  $250\text{--}260^{\circ}$ , strongly acid in character, giving no compounds with mineral acids and dissolving in alkalis with a red colour. When heated with dilute sulphuric acid in a sealed tube the nitroso-compound gives 2-hydroxynicotinic acid, whilst the action of the concentrated reagent in an open vessel leads to 2-aminonicotinic acid. When the acid (II) is oxidised in ammoniacal solution with potassium ferricyanide or permanganate, the *dehydro* compound (III) is obtained, forming small, red needles, m. p.  $259\text{--}260^{\circ}$  (decomp.). The compound shows a fine violet-red colour in solution and dyes wool from an acid bath. It readily undergoes reduction. The *dehydro*-compound is also obtained by the action of atmospheric oxygen on solutions of the acid (II) in ammonia, but not in potassium or sodium hydroxides.

It is pointed out that the acid (I) differs from phenylglycine carboxylic acid by the greater stability of the carboxyl group in position 3 and the more ready formation of the indole derivative (II), whilst the latter shows characteristic behaviour on oxidation.

G. A. R. K.

**Hydroxylamine, Hydrazine, and their Derivatives as "Oxidising Agents" in the Formation of Induline.** K. A. HOFMANN, F. HARTMANN, and F. KROLL (*Ber.*, 1924, 57, [B], 945—963).—The formation of indulines of the benzene and naphthalene series from aniline and  $\alpha$ -naphthylamine occurs, not only with typical oxidising agents, such as oxygen, but also with compounds of nitrogen which are generally placed among the strongest reducing agents, such as hydroxylamine, phenylhydroxylamine, hydrazobenzene, phenylhydrazine, and hydrazine. The latter substances are constrained by the energy conditions of ammonium salt formation to withdraw hydrogen from aniline and  $\alpha$ -naphthylamine, thus leading to oxidation and production of indulines.

H. W.

**Derivatives of Mono- and Di-substituted Hydrazodithiocarbonamides.** E. FROMM and P. JOKL (*Monatsh.*, 1924, 44, 298—305; cf. Fromm, Nerz, and Layer, A., 1923, i, 1239).—Mono-phenylhydrazodithiocarboxylamide on boiling with 10% hydrazine hydrate solution and acidifying, yielded a mixture of 2-amino-5-thiol-1-phenyl-1:3:4-triazole, and 2:5-dithiol-1-phenyl-1:3:4-triazole (cf. Arndt, A., 1922, i, 375). The former substance yielded an *acetyl* derivative, m. p.  $187^{\circ}$ . The dithioltriazole was converted by methyl sulphate and ammonia into 2:5-dimethylthiol-1-phenyl-1:3:4-triazole, which was oxidised cautiously by permanganate to 2:5-dimethylsulphonyl-1-phenyl-1:3:4-triazole, m. p.  $218^{\circ}$ , the latter, when hydrolysed by alkali, giving 2-hydroxy-5-methylsulphonyl-1-phenyl-1:3:4-triazole, white prisms, m. p.  $221^{\circ}$ . 2:5-Dithiol-1-phenyltriazole gives with benzyl chloride and sodium ethoxide 2:5-dibenzylthiol-1-phenyl-1:3:4-triazole, m. p.  $110^{\circ}$ .

Diallylhydrazodithiocarboxylamide when heated with hydrazine hydrate is converted into allylamine and 2:5-dithiol-1-allyl-1:3:4-triazole, m. p. 148° (*lead* derivative,  $C_5H_5N_3S_2Pb$ , decomp. 290°; *mercury* derivative,  $C_5H_5N_3S_2Hg$ , m. p. 188°, decomp. 280°). The allyltriazole is oxidised by bromine water to the *polysulphide*,  $(C_5H_5N_3S_2)_n$ , yellow crystals, m. p. 175°. Monoallylhydrazodithiocarboxylamide when heated with 10% hydrazine hydrate solution yields 1-amino-2-allylamino-5-thiol-1:3:4-triazole, white prisms, m. p. 202° (*benzylidene* derivative, m. p. 204°). Monophenylhydrazodithiocarboxylamide when oxidised by cold alkaline hydrogen peroxide affords 2-amino-5-phenylamino-1:3:4-thiodiazole, m. p. 205°, which forms a *benzylidene* derivative, yellow needles, m. p. 238°, a *benzoyl* derivative, m. p. 278°, and with acetic anhydride affords 2-diacetamido-5-phenylamino-1:3:4-thiodiazole, m. p. 264°. Monophenylhydrazodithiocarboxylamide on treatment with hydrochloric acid in glacial acetic acid yields 2-acetamido-5-thiol-1:3:4-thiodiazole, m. p. 282°, which when treated with benzyl chloride and sodium ethoxide, gives 2-acetamido-5-benzylthiol-1:3:4-thiodiazole, m. p. 164°; the compound of m. p. 282° forms a *lead* derivative,  $C_8H_8O_2N_6S_4Pb$ , decomp. 250°, and with acetic anhydride yields 2-diacetamido-5-thiol-1:3:4-thiodiazole, m. p. 202°. F. A. M.

**Derivatives of 1:3:8-Benztriazine and the Preparation of 2-Aminonicotinic Anhydride.** L. KLISIECKI and E. SUCHARDA (*Roczniki Chemji*, 1923, **3**, 251—260).—2-Aminonicotinic acid behaves in a manner analogous to that of anthranilic acid and condenses with formamide and acetamide, although the yield of condensation product is small. Thus on heating with formamide it yields 4-hydroxy-1:3:8-benztriazine (I), sparingly soluble, colourless prisms which do not melt at 385° (*hydrochloride*, colourless crystals). The 2-methyl derivative is obtained by substituting acetamide for formamide in the original condensation and forms colourless needles, m. p. 258°; the *hydrochloride* is somewhat sparingly soluble and was obtained in colourless needles. In contrast to the parent substance, the methyl derivative is readily soluble in water, etc., as well as in mineral acids and alkalis. This difference is accounted for by assuming the methyl derivative to have a lactim and the parent substance a lactam structure.

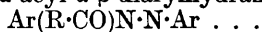


The alternative structure (II) is disproved because the substance does not show any of the characteristic reactions of the primary amino group. Moreover, the more acid nature of the above methyl derivative is shown by the fact that the chlorine in the hydrochloride cannot be estimated by direct titration as in the case of (I).

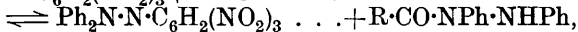
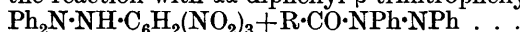
An attempt to condense methyl 2-aminonicotinate with ethyl acetate by means of sodium failed, the product forming colourless

prisms, m. p.  $378^{\circ}$  (decomp.); on acid or alkaline hydrolysis, it reverts to 2-aminonicotinic acid, of which it appears to be the *anhydride*, probably of the formula  $C_{12}H_8O_2N_4$ . G. A. R. K.

**Amine Oxidation. IX. Hydrazyls.** S. GOLDSCHMIDT (*Annalen*, 1924, **437**, 194—226; cf. A., 1920, i, 257; 1922, i, 475, 476).—A further series of investigations on different types of hydrazyls has revealed equilibrium conditions which do not conform to the Thiele-Werner principle, and the regularities observed by Wieland in the dissociation of tetra-arylhydrazines (A., 1911, i, 567; 1912, i, 904) do not hold for the substituted hydrazyls. The tetrazans of the  $\alpha$ -acyl- $\alpha$ - $\beta$ -diarylhydrazyls,



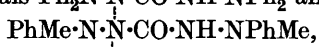
are much less dissociated than the hexa-aryltetrazans, and the following order is given:  $\alpha\alpha'$ -diacetyl- $\alpha\beta\alpha'\beta'$ -tetraphenyltetrazen  $<$   $\alpha'\alpha$ -dibenzoyl- $\alpha\beta\alpha'\beta'$ -tetraphenyltetrazen  $<$   $\alpha\alpha'$ -diacetyl- $\alpha\beta\alpha'\beta'$ -tetra-tolyltetrazen  $<$   $\alpha\alpha'$ -dibenzoyl- $\alpha\beta\alpha'\beta'$ -tetratolyltetrazen. Dissociation of the tetrazen is thus weakened when the phenyl group is replaced by tolyl, and the  $\alpha\alpha'$ -diacetyl- $\alpha\beta\alpha'\beta'$ -tetra(*m*-dimethylaminophenyl)tetrazen is almost completely dissociated into the hydrazyl. A further study of the effect of different acyl groups on the dissociation of diacyl- $\alpha\alpha'\beta\beta'$ -tetraphenyltetrazen, based on the reaction with  $\alpha\alpha$ -diphenyl- $\beta$ -trinitrophenylhydrazine:



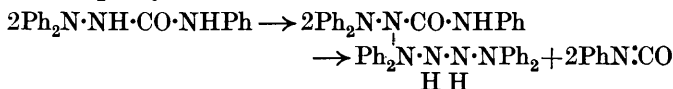
showed that the dissociation did not depend on the dissociation constant of the acid, nor was a simple connexion observed between the solubility of the tetrazen and its degree of dissociation. The  $\beta$ -acyl- $\alpha\alpha$ -diarylhydrazyls readily decomposed, and their behaviour was therefore studied in solution. Equilibrium between the hydrazyl and the tetrazen is a definite time reaction. The free hydrazyl reacts instantly with quinol:  $2R_2N\cdot NR' \dots + C_6H_4(OH)_2 \rightarrow 2R_2N\cdot NHR' + C_6H_4O_2$ , the solution being decolorised. The red colour, however, at once begins to reappear as the tetrazen dissociates, and the velocity of the dissociation increases greatly with the temperature, but decreases with dilution. The dissociation is also dependent on the nature of the solvent, and in the case of the tetrazen obtained from diphenylacetylhydrazine it was found that the dissociation and the solubility of the tetrazen are roughly proportional. With the dibenzoyltetrazans, the dissociation corresponds with Ostwald's dilution law. Confirmation of these results was obtained by a colorimetric method. Two formulæ are discussed for the acyl- $\alpha\alpha$ -diarylhydrazyls, but in the absence of any satisfactory criteria for bivalent nitrogen and univalent oxygen, and in the absence also of evidence to the contrary, preference is given to the formula  $R_2N\cdot N\cdot CO\cdot R$  previously used.

The behaviour of carbonic acid derivatives on oxidation has also been studied. Tetraphenylsemicarbazide and diphenyldimethylsemicarbazide yield deep blue solutions, which react at once (with decolorisation) with nitrogen dioxide, bromine, and triphenyl-

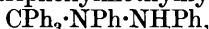
methyl. By the reaction with quinol these solutions are shown to contain the radicals  $\text{Ph}_2\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{NPh}_2$  and



respectively. Both radicals are completely unimolecular in solution and at  $-70^\circ$  obey Beer's law. They are distinguished by their reactivity towards hydrogen. The dimethyldehydro compound reacts quantitatively with quinol whilst only the tetraphenyldehydrocarbazide was isolated in the free state by the reaction with trinitrophenylhydrazyl. The dehydrogenation of the second nitrogen in the carbazide is probably possible although with difficulty, but the formation of hydrazyls from the corresponding urethane,  $\text{RR}'\text{N}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , or chloride,  $\text{RR}'\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{Cl}$ , was not observed. Triphenylsemicarbazide,  $\text{Ph}_2\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , on oxidation with lead peroxide in benzene solution, leads exclusively to tetraphenyltetrazen,



Experiments on the oxidation of alkylarylhydrazines showed that the presence of the alkyl group diminished the capacity for oxidation of the hydrazine, and the expected alkyl-substituted hydrazyls were not obtained. By condensation of triphenylchloromethane with diphenylhydrazine,  $\alpha\alpha$ -diphenyl- $\beta$ -triphenylmethylhydrazine,  $\text{Ph}_2\text{N}\cdot\text{NH}\cdot\text{CPh}_3$ , was obtained, which on oxidation loses hydrogen, probably yielding the unsaturated radical,  $\text{Ph}_2\text{N}\cdot\underset{\textstyle |}{\underset{\textstyle |}{\text{N}}}\text{CPh}_3$ , which at once gives triphenylcarbinol and tetraphenyltetrazen. The condensation of triphenylchloromethane with hydrazobenzene yielded similarly  $\alpha\beta$ -diphenyl- $\alpha$ -triphenylmethylhydrazine,



which on oxidation yielded triphenylcarbinol and azobenzene. It is probable therefore that exchange of an aryl group for alkyl renders the hydrazyls too unstable to exist.

A comparison of the known hydrazyls indicates that the nitrogen atom in the tertiary hydrazines possesses no basic properties and that the hydrogen atom attached to it is acidic. This appears to be a fundamental condition for the formation of hydrazyls.

[With A. WOLF.]— $\alpha\alpha'$ -Diphenyl- $\beta\beta$ -*p*-chlorophenylhydrazine, prismatic needles, m. p.  $114$ — $116^\circ$  (decomp.), obtained by the action of ethyl hypochlorite on triphenylhydrazine at  $-80^\circ$  in ethereal solution, yields *p*-chloroaniline on reduction. Oxidation with lead peroxide in methyl ether at  $-70^\circ$  yields  $\alpha\alpha$ -diphenyl-*p*-chlorophenylhydrazyl, a deep blue solution which obeys Beer's law at  $-20^\circ$ , but not at  $-70^\circ$ .

[With I. DRIMMER.]—Chloroacetyl chloride and hydrazobenzene in ethereal solution give  $\alpha$ -chloroacetyl- $\alpha\beta$ -diphenylhydrazine,  $(\text{CH}_2\text{Cl}\cdot\text{CO})\text{NR}\cdot\text{NHPh}$ , plates, m. p.  $163^\circ$  (decomp.), which on oxidation with lead peroxide in benzene yield  $\alpha\alpha'$ -dichloroacetyl- $\alpha\beta\alpha'\beta'$ -tetraphenyltetrazen, yellow prisms, m. p.  $111$ — $112^\circ$  (decomp.). Similarly, from dichloroacetyl chloride is obtained  $\alpha$ -dichloro-

*acetyl- $\alpha\beta$ -diphenylhydrazine*, m. p.  $134^{\circ}$ , and on oxidation,  *$\alpha\alpha'$ -dichloroacetyl- $\alpha\beta\alpha'\beta'$ -tetraphenyltetrazen*, m. p.  $102$ — $104^{\circ}$  (decomp.).  *$\alpha$ -Propionyl- $\alpha\beta$ -diphenylhydrazine*, tablets, m. p.  $140.5^{\circ}$ , on oxidation yields  *$\alpha\alpha'$ -propionyl- $\alpha\beta\alpha'\beta'$ -tetraphenyltetrazen*, yellow rhomboids, m. p.  $117^{\circ}$  (decomp.).

[With R. WAGNER.]— $\alpha\beta$ -Bis-*m*-dimethylaminophenylhydrazine with acetic anhydride is converted into  $\alpha$ -acetyl- $\alpha\beta$ -bis-*m*-dimethylaminophenylhydrazine, needles, m. p.  $123^{\circ}$ , which on oxidation with lead peroxide in chloroform solution at  $-20^{\circ}$  yields a deep blue solution of the *hydrazyl*.

[With E. WOLFFHARDT.]— $\beta$ -Acetyl- $\alpha\alpha$ -diphenylhydrazine, obtained by acetylation of  $\alpha\alpha$ -diphenylhydrazine (Fischer, A., 1878, 190) on oxidation with lead peroxide in acetone solution, yields  $\beta\beta'$ -diacetyl- $\alpha\alpha\alpha'\alpha'$ -tetraphenyltetrazen, prismatic plates, m. p.  $141^{\circ}$  (decomp.), which on reduction with quinol yield the original hydrazine (m. p.  $185^{\circ}$ ). With triphenylmethyl in chloroform solution the tetrazen yields triphenylmethyl peroxide and a *substance*,  $C_{33}H_{28}ON_2$ , dense crystals, melting at  $159^{\circ}$  to a red liquid, which on boiling with acetic acid yields triphenylcarbinol and acetyldiphenylhydrazine. In benzene solution a *substance*,  $C_{33}H_{28}ON_2$ , was obtained, darkening at  $250^{\circ}$ , m. p.  $256^{\circ}$ .  $\beta$ -Benzoyl- $\alpha\alpha$ -diphenylhydrazine on oxidation with potassium ferricyanide in alcoholic solution yields the  $\beta$ -benzoyl- $\alpha\alpha$ -diphenylhydrazyl, deep blue solutions, reconverted to hydrazine with quinol.  $\beta$ -Anisoyl- $\alpha\alpha$ -diphenylhydrazine (from anisoyl chloride and diphenylhydrazine), m. p.  $217^{\circ}$ , on rapid treatment with sodium ethoxide in alcoholic solution is converted into the tetrazen, the original anisoyl hydrazine being very readily reprecipitated.  $\beta$ -*o*-Nitrobenzoyl- $\alpha\alpha$ -diphenylhydrazine, citron-yellow needles, m. p.  $203^{\circ}$ ,  $\beta$ -*m*-nitrobenzoyl- $\alpha\alpha$ -diphenylhydrazine, yellowish-green needles, m. p.  $205^{\circ}$ , and  $\beta$ -*p*-nitrobenzoyl- $\alpha\alpha$ -diphenylhydrazine, orange-yellow needles, m. p.  $206^{\circ}$ , are similarly prepared. The *o*-nitrobenzoylhydrazine on oxidation in toluene solution yields the *tetrazen*, bright yellow crystals rapidly changing to violet in the light.

[With A. WOLF.]—On oxidation with lead peroxide in a mixture of tetrachloroethane and toluene, tetraphenylcarbazine yields a deep blue solution stable at  $-25^{\circ}$  but rapidly decomposing at the ordinary temperature. The *N*-dehydrotetraphenylcarbazine is isolated by the addition of  $\alpha\alpha$ -diphenyltrinitrophenylhydrazyl, the product, after washing from diphenyltrinitrophenylhydrazine with toluene, giving a dark violet solution in chloroform. Diphenyldimethylcarbazine on oxidation in chloroform-ether solution similarly yields a deep lavender-blue solution, from which the *N*-dehydrodiphenyldimethylcarbazine may be isolated as in the case of triphenylhydrazyl.

[With S. NATHAN.]—Triphenylchloromethane and  $\alpha\alpha$ -diphenylhydrazine in benzene solution yield  $\alpha\alpha$ -diphenyl- $\beta$ -triphenylmethylhydrazine, m. p.  $136$ — $137^{\circ}$  (turning brown at  $126^{\circ}$ ), which on oxidation with lead peroxide in benzene solution yields tetraphenyltetrazen and triphenylcarbinol. Similarly, triphenylmethyl chloride and  $\alpha\beta$ -diphenylhydrazine in ethereal solution give  $\alpha\beta$ -diphenyl- $\alpha$ -triphenylmethylhydrazine, prismatic plates, m. p.  $107^{\circ}$ ,

which is converted into triphenylcarbinol and azobenzene on oxidation with lead peroxide in alcoholic solution.  $\alpha\alpha$ -Dibenzyl- $\beta$ -tert.-butylhydrazine, rhombic plates, m. p.  $85^\circ$ , from  $\alpha\alpha$ -dibenzylhydrazine and tert.-butyl bromide, yields only the unchanged hydrazine on oxidation.  $\alpha\alpha$ -Dibenzyl- $\beta$ -trinitrophenylhydrazine, m. p.  $176^\circ$ , similarly prepared from picryl chloride, on oxidation yields trinitrophenylbenzylidenehydrazine, m. p.  $262^\circ$  (cf. Curtius and Dedichen, A., 1895, i, 29).  $\alpha$ -Phenyl- $\beta$ -trinitrophenyl- $\alpha$ -methylhydrazine on oxidation in chloroform solution at  $-70^\circ$  yields a transient, dark violet solution, becoming yellowish-brown. At room temperature, oxidation yields a substance,  $C_{26}H_{18}O_9N_{10}$ , yellowish-red, rhombic crystals, m. p.  $150^\circ$ .  
R. B.

**Halogenated Aromatic Hydrazines. I. 3:4-Dibromophenylhydrazine.** E. VOTOČEK and P. JIRŮ (*Chem. Listy*, 1924, **18**, 113—117).—The 3:4-dibromophenylhydrazine prepared by Meyer (A., 1893, i, 155) by the bromination of acetone phenylhydrazone is shown to be the *p*-monobromo compound. The dibromo compound has now been prepared by reducing diazotised 3:4-dibromoaniline with stannous chloride; it forms fairly stable, yellow needles, m. p.  $75^\circ$ . It forms a *hydrochloride*, decomp.  $215^\circ$ , a *sulphate*, needles, decomp.  $180^\circ$ , an *oxalate*, decomp.  $162$ — $163^\circ$ , and a *picrate*, decomp.  $154$ — $156^\circ$ . The *acetyl* derivative forms red needles, m. p.  $181$ — $182^\circ$ . The base forms *hydrazones* with the following compounds: benzaldehyde, yellow crystals, m. p.  $128^\circ$ ; salicylaldehyde, reddish-yellow crystals, m. p.  $190^\circ$ ; acetone, an oil; arabinose, a solid difficult to purify, decomp.  $82$ — $83^\circ$ ; rhamnose, m. p.  $153$ — $154^\circ$ ; dextrose, colourless crystals, m. p.  $165$ — $167^\circ$ , and a colourless *compound*, m. p.  $70^\circ$ , containing less bromine; the compounds obtained from lævulose and galactose could not be obtained pure. The *osazone* prepared from dextrose or lævulose and the hydrochloride of the base forms yellow crystals, m. p.  $225$ — $226^\circ$  (decomp.).

It is shown that both 3:4- and 2:4-dibromophenylhydrazine and also the *p*-bromophenylhydrazine obtained by Meyer give *p*-bromoaniline on reduction with zinc and hydrochloric acid.

G. A. R. K.

**Preparation of *p*-Dialkylaminoarylphosphinous Acids.** L. CASSELLA & Co., G.M.B.H. (Brit. Pat. 214836).—Phosphorus trichloride is heated with an excess of a dialkylarylamine and the resulting arylphosphorus chloride is converted into the *p*-dialkylaminoarylphosphinous acid or a salt of the same in the usual way (e.g., with sodium hydroxide). The reaction is smooth and almost quantitative, and the products, which possess therapeutic properties, are of a high degree of purity. Details are given for the preparation of sodium 1-dimethylamino-4-phenylphosphinite, colourless needles ( $+2H_2O$ ). Sodium 1-dimethylamino-4-phenyl-3-methylphosphinite forms scales, needles, or prisms ( $+3H_2O$ ). Sodium 1-diethylamino-4-phenyl-3-methylphosphinite forms prisms ( $+3H_2O$ ). Other salts of these acids are also described.

W. T. K. B.

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**Compounds of the Diethylarsine Series.** N. I. WIGREN (*Annalen*, 1924, **437**, 285—296).—Dehn's method (A., 1906, i, 150) failed for the diethylarsine series but *iododiethylarsine* (a yellow, irritating liquid, b. p. 70—71°/10 mm.) was prepared from diiodoethylarsine by Auger's method, as modified by McKenzie and Wood (T., 1920, **117**, 406). Oxidation of iododiethylarsine by hydrogen peroxide gives a diethylarsinic acid possessing properties sharply distinguished from those of the (probably impure) diethylarsinic acid described by Landolt (*J. pr. Chem.*, 1854, **63**, 283). It gives no precipitate with silver, ferric, lead, or copper salt solutions, whilst the acid barium salt described by Landolt could not be obtained. The behaviour of diethylarsine and bisdiethylarsine-oxide (below) with mercuric chloride in hydrochloric acid shows that, contrary to the assumptions of Biginelli (A., 1901, i, 20) and Klason (A., 1915, i, 486), neither of these compounds can be the volatile arsenic compound produced by different arsenic moulds. The above iodo compound is converted by alkali into *bisdiethylarsineoxide*,  $(\text{AsEt}_2)_2\text{O}$ , a colourless, highly refracting liquid, b. p. 97—98°/10 mm., which has an unbearable, irritating odour, and oxidises to diethylarsinic acid in the air. Reduction of iododiethylarsine with zinc copper couple and alcohol (cf. Palmer, A., 1894, i, 400) in a specially designed apparatus affords *diethylarsine*, a colourless liquid, b. p. 105°, which undergoes spontaneous oxidation in air and has a garlic odour. With Biginelli's solution, it yields lustrous needles of the *mercurosochloride*,  $\text{AsEt}_2\text{Cl}_2\text{HgCl}$ , this, with boiling water, yielding chlorodiethylarsine. Diethylarsinic acid, colourless needles, m. p. 133—134° (Landolt gives 190°), forms a soluble *silver* salt (needles), and a *nitrate*,  $\text{Et}_2\text{AsO}_2\text{H}\cdot\text{HNO}_3$ , prisms, m. p. 71—72°. The constants for the acid (by the methyl acetate, and Sørensen's indicator method [A., 1909, i, 861]) are  $K_a = 3.7 \times 10^{-13}$ .  $K_a = 3.0 \times 10^{-7}$ . R. B.

**3-Amino-4 : 4'-dihydroxyarsenobenzene, and its N-Methylenesulphinate and N-Methylenesulphonate Derivatives.** M. C. HART and W. B. PAYNE (*J. Amer. Pharm. Assoc.*, 1923, **12**, 688—695).—The preparation of 3-amino-4 : 4'-dihydroxyarsenobenzene and the determination of its toxicity are described, together with similar experiments with the (unstable) sodium *N*-methylenesulphinate and (more stable) sodium *N*-methylenesulphonate. The reduction with sodium hyposulphite of an equimolecular mixture of the two arsinic acids is not a general method for the production of unsymmetrical derivatives.

The loss of one of the essential anchoring groups from salvarsan does not impair its therapeutic efficiency.

#### CHEMICAL ABSTRACTS.

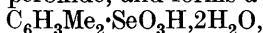
**3-Amino-4-hydroxyarsenophenyl-4'-glycine and its N-Methylenesulphinate and N-Methylenesulphonate Derivatives.** M. C. HART and W. B. PAYNE (*J. Amer. Pharm. Assoc.*, 1923, **12**, 759—768).—The toxic and maximum tolerated doses of 3-amino-4-hydroxyarsenophenyl-4'-glycine and its *N*-methylenesulphonate and *N*-methylenesulphinate have been determined;

the toxicity and trypanocidal activity decrease in the order given. The effect of the introduction of these groups (yielding soluble compounds) on the therapeutic activity is parallel to that in the case of salvarsan. Although these compounds are as effective therapeutically as the corresponding compounds of the salvarsan series, they are deficient in some of the essential anchoring groups considered by Ehrlich to be necessary for the highest type of therapeutic efficiency claimed to have been reached in salvarsan.

## CHEMICAL ABSTRACTS.

**Aromatic Selenonic Acids. II. *m*-Xyleneselenonic Acid.**

R. ANSCHÜTZ and F. TEUTENBERG (*Ber.*, 1924, **57**, [B], 1018—1023; cf. A., 1919, i, 24).—By the action of selenic acid on *m*-xylene in the presence of acetic anhydride a crystalline *m*-xylene-4 (?) -selenonic acid, m. p. 130—130.5°, is obtained which presents analogies with *m*-xylene-4-sulphonic acid, but the position of the selenonic group has not been definitely determined. Fractional crystallisation gave no indication of the formation of the two possible isomerides. The yield, one of 75%, could not be improved, since concentration of the mother-liquor in a vacuum led to an explosion. *m*-Xylene-4-selenonic acid is stable towards boiling sodium hydroxide, is not attacked by hydrogen peroxide, and forms a *dihydrate*,

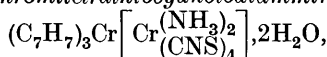


similar *dihydrates* of the *o*- and *p*-xylene-4-selenonic acids being described. The *o*-, *m*-, and *p*-xylene-4-sulphonic acids also yield *dihydrates*. The *salts* of 10 metals and *m*-xylene-4-selenonic acid are described, and the corresponding *m*-xylene-4-sulphonates, most of which are new (cf. Jacobsen, *Ber.*, 1878, **11**, 18), particular attention being directed to the number of molecules of water of crystallisation.

R. B.

**Organo-chromium Compounds. V. Chromium Toly Compounds.**

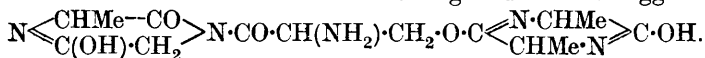
F. HEIN and R. SPAETE (*Ber.*, 1924, **57**, [B], 899—908; cf. A., 1921, i, 826; 1922, i, 76, 77; this vol., i, 437).—The action of an ethereal solution of magnesium *p*-tolyl bromide on chromium chloride yields a mixture of chromium polyphenyl bromides from which the following substances are derived by methods which are somewhat modified from those used previously (*loc. cit.*): *chromiumpenta-p-tolyl carbonate*,  $[\text{Cr}(\text{C}_7\text{H}_7)_5]_2\text{CO}_3\cdot 6\text{H}_2\text{O}$ , orange crystals, m. p. 139—140°, and the corresponding tetrahydrate; the additive compound of chromiumpenta-*p*-tolyl bromide and mercuric chloride; *chromiumpenta-p-tolyl hydrogen anthranilate*,  $2\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Cr}(\text{C}_7\text{H}_7)_5\cdot\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , m. p. 170° after previous softening; *chromiumtetra-p-tolyl hydrogen anthranilate*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Cr}(\text{C}_7\text{H}_7)_4\cdot\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , m. p. 176° after previous softening; *chromiumtri-p-tolyl hydroxide*, *chromiumtri-p-tolyl iodide*,  $2\text{Cr}(\text{C}_7\text{H}_7)_3\text{I}\cdot\text{Et}_2\text{O}$ , m. p. 115—119° (decomp.); *chromiumtri-p-tolyl hydrogen anthranilate*, an orange-yellow, amorphous substance, m. p. 145—149°; *chromiumtri-p-tolyl picolonate*; *chromiumtri-p-tolylchromitetrahiocyanotodiammine*,





an unstable, amorphous substance. The *p*-tolyl compounds are all considerably less stable than the corresponding phenyl derivatives, and this difference is even more noticeable with the *o*-tolyl compounds, of which *chromiumtetra-o-tolyl hydrogen anthranilate*, m. p. 75—110°, and *chromiumpenta-o-tolyl hydrogen anthranilate*,  $C_{91}H_{89}O_6N_3Cr_2$ , m. p. 151° (decomp.), are described. H. W.

**Structure of the Protein Molecule.** E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1924, **136**, 134—146).—When proteins are subjected to progressive partial hydrolysis with dilute hydrochloric acid or water alone at 150—160° for 7 hours, the greater part goes into solution. If the hydrolysate be then evaporated to dryness and the residue mixed with sand and extracted successively with ethyl acetate, chloroform, acetone, and methyl alcohol, it yields characteristic crystalline compounds having an anhydride structure, which can be readily isolated in the pure condition. They are optically inactive and do not give the ninhydrin reaction, indicating the absence of free amino and carboxyl groups. Regarding these compounds as fragments of the original protein molecule, it is concluded that in the protein molecule in addition to the polypeptide chains, anhydride-like residues having the diketopiperazine structure are also present. It is conceivable that these diketopiperazine residues are capable of existing in tautomeric forms,  $-NH\cdot CO- \rightarrow -N\cdot C(OH)-$ , and the changes in the physico-chemical properties of proteins accompanying denaturation may be in part ascribed to this cause. When silk fibroin is hydrolysed with 0.5% hydrochloric acid as mentioned above, only a very small quantity of it is dissolved, but if the residue be then hydrolysed under the same conditions with four times its quantity of 2% hydrochloric acid it goes completely into solution. The first hydrolysate yields on extraction with ethyl acetate an *anhydride* containing (1 mol. of serine+1 mol. of glycine+3 mols. of alanine, less  $5H_2O$ ). It forms needles, m. p. 213—215° (subl.). On treatment with alkali one-fourth of the total nitrogen appears as amino-nitrogen, and from this and other considerations the following structure is suggested :



The residue from the above and the second hydrolysate on extraction with chloroform yield alanylglycine anhydride, m. p. 236°. The acetone and methyl alcohol extracts did not yield any characteristic products. Blood proteins on heating with water under pressure are completely dissolved and the hydrolysate on appropriate extraction yields leucine-imide, *isoleucyl-leucine* anhydride, and *leucylglycine* anhydride. D. R. N.

**Reductive Decomposition of Proteins and Toxicity of their Decomposition Products.** V. N. TROENSEGAARD (*Z. physiol. Chem.*, 1924, **134**, 100—112; cf. A., 1923, i, 615, 1243; this vol., i, 581).—Acetylated or methylated proteins (casein or gliadin) are reduced, hydrolysed, and fractionated as previously described. The basic fractions show marked toxic properties when injected into guinea-pigs. For the preparation of these hydrated protein deriv-

atives in addition to the methods previously described, acetylgladin or acetylgelatin may be hydrogenated with magnesium in acetic acid solution and acetylcasein with zinc dust in acetic acid.

W. O. K.

**Oxidative and Reductive Scission of Proteins.** S. EDL-BACHER (*Z. physiol. Chem.*, 1924, **134**, 129—139).—Oxyprotosulphonic acid formed from casein by the action of potassium permanganate contains, as compared with casein, about 10% more humin nitrogen and about 10% less monoamino-nitrogen. After oxyprotosulphonic acid is hydrolysed by trypsin, the ratio of the number of methyl groups introduced by methyl sulphate to the formol titration number is the same as before hydrolysis. Further oxidation by hydrogen peroxide results in the formation of "apocasein," in which deep-seated changes, as shown by the distribution of nitrogen, have taken place. "apoGelatin," "apoarachin," and "apoclupein" are also described.

[With K. ERBACH.]—The results of Troensegaard on the methylation, reduction, and subsequent hydrolysis of casein are confirmed (cf. preceding abstract).

W. O. K.

**Structure of the Protein Molecule.** E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1924, **134**, 113—120; 121—128).—(I) From hog's bristles, hydrolysed in an autoclave with double their weight of 2% hydrochloric acid at 120° for 10 hours, the following compounds have been isolated, using the methods previously described (cf. this vol., i, 227): *Di(hydroxypropyl)glycine anhydride*,  $C_{12}H_{17}O_5N_3$ , m. p. 174°,  $[\alpha]_D^{25} -31.65^\circ$  in alcohol; *isoleucyl-leucine anhydride*, m. p. 273—277°,  $[\alpha]_D^{20} -15.96^\circ$  in aqueous solution, and a product, m. p. 205—210°, possibly impure alanyl-glycine anhydride. From the proteins of blood, heated for 7 hours in an autoclave at 180° at 10 atm. pressure, the following products have been obtained: *leucylserine anhydride*, m. p. 201—204°,  $[\alpha]_D^{20} +0.87^\circ$  (in methyl-alcoholic solution), *leucyl glycine anhydride*, m. p. 233°,  $[\alpha]_D^{20} -2.58^\circ$  in alcoholic solution, and *dipropylvaline anhydride*,  $[\alpha]_D^{20} +2.6^\circ$ .

(II) In order to ascertain whether anhydrides such as are obtained from protein after partial hydrolysis may owe their existence to the conditions of hydrolysis, certain amino-acids and polypeptides have been heated with water for 7 hours at 150°. *l-Leucylglycyl-l-leucine*, *dl-leucyldiglycylglycine*, and *glycyl-dl-leucylglycine*, and probably *glycyl-dl-leucine*, yield *leucylglycine anhydride*. *Diglycylcystine* yielded no definite product and *glycyl-dl-tyrosine* only the component amino-acids. From the amino-acids, *glycine*, *d-alanine*, *dl-leucine*, and *l-tyrosine*, after heating with water under the same conditions by themselves or in mixtures, no trace of anhydride could be isolated.

W. O. K.

**Amide Nitrogen of Caseinogen.** J. M. LUCK (*Biochem. J.*, 1924, **18**, 679—692).—Only two-thirds of the ammonia liberated by acid hydrolysis of caseinogen is obtained when this protein is submitted even to prolonged tryptic digestion. This undigested residue can be partly precipitated by alcohol and totally precipitated

by phosphotungstic acid and alcoholic mercuric chloride. The isolated residue entirely resists tryptic hydrolysis. When it is submitted to acid hydrolysis, glutamic acid and lysine are obtained. Eight to 10% of its total nitrogen occurs as ammonia, which is not associated with the lysine, but is present in amide form. It is concluded that glutamine or a glutamine-containing peptide is present in the tryptic digestion product of caseinogen. The possibility that this compound is a secondary product of enzymic synthesis cannot be excluded. S. S. Z.

**Chemistry of Blood Pigments.** F. HAUROWITZ (*Z. physiol. Chem.*, 1924, 136, 147—159).—A method is described whereby oxyhæmoglobin can be prepared in the crystalline state in considerable quantity from horse-blood (cf. A., 1918, i, 316; 1921, i, 749; 1922, i, 962). The corpuscles are washed thrice by centrifuging with isotonic sodium chloride solution and then dialysed for 2 days against running ice-cold tap water and for 3 days subsequently against distilled water. The corpuscles are then hæmolyzed and the dark red liquid is freed from the stroma by centrifuging, cooled with ice, and a current of air is passed through it, when within 10—20 minutes a dark red, crystalline magma begins to separate. The crystals are removed by centrifuging and further freed from moisture on unglazed porcelain tile and brought to 20% moisture content by pressing in a hydraulic press under a pressure of 300 atms. The above operations must be carried through as rapidly as possible as otherwise the product will not crystallise. The needles of oxyhæmoglobin are identical with those obtained by other methods (*loc. cit.*). Hæmoglobin can be readily prepared in a crystalline state without using alcohol by exposing a 40% oxyhæmoglobin paste in a vacuum until complete reduction is effected, when after one or two days it crystallises in hexagonal plates. Crystalline carbon monoxide-hæmoglobin can also be obtained by passing carbon monoxide through oxyhæmoglobin paste and keeping in a cool place. Nitric oxide-hæmoglobin can be prepared by passing nitric oxide free from the higher oxides of nitrogen through a 20% hæmoglobin solution, from which it rapidly crystallises on keeping in the cold. It decomposes on keeping into nitric oxide and hæmoglobin. The so-called water of crystallisation of oxyhæmoglobin preparations obtained by different methods is found to vary between 8.9 and 9.8%. D. R. N.

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### Biochemistry.

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Pharmacology of Cell Respiration. IV. Influence of Temperature on the Spontaneous Oxidation of Hydrocyanic Acid in "Brennorten" ("Combustion Regions") and on the Curve of Oxygen Consumption of Tissues Poisoned by Potassium Cyanide. P. ELLINGER (*Z. physiol. Chem.*, 1924, 136, 19—29).—In the presence of charcoal and a phosphate solution

of  $p_H$  7.2, potassium cyanide absorbs oxygen at a rate which, for any given temperature, is proportional to the cyanide concentration. The rate of oxidation increases by 90—100% for a rise in temperature of  $10^\circ$ . A suspension of frog muscle pulp at  $p_H$  7.2 shows an increase in rate of oxidation from  $20$ — $30^\circ$  and a fall from  $30$ — $35^\circ$  which becomes rapid between  $35^\circ$  and  $40^\circ$ , whilst in the presence of various cyanide concentrations frog-muscle shows a minimum rate of oxidation when the concentration of cyanide is 4.5 millimols. per litre at temperatures between  $20^\circ$  and  $35^\circ$ , and when the concentration is 2.25 millimols. at  $40^\circ$ . It is concluded that in addition to inhibiting cell oxidation, potassium cyanide is itself spontaneously oxidised in the tissues (cf. Meyerhof, *Pflüger's Archiv*, 1923, 200, 1). J. P.

**Respiration and Fermentation.** H. F. HOLDEN (*Biochem. J.*, 1924, 18, 536—542).—The "respiration substance" of Meyerhof, obtained by extracting mammalian muscle with boiling water, is destroyed by aëration in contact with washed rabbit, rat, or frog muscle. The alcoholic co-enzyme in yeast or muscle is also destroyed in this way, although it is not readily oxidised by air alone. Neither glutathione nor pancreatic insulin can act as the alcoholic co-enzyme to washed "acetoned" yeast in the presence of potassium phosphate, at a suitable hydrogen-ion concentration at which the natural co-enzyme acts. The "respiration substance" seems to be a collection of irreversibly oxidisable substances, although not in the main lactic acid. A new method of preparation of "acetoned" yeast is described. S. S. Z.

**Properties of an alleged Erythropoietic Hormone.** C. D. LEAKE and F. J. BACON (*J. Pharm. Exp. Ther.*, 1924, 23, 353—363).—An erythropoietic substance was obtained by extracting with water a mixture of equal parts of desiccated preparations of spleen and red bone-marrow. The activity of the substance was not affected by boiling in aqueous solution or by keeping for long periods in sterile solution, but was destroyed by precipitation with alcohol and ether. The desiccated material, from which the hormone was obtained, contained about 0.24% of water-soluble iron and 2.89% of lecithin-phosphatides. C. R. H.

**Spectroscopic Chemical Reactions of some Porphyrins and their Methyl Esters.** O. SCHUMM (*Z. physiol. Chem.*, 1924, 136, 243—278).—The occurrence of porphyrin (uroporphyrin), kotporphyrin (coproporphyrin), and chloroform-soluble porphyrin is reviewed and an account given of their spectroscopic reactions. Chloroform is not such a suitable solvent for the methyl esters of uroporphyrin and coproporphyrin as is phenol. In this case, the acidity is an important factor, and consequently, different results were shown with different samples of phenol. A phenol-alcohol mixture shows definite differences between the two esters, as does also a pyrrole-alcohol mixture. The latter, however, is unsatisfactory, owing to the brown coloration which develops in the  
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pyrrole itself. Less conclusive results were obtained with toluene, acetone, aniline, and benzene. Carbon tetrachloride, in which the esters are only very slightly soluble, gave definite differences.

The porphyrin prepared from normal faeces differs from both uroporphyrin and coproporphyrin, but is very similar to a preparation made from sulphur-haemoglobin, and this, in turn, has spectroscopic properties very similar to those of ooporphyrin.

O. O.

**Formation of Porphyrin from the Colouring Matter of Blood.** O. SCHUMM and A. PAPENDIECK (*Z. physiol. Chem.*, 1924, **137**, 103—104; cf. this vol., i, 440, and preceding abstract).—In the preparation of a colouring matter allied to porphyrin, by the treatment of oxygen-free blood with hydrochloric acid, the authors have used chloroform to extract the substance from the reaction mixture. The substance thus obtained behaved in a somewhat anomalous manner, and it is now shown that this is probably due to partial esterification during the extraction with chloroform containing some alcohol. The solubility of the porphyrin derivative is greater in such chloroform than in pure chloroform. To avoid esterification, specially purified chloroform should be used. The preparation of the substance under discussion is greatly facilitated by the use of chloroform to which some alcohol has been added.

B. F.

**Occurrence of Porphyrin in Blood-serum.** A. PAPENDIECK (*Z. physiol. Chem.*, 1924, **136**, 293—306).—Contrary to the findings of Fischer and Zerweck (this vol., i, 459), and following their procedure, the author could find no positive spectroscopic evidence of the presence of porphyrin in a large number of samples taken from subjects in various conditions.

O. O.

**Porphyrins from Blood-pigment.** A. PAPENDIECK (*Z. physiol. Chem.*, 1924, **134**, 158—159).—Treatment of blood, saturated with hydrogen sulphide by fuming hydrochloric acid, yields a porphyrin, isolated by neutralising the solution with sodium carbonate, and acidifying with acetic acid, which precipitates the porphyrin. Treatment of the porphyrin with 1% methyl-alcoholic hydrochloric acid results in the formation of a *methyl* ester, insoluble in alkali, dense, prismatic rods, from methyl alcohol, m. p. 221°.

W. O. K.

**Natural Porphyrins. VI. Distribution of Porphyrins in Organs. Detection of a Porphyrin in Yeast.** H. FISCHER and K. SCHNELLER (*Z. physiol. Chem.*, 1924, **135**, 253—293).—Coproporphyrin accompanies Kämmerer's porphyrin in the products resulting from the putrefaction of calf liver, heart, and flesh, of ox flesh, and of human liver, spleen, lung, heart, and uterus. In human back-muscle, after removal of blood, coproporphyrin is alone demonstrable. Kämmerer's porphyrin is detectable in blood-corpuscles washed with physiological salt solution and subjected to putrefaction, whilst coproporphyrin may also be present in

traces if the serum has not been completely removed. Only one porphyrin is therefore derivable from red blood-corpuscles. The breast-muscle of the pigeon yields after putrefaction coproporphyrin, of which the origin is ascribed to degradation of the muscle pigment (myohæmoglobin) by lactic acid. Hydrolysis of fresh blood-corpuscles by hydrochloric acid, by pepsin, and by trypsin did not lead to the definite identification of the porphyrin. Coproporphyrin is present in putrefying fish flesh and in yeast, both fresh and putrefying. This evidence is regarded as lending support to the view that blood pigments are derived from leaf pigments with porphyrins occurring as intermediates. A possible parallelism between the dualism shown by the porphyrins and chlorophylls A and B is suggested. Kämmerer's porphyrin left in glacial acetic acid and ether for some months shows a band ( $623 \mu\mu$ ) characteristic of hæmatoporphyrin. Coproporphyrin has been isolated as the crystalline methyl ester from fæces derived from a purely vegetarian diet (cf. A., 1923, i, 1244; this vol., i, 459).

J. P.

**Changes of Reaction of Sera.** H. PLOTZ and M. SCHOEN (*Compt. rend.*, 1924, **178**, 1926—1928).—Exposure of normal horse-serum in open tubes caused an increase in  $p_H$  value, owing to the escape of carbon dioxide. A decrease in  $p_H$  took place when serum was stored aseptically in closed tubes; in one case the  $p_H$  changed from 7.33 to 6.89 after storage for 51 days at  $37^\circ$ .

E. M. C.

**Glycolysis in Blood of Normal Subjects and of Diabetic Patients.** E. TOLSTOI (*J. Biol. Chem.*, 1924, **60**, 69—75).—The blood of eight normal subjects and of eleven diabetic patients was examined. Determinations of sugar at intervals up to 24 hours in the blood kept at  $37^\circ$  with aseptic precautions showed no difference in the glycolytic power of diabetic and normal blood. At room temperature, the glycolytic rates were diminished to about the same extent in both types of blood. Counts of the red and white corpuscles gave figures within normal limits and bearing no relationship to the rate of glycolysis.

C. T. G.

**Relation of  $p_H$  to Tungstic Acid Precipitation of Protein.** A. T. MERRILL (*J. Biol. Chem.*, 1924, **60**, 257—259).—In serum, the maximum precipitation of nitrogenous substances occurs on the acid side of  $p_H$  5; in peptone solutions the zone of maximum precipitation is not reached until the acidity is greater than  $p_H$  1.

C. R. H.

**Neutral and Oxidised Sulphur in the Blood.** J. BROWNSKI (*Bull. Soc. Chim. biol.*, 1924, **6**, 352—356).—The deproteinised blood of horses and cattle was found to contain 9.5 to 12.0 mg. % of sulphur as sulphates and also a considerable quantity of unoxidised (neutral) sulphur. Ethereal sulphates were not found. Sulphates were precipitated and weighed as barium sulphate in the blood or serum previously deproteinised by means of trichloroacetic

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acid. Allowance was made for the amount of barium trichloroacetate precipitated. Neutral sulphur was determined by subtracting the sulphur as sulphates from the total sulphur found by fusion with sodium peroxide and subsequent precipitation with barium. The results do not agree with those of Denis (A., 1922, ii, 225), who found much less sulphur as sulphates and no neutral sulphur in blood. The analytical methods employed by Denis are criticised.

C. T. G.

**Effect of Inorganic Salts on the Chemical Changes in the Blood of the Dog after Obstruction of the Duodenum.** R. L. HADEN and T. G. ORR (*J. Exp. Med.*, 1924, **39**, 321—330; cf. *ibid.*, 1923, **37**, 365, 377; **38**, 55).—Life is prolonged by sodium chloride; ammonium chloride produces an acidosis. Potassium, calcium, and magnesium chlorides do not prevent the usual rise of non-protein nitrogen and fall in chlorides, followed by death. The toxic process is hastened by iodides; the inhibitory effect of sodium bromide is much less than that of the chloride.

CHEMICAL ABSTRACTS.

**Blood Changes and Clinical Symptoms following Oral Administration of Phosphates.** H. A. SALVESEN, A. B. HASTINGS, and J. F. MCINTOSH (*J. Biol. Chem.*, 1924, **60**, 311—326).—Oral administration to dogs of small doses of phosphates over a long period produced no clinical symptoms; if alkaline phosphates were used no change in the composition of the blood was observed, whereas with acid phosphates there was an increase in the phosphate concentration of the serum. The rapid administration of large doses of phosphate, acid or alkaline, produced violent symptoms of tetany, accompanied by a rise in the phosphate and a fall in the calcium of the serum. The tetany resembled that previously observed in parathyroidectomised dogs (cf. A., 1923, i, 979) and, in this case also, could be relieved by injection of calcium chloride. It is therefore probably due to a decrease in the calcium concentration of the blood.

C. R. H.

**Effect of Administration of Calcium Salts on the Inorganic Composition of the Blood.** H. A. SALVESEN, A. B. HASTINGS, and J. F. MCINTOSH (*J. Biol. Chem.*, 1924, **60**, 327—339).—Ingestion of calcium chloride produces an acidosis owing to the replacement of hydrogen carbonate ions by chloride ions in the blood. The intravenous injection of small quantities of calcium chloride produced no change in the acid-base equilibrium of the blood, but a rise in the phosphate concentration was observed. Although the calcium disappeared rapidly from the blood, it could not be subsequently recovered from the urine or faeces. In cases of Bright's disease, it was not found possible to restore the calcium content of the blood to normal by means of oral administration of calcium lactate.

C. H. R.

**Calcium Content of the Blood during Pregnancy. II.** S. T. WIDDOWS (*Biochem. J.*, 1924, **18**, 555—561).—The results



for abnormal pregnancies support the observation for normal pregnancies; a heavy demand of the foetus for calcium at certain stages of its development is met by a perfectly balanced calcium metabolism. S. S. Z.

**Relation between the Pancreas and the Carbohydrate Metabolism of Muscle. Effect of Extracts from the Gland on Lactic Acid Production *in vitro*.** D. L. FOSTER and C. E. WOODROW (*Biochem. J.*, 1924, **18**, 562—574).—The pancreas contains a factor capable of causing marked inhibition in the lactic acid production of chopped muscle. This factor is not identical with trypsin or insulin, and is probably not antiglyoxalase. A method is described for making a stable preparation of the pancreas with all its enzymes intact, and details are given for making an extract of this preparation with 70% alcohol which contains the inhibitory factor in high concentration. S. S. Z.

**Behaviour of  $\beta$ -Glucose in the Human Body and the Nature of the Glucose in Serum.** S. J. THANNHAUSER and M. JENKE (*Munch. med. Woch.*, 1924, **71**, 196—198; from *Chem. Zentr.*, 1924, i, 1687).—Intravenous injection of  $\beta$ -glucose had the same effect on the blood-sugar curve and the excretion of sugar in the urine as  $\alpha\beta$ -glucose. The elimination of acetone in diabetes is not diminished to the same extent by  $\beta$ -glucose as by  $\alpha\beta$ -glucose.  $\beta$ -Glucose is probably a stage in the degradation of sugar.

G. W. R.

**Type of Sugar Excreted in the Urine of Normal Persons.** K. TALLERMAN (*Biochem. J.*, 1924, **18**, 583—585).—The sugar excreted in the urine of the normal subject as a result of an injection of phloridzin is not  $\gamma$ -glucose, but the ordinary  $\alpha\beta$ -variety. Sugar of the same nature is found in the urine of diabetics after such an injection.  $\gamma$ -Glucose is therefore unlikely to be present in normal blood. S. S. Z.

**Physiological Testing of Insulin Preparations.** H. PÉNAU and H. SIMONNET (*J. Pharm. Chim.*, 1924, **29**, 473—481; cf. *B.*, 1924, 74).—Exception is taken to certain details of the Canadian physiological unit for insulin, and a modified test is described.

W. T. K. B.

**Insulin from the Cod Fish. Direct Application of Picric Acid to Islet Tissue.** H. W. DUDLEY (*Biochem. J.*, 1924, **18**, 665—668).—The islet tissue of the cod contains, weight for weight, about ten times as much insulin as mammalian pancreas. The insulin can be obtained by treating the tissue directly with picric acid and then extracting the insulin-containing picrate with aqueous acetone and converting the picrate into a soluble hydrochloride as previously described by the author. The islet tissue of the cod collected from fish caught at varying intervals up to 24 hours previously yielded 13.1 rabbit units per g. of tissue. S. S. Z.

**Preparation of Insulin.** M. SOMOGYI, E. A. DOISY, and P. A. SHAFFER (*J. Biol. Chem.*, 1924, **60**, 31—58; cf. *ibid.*, 1923, **55**, 31).—The activity of purified preparations of insulin from ox pancreas is associated always with a single, fairly well-characterised protein and probably is a property of this protein. "Insulin-protein" is relatively insoluble at a reaction of about  $p_H$  5. Crude insulin contains, in addition, two other "isoelectric-proteins" which are inactive, one with optimum precipitation, in absence of salts, at  $p_H$  7 or 8, and the other at  $p_H$  4. In the pancreas extracts, there is also an "alcohol-protein," readily soluble in alcohol up to 80% and insoluble in higher concentrations, which is not precipitated on adjusting the reaction, but tends to interfere with the precipitation of "insulin-protein."

The solubility relationships, in presence and in absence of salts, of "insulin-protein" and the associated inactive proteins and the choice of acid for extraction, having been studied, a simplified method for the separation of active insulin has been worked out. Data are given illustrating the activity of different preparations.

C. T. G.

**Chemical Reactions of Insulin.** C. H. BEST and J. J. R. MACLEOD (*Amer. J. Physiol.*, 1923, **63**, 390—391).—Insulin, when free from protein, does not respond to any of the colour reactions for the latter, or for adrenalin. It is not appreciably affected by moderate heat in solution of  $p_H$  5—6; it may be heated on a boiling water-bath for 10 minutes, but is destroyed by actual boiling for 3 minutes. Insulin is absorbed from acid solution by kaolin, charcoal, etc.; it could not be shown to dialyse through a collodion membrane. The potency of insulin preparations is greatly reduced by passage through a Berkefeld filter. Insulin preparations do not contain proteolytic enzymes.

A. A. E.

**Chemistry of Amino-acid Deamination.** W. R. FEARON and E. G. MONTGOMERY (*Biochem. J.*, 1924, **18**, 576—582).—Cyanic acid is an important factor in the production of urea and in the maintenance of neutrality in the organism, since it is shown that the acid is formed during the oxidative deamination of glycine, sarcosine, and alanine and that it is an intermediate product of  $\alpha$ -deamination of glycine.

S. S. Z.

**Biochemistry of Experimental Tetany. Urinary and Muscle Creatine in Guanidine and Parathyroid Tetany with and without Calcium Treatment.** A. PALLADIN and L. GRILICHES (*Biochem. Z.*, 1924, **146**, 458—466).—In experimental guanidine and parathyroid tetany, muscle creatine is increased and appears in the urine, whilst the excretion of creatinine is unaffected or but slightly increased. A direct relationship between muscle creatine and urinary creatine and creatinine is inferred. The abolition of tetanic symptoms by injection of calcium salts into rabbits, previously treated with guanidine, arrests the excretion of creatine and restores muscle creatine to normal limits. The increase of the latter in tetany is not ascribed to its increased formation from guanidine (cf. Paton, *Quart. J. Expt. Physiol.*, 1916, **10**),

since if calcium be administered simultaneously with guanidine the muscle creatine is not increased. J. P.

**Sulphur Metabolism of the Dog. II. Constancy of the Relative Output of Ethereal Sulphate and of Neutral Sulphur after Oral Administration of Halogen-substituted Benzenes.** T. S. HELE (*Biochem. J.*, 1924, **18**, 586—612).—Chlorobenzene administered by the mouth has an approximately constant quantitative effect on the sulphur metabolism of the dog. The "extra" ethereal sulphate bears a constant proportion to the "extra" neutral sulphur (about 2 to 3). This ratio may be altered by repeated doses of chlorobenzene if no cystine or sodium sulphate is given at the same time. The simultaneous oral administration of these latter compounds alone does not alter the ratio. The ratio of "extra" free phenol to "extra" total phenol also appears to be constant. There is no increase of free or conjugated phenols in the faeces after administration of chlorobenzene. The action of bromobenzene is similar to that of chlorobenzene. The oral administration of cystine always produces a small rise in the output of neutral sulphur. A rise in the protein intake may produce a considerable rise in the output of neutral sulphur. Guaiacol seems to have a slight toxic effect on sulphur metabolism. S. S. Z.

**(Biological) Action of Sulphur.** A. HOTTINGER (*Schweiz. med. Woch.*, 1923, **53**, 429—432; from *Chem. Zentr.*, 1924, i, 1826—1827).—A theoretical discussion of the rôle of sulphur and sulphides in biological oxidations and reductions. G. W. R.

**Formation of Ethereal Sulphates.** G. J. SHIPLE, J. A. MULDOON, and C. P. SHERWIN (*J. Biol. Chem.*, 1924, **60**, 59—67).—The feeding of bromobenzene, phenol, or *p*-chlorophenol to a pig maintained on a carbohydrate diet in a condition of endogenous nitrogen catabolism definitely increased the output of ethereal sulphates in the urine. Sodium sulphate, fed with the aromatic poisons, did not cause any further increase in ethereal sulphates; with phenol and bromobenzene there was actually a decrease. Cystine, given with phenol, caused an increase beyond that obtained with phenol alone, whilst cystine with bromobenzene or *p*-chlorophenol caused a marked decrease. Ethereal sulphates are therefore not formed simply at the expense of inorganic sulphates: the sulphur required must come from the tissues, presumably from tissue-cystine, although if cystine be present in the diet, it may be utilised. It is thought that when ethereal sulphates are formed from endogenous sulphur, the phenolic poison is first linked to an intermediary product of the metabolism of tissue-cystine and the whole eventually oxidised to the sulphate stage. If exogenous cystine is available, a complex analogous to *p*-bromophenylmercapturic acid may be formed and either excreted as such or oxidised to a sulphate. C. T. G.

**Influence of Salts on Metabolism. II. Blood-sugar and Liver Glycogen.** M. HÄNDEL (*Biochem. Z.*, 1924, **146**, 438—445).—Withholding of cell salts from the dietary of rats produces

a slight diminution in liver glycogen and a slight increase in blood-sugar. The addition of potassium has no appreciable effect, whilst calcium produces a slight increase in blood-sugar, but has no influence on the liver glycogen. The latter is likewise not affected by the addition of phosphates, which, however, produce a normal blood-sugar value. J. P.

**Influence of Variations in the Sodium-Potassium Ratio on the Nitrogen and Mineral Metabolism of the Growing Pig.** M. B. RICHARDS, W. GODDEN, and A. D. HUSBAND (*Biochem. J.*, 1924, **18**, 651—660).—The addition of sodium chloride or sodium citrate to a ration of cereal grain fed to a growing pig leads to increased assimilation and retention of nitrogen, calcium, and phosphorus. The increase of sodium salts in the ration causes increased excretion of potassium in the urine, which is, however, counterbalanced by the diminution of this element in faecal excretion, and the balance is therefore normal. S. S. Z.

**Mechanism of Acidosis in Anæsthesia.** R. L. STEHLE and W. BOURNE (*J. Biol. Chem.*, 1924, **60**, 17—29).—A study of the relation between ether anæsthesia and increased excretion of phosphoric acid. C. T. G.

**Classification and Grouping of Vitamins.** W. TÖNNIS (*Z. physiol. Chem.*, 1924, **136**, 89—104).—In mice and rats, normal growth and duration of life are observed only when the diet comprises sources of all three vitamins, *A*, *B*, and *C*. The simultaneous administration to avitaminosed animals of two vitamins has a definite improving effect on the growth curve—*A* and *B* exerting a more marked effect than *A* and *C*—only during the early stages of avitaminosis. Alcoholic and weakly acidic extracts of yeast produce in adult rats, in addition to the curative effect on the paresis due to lack of vitamin-*B*, an increase in body-weight, an effect which is also shown by the extracted yeast. The presence of the supposed vitamin-*D* in yeast is therefore not confirmed. Alcoholic and aqueous yeast extracts exert no effects on the growth of young rats and mice which are not also shown by the extracted yeast itself, from which it is concluded that no evidence is forthcoming in support of the possible separation of the water-soluble growth vitamin from the anti-beri-beri vitamin, and the general conclusion is drawn that only the three vitamins, *A*, *B*, and *C*, exist. J. P.

**Association of Manganese with Vitamins.** J. S. MCHARGUE (*J. Agric. Res.*, 1924, **27**, 417—424).—Manganese has been shown (cf. A., 1922, i, 906) to be an essential element in plant economy. In the animal body it is found most abundantly in the liver, kidney, and pancreas. The pericarp and germ of rice, barley, and wheat contain considerable amounts of manganese, which is largely removed during the polishing and milling processes. Cod-liver tissue, fish roe, the yolks of eggs, tomatoes, oranges, and lemons are relatively rich in manganese, whilst purified cod-liver oil and the whites of eggs contain negligible amounts. Colostrum is much

richer in manganese than milk. The fact that it is found in largest quantities in those plant- and animal-tissues which show the greatest vitamin potency suggests the existence of a relationship between manganese and these vital factors. E. M. C.

**Preparation of a Crystalline Picrate having the Antineuritic Properties of Vitamin-B.** A. SEIDELL (*U.S. Public Health Rep.*, 1924, 294—299; cf. Bertrand and Seidell, *Bull. Soc. Chim. biol.*, 1923, 5, 794).—The mixture of picrates, previously described as resulting from the treatment of an aqueous-alcoholic extract of yeast with methyl-alcoholic picric acid, can be separated to some extent by repeated extraction with acetone. From the acetone-soluble portion there was obtained a picrate crystallising in reddish-yellow flakes, m. p. (decomp.) below  $160^{\circ}$ . A daily dose of 2 mg. of this picrate is sufficient to protect pigeons against loss of weight on a diet of polished rice. The residue from the acetone extraction crystallises in pale yellow rods and prisms, m. p.  $202^{\circ}$ , and is physiologically inert. Both picrates, on combustion, give figures corresponding with the formula  $C_6H_{18}O_2N_3, C_6H_2(OH)(NO_2)_3$ . C. R. H.

**Antiscorbutic Fraction of Lemon Juice. II.** S. S. ZILVA (*Biochem. J.*, 1924, 18, 632—637).—When decitrated lemon juice is fermented in order to remove the sugar an active solution is obtained. On concentrating such a solution and precipitating with absolute alcohol, further non-active matter is removed in the precipitate. When such purified solution is treated with basic lead acetate, the entire antiscorbutic vitamin is precipitated. On removing the lead and bringing the solution up to its original volume, a preparation is obtained which contains the entire antiscorbutic activity of the original lemon juice, but only 0.03—0.07% of solids. Basic lead acetate also brings down the vitamin entirely in unfermented decitrated lemon juice, but in this case more extraneous matter (sugar, etc.) is also precipitated with it. These active preparations reduce ammoniacal silver nitrate in the cold and decolorise potassium permanganate. A new method for the removal of acids and other non-active matter from lemon juice without vitiating its antiscorbutic activity is described.

S. S. Z.

**Reducing Properties of Antiscorbutic Preparations.** S. J. B. CONNELL and S. S. ZILVA (*Biochem. J.*, 1924, 18, 638—640).—The destruction of the reducing properties of antiscorbutic solutions observed by Zilva (see preceding abstract) by heat and by alkalinity in the presence of air does not proceed at the same rate as the inactivation of the vitamin by the same means. Further evidence is produced which shows that the modified Folin's reagent suggested by Bezssonoff (this vol., i, 686, 789) for the detection of the antiscorbutic factor is untrustworthy. S. S. Z.

**Differential Dialysis of the Antiscorbutic Factor. II.** S. J. B. CONNELL and S. S. ZILVA (*Biochem. J.*, 1924, 18, 641—646).—The diffusion of the antiscorbutic factor proceeds differently

from that of the sugar and the nitrogenous substances present in decitrated lemon juice. The antiscorbutic factor in swede juice and in lemon juice diffuses through membranes of the same permeability. There are indications that the size of the active molecule cannot be far removed from that of the hexoses. S. S. Z.

**Antiscorbutic Value of Fresh and Canned English Tomatoes.** E. M. DELF (*Biochem. J.*, 1924, **18**, 674—678).—Raw fresh juice of English tomatoes is not quite as effective an antiscorbutic as fresh orange- or lemon-juice. Bottled tomatoes stored for six months were found to have lost about two-thirds of their original activity. Canning causes a loss of nearly three-quarters of the original value. A further but smaller loss takes place after storage for about 4 years. Canned tomato purée retains only about one-seventh of its original activity. S. S. Z.

**Creatine Content of Brain.** V. J. HARDING and B. A. EAGLES (*J. Biol. Chem.*, 1924, **60**, 301—310).—The percentage of creatine in the brain as a whole is a constant for any individual species; it is always higher in the cerebellum than in the cerebral hemispheres; it is independent of the amount of creatine in the diet, and it is rapidly reduced by autolysis of the brain-tissue. C. R. H.

**Isolation of Arachidonic Acid from Brain-tissue.** L. G. WESSON (*J. Biol. Chem.*, 1924, **60**, 183—187).—Bromine is added in slight excess to the ether extract of ground brain-tissue previously dehydrated with acetone. The white precipitate is removed, digested at 37° for 24 hours with 50% alcohol containing 5% of hydrochloric acid, washed, and dried at 100°. Analysis shows this substance to be the octabromide of arachidonic acid. The yield is about 3.5 g. per kg. of wet brain-tissue. The compound may be debrominated by boiling an alcohol solution for about 4 hours with copper-coated zinc (if the ethyl ester is required, dry hydrogen chloride is passed slowly through the boiling alcohol solution for 1 hour); water is then added and the acid (or ester) extracted with ether. The free acid thus obtained has all the properties of arachidonic acid, and there is little reason to suspect that it is different from the acid present as glyceride in the tissues. C. T. G.

**Gelatinolytic Liver Enzyme.** TSOU-HIA HSÜ (*Biochem. Z.*, 1924, **146**, 540—544).—The gelatin-liquefying enzyme present in liver extracts (Hata, A., 1909, ii, 416) may be precipitated from fresh preparations, but not from old extracts, by ammonium sulphate. Various attempts to isolate the enzyme by precipitation with uranyl acetate, and by separation of the accompanying proteins by means of cholesterol, are described. J. P.

**Hippuric Acid Balance in Renal Diseases.** J. SNAPPER and A. GRÜNBAUM (*Klin. Woch.*, 1924, **3**, 101—104; from *Chem. Zentr.*, 1924, i, 1689).—After administration of 3—5 g. of sodium hippurate

to healthy men, only traces of hippuric acid were found in the blood, whilst in certain renal diseases 4—40 mg. % were found. Both diseased and healthy kidneys produced hippuric acid, but in the former case it was eliminated with difficulty.

G. W. R.

**Extractives of Ox Spleen.** J. HAGIHARA (*Z. physiol. Chem.*, 1924, 136, 232—234).—A hot-water extract of ox spleen, after removal of the protein, gave no crystallisable substances in the arginine, histidine, and lysine fractions.

O. O.

**Nuclein Substance of the Spleen.** J. HAGIHARA (*Z. physiol. Chem.*, 1924, 135, 294—316).—Extracts of dried ox spleen with 10% sodium chloride, yielded, on treatment with copper sulphate or calcium chloride, precipitates with a phosphorus:nitrogen ratio of 1:1.5 to 1:2.5. On hydrolysis with 5% sulphuric acid and precipitation with ammoniacal silver nitrate, the presence of purine bases could not be established with certainty, the supposed guanine fraction giving nitrogen values which were too low. Guanylnucleic acid was not detected in the original dried gland. Various other methods of precipitating nucleic acids were applied to the preparations of the spleen, but the material obtained showed a variable composition and no very definite conclusions are drawn.

J. P.

**Significance of Ions in Muscular Function.** G. EMBDEN and E. LEHNARTZ (*Z. physiol. Chem.*, 1924, 134, 243—275).—A comparison was made of the effects of the sodium salts of various acids on the breakdown of lactacidogen in freshly-chopped muscle, to give lactic and phosphoric acids. In this respect, the ions arrange themselves according to the Hofmeister series, the greatest effect being obtained with thiocyanate and iodide and scarcely any with sulphate and tartrate. Sodium citrate and, especially, sodium fluoride, bring about the reverse reaction, viz., a disappearance of inorganic phosphate and synthesis of lactacidogen. The power of the different ions to stimulate breakdown of lactacidogen is found to correspond with their power to restore activity to a frog's muscle which has been inhibited by keeping in sucrose solution or otherwise.

C. R. H.

**Significance of Ions in Muscle Functions. II. Influence of Sodium Fluoride Solutions on Lactic Acid Formation in Frog-muscle Pulp.** G. EMBDEN, A. ABRAHAM, and H. LANGE (*Z. physiol. Chem.*, 1924, 136, 308—312).—Sodium fluoride in concentrations of  $M/100$ ,  $M/10$ , and  $M/1$  favoured the formation of lactacidogen but inhibited the lactic acid formation almost completely. At low concentrations ( $M/1000$ — $M/10,000$ ), the formation of lactacidogen is diminished and lactic acid formation increased. When the sodium fluoride solutions contained 2% of sodium hydrogen carbonate similar relations held, but the extent to which lactacidogen synthesis or lactic acid formation occurred was usually greater.

O. O.

**Hydrolysis of Protein by a Heat-stable Catalyst Present in Muscle.** W. M. CLIFFORD (*Biochem. J.*, 1924, **18**, 669—673).—Cod muscle contains a heat-stable catalyst which hydrolyses protein. S. S. Z.

**Possible Significance of Hexosephosphoric Esters in Ossification. II. The Phosphoric Esterase of Ossifying Cartilage.** R. ROBISON and K. M. SOAMES (*Biochem. J.*, 1924, **18**, 740—754).—The phosphoric esterase described by Robison which is present in bone and ossifying cartilage is also present in equally high degree in teeth, especially in those of very young animals. This enzyme also hydrolyses ethyl butyrate and triacetin, but not olive oil. It is distinct from the esterase of pancreas, which is relatively inactive towards phosphoric esters. The optimum reaction of the enzyme is  $p_H$  8.4—9.4—a reaction favourable for the precipitation of tertiary calcium phosphate and calcium carbonate. The deposition of fresh calcium phosphate has been demonstrated in bones taken from rachitic rats in solutions of calcium hexosemonophosphate or calcium glycerophosphate at 37° at the above reaction. It is argued that the enzyme is secreted in the region of the osteoblasts and hypertrophic cartilage cells and is actively concerned in ossification. It is suggested that the reaction of the tissue fluid in the region of ossification is rendered more alkaline than the blood by some mechanism, thereby increasing the activity of the enzyme, and favouring the deposition of both calcium phosphate and carbonate. S. S. Z.

**Possible Significance of Hexosephosphoric Esters in Ossification. III. Action of the Bone Enzyme on the Organic Phosphorus Compounds in Blood.** H. D. KAY and R. ROBISON (*Biochem. J.*, 1924, **18**, 755—764).—The acid-soluble organic phosphorus compounds present in the blood of various animals consist of at least two phosphoric esters, one of which is rapidly hydrolysed by the enzyme of ossifying cartilage (see preceding abstract), whilst the other is very resistant to the action of this enzyme. Both esters are hydrolysed by boiling with 0.2*N*-sulphuric acid. A method has been worked out by which the respective amounts of these esters may be determined and results of such determinations are given for the blood of human adults and children, and of rats, rabbits, and cockerels. The amount of ester hydrolysed by the bone enzyme varies between 14 and 36% of the total acid-soluble phosphorus. This ester is present almost entirely in the corpuscles. Attempts to demonstrate the presence of hydrolysable esters in the plasma lead to inconclusive results. There are indications that the esters are able to diffuse from the corpuscles to the plasma. The phospholipins present in the blood are not hydrolysed by the bone enzyme. S. S. Z.

**Cholesteryl Palmitate, a Constituent of Corpus Luteum.** M. C. HART and F. W. HEYL (*J. Amer. Pharm. Assoc.*, 1924, **13**, 17—22).—Dried corpus luteum contained 4.5—5.4% of ash.



Cholesteryl palmitate, potassium stearate, free fatty acids, and possibly cholesteryl stearate were identified in the acetone extract.

CHEMICAL ABSTRACTS.

**Microchemical Detection of a Nucleic Acid of the Thymonucleic Acid Type and the Selective Coloration Dependent Thereon in Microscopic Preparations.** R. FEULGEN and H. ROSSENBECK (*Z. physiol. Chem.*, 1924, **135**, 203—248).—A colour test called the “nucleal reaction” is described, whereby the presence of nucleic acids of the type of thymonucleic acid may be demonstrated in micro-preparations by the development of a red colour after these have been submitted to mild hydrolysis (4 minutes at 60° with 0.1*N*-hydrochloric acid), followed by treatment with fuchsin-sulphurous acid. The reaction is given by nucleic acids containing a hexose residue, such as thymus-nucleic acid, but not by the nucleic acids containing a pentose such as yeast-nucleic acid and triticonucleic acid. Nevertheless, certain of the higher plants (wheat embryos, bulbous plants) give a positive reaction, and it is inferred that in these cases a hexose acid must be present in addition to the well-established pentose acid. This is paralleled by the occurrence in animal cells of such pentose nucleotides as inosinic and guanylic acids. The nuclei of ciliate protozoa (infusoria) give the nucleal coloration, but in still lower representatives of the class (trypanosomes) it is absent. Bacteria are also, like yeast-cells, “anucleal.” Yeast-nucleic acid, typical of the lower plants, is regarded as being the primitive form of the substance; it becomes partly replaced in the higher plants by the “nucleal” acid, and the primitive form almost entirely disappears in the animal world, surviving only in the form of the pentose nucleotides. The nucleic material occurring in rye and responsible for the nucleal reaction in the higher plants has been isolated in an impure condition. It is rich in phosphorus and gives a marked reaction with fuchsin-sulphurous acid after mild hydrolysis just as does thymus-nucleic acid. J. P.

**Mechanism of “Nucleal” Staining. I. Detection of Reducing Groups in the Nuclei of Partly Hydrolysed Micro-preparations.** R. FEULGEN and K. VOIT (*Z. physiol. Chem.*, 1924, **135**, 249—252).—The nuclei of partly hydrolysed preparations of frog erythrocytes give a brown coloration, due to reduced colloidal silver when treated with a saturated aqueous solution of silver oxide. The reaction is not given by non-hydrolysed preparations. The presence of reducing groups liberated by hydrolysis of the nuclear material is inferred. J. P.

**Mechanism of “Nucleal” Staining. II. Behaviour of the Nucleus of Partly Hydrolysed Microscopic Preparations to Magenta-Sulphurous Acid after Preliminary Treatment with Phenylhydrazine.** R. FEULGEN and K. VOIT (*Z. physiol. Chem.*, 1924, **136**, 57—61).—The “nucleal” colour reaction (cf. preceding abstracts) is given by partly hydrolysed (4 mins. at 60° in 1.0*N*-hydrochloric acid) micro-preparations, but not after

these have been treated with phenylhydrazine acetate. Preparations treated with acid for 1 min., then with phenylhydrazine, and subsequently hydrolysed further, give the reaction, which is therefore ascribed to a chemical combination between magenta-sulphurous acid and the aldehyde groups liberated by separation of the purine residues of the nucleic acids during mild hydrolysis. J. P.

**Iron Content of Nucleoproteins.** T. TAKAHATA (*Z. physiol. Chem.*, 1924, **136**, 214—218).—The rôle of iron which occurs in the precipitate of nucleoproteins obtained with acetic acid from an aqueous extract of an organ is not quite clear. In analogy with the iron of the blood pigments, it may have some significance in oxidation processes or it may have a direct relation with the red blood-corpuscles and their genesis. It appears very doubtful whether the iron of the nucleoproteins can participate at all in oxidation processes. As nucleic acids are known to be free from iron and most proteins contain it only in traces, the iron content of different nucleoproteins has been examined. It is found that most extracts of different organs contain a sufficient amount of inorganic iron salts, a certain amount of which is precipitated with the nucleoprotein.

D. R. N.

**Production of Ammonia and Urea in Autolysis.** R. A. McCANCE (*Biochem. J.*, 1924, **18**, 486—497).—The optimum hydrogen-ion concentration for the production of ammonia and urea by autolysis from spleen and kidney is  $p_H$  6. When liver is employed in the winter the optimum  $p_H$  for ammonia production is the same but it is not so marked. The optimum for urea production lies in the region of  $p_H$  5—5.5. During the summer, the ammonium curves are unchanged, but the production of urea at  $p_H$  5—5.5 falls to a value often lower than that at  $p_H$  6. When the tissues are autolysed in the presence of oxygen and hydrogen, the total nitrogen is always the same, and also the  $p_H$ . The ammonia is sometimes the same and sometimes slightly higher in the hydrogen filtrate. The urea is always very much greater in the hydrogen filtrate, and the amount of urea produced in an autolysis in hydrogen is the same as when the gas is not present during the process. Nitrogen and hydrogen give identical results. The production of ammonia is common to all autolyses; that of urea occurs only in certain organs. It is not produced in the case of mammalian pancreas (bullock, pig), lung, skeletal muscle (bullock), heart-muscle (sheep) or avian liver (hen). Ammonia and urea are formed by separate processes. Their precursors are discussed. An enzyme which forms part of the urea-producing system and is strongly inhibited by gaseous oxygen is described and discussed. S. S. Z.

**Occurrence of Agmatine in Lower Animals.** F. HOLTZ (*Z. Biol.*, 1924, **81**, 65—67).—An extract of the giant siliceous sponge, *Geodia gigas*, was found to contain agmatine, a base already known to occur in vertebrates and in some lower plants, but not hitherto found in any invertebrate. The substance was isolated as the picrate

from the arginine fraction of the extract. It was identified by the composition and properties of the picrate, chloroaurate, and carbonate. Arginine was not found in the extract of *G. gigas*.

C. T. G.

**Occurrence of Trigonelline in the Animal World.** F. HOLTZ, F. KUTSCHER, and F. THIELMANN (*Z. Biol.*, 1924, **81**, 57—60).—Trigonelline, hitherto found only in plants, is now reported as occurring in the sea-urchin *Arbatia pustulosa*. The extract of 109.5 kg. of the animals was treated according to Kutscher's method (*Z. Nahr. Genussm.*, 1905, **10**, 528; A., 1906, ii, 562) and 13 g. of the gold salt of the alkaloid were isolated from the "lysine fraction." The alkaloid was identified by analyses and m. p. of the chloroaurate, chloroplatinate, chloride, and of the free base. Roeder's observation (A., 1914, i, 25) that the potassium ferrocyanide compound of trigonelline crystallises as red, lustrous prisms (the corresponding compound of glycine-betaine being white) was confirmed with trigonelline prepared from nicotinic acid and from sea-urchins.

The discovery of trigonelline in the animal world makes the occurrence of methylpyridinium hydroxide in crabs, sea-anemones, and other animals more easily intelligible, since this compound may be formed from trigonelline by addition of water and loss of carbon dioxide.

C. T. G.

**Recognition of Arginine, Betaine, Choline, and Acanthine in the Embryos and Liver of the Spiny Dog-fish (*Acanthias vulgaris*).** E. BERLIN and F. KUTSCHER (*Z. Biol.*, 1924, **81**, 87—92).—The presence in various cold-blooded animals of certain "intermediate" products of metabolism such as betaines and methylpyridinium hydroxide, which normally occur in plants, has recently been demonstrated. From the aqueous extract of about 1 kg. of the embryos of the common dog-fish (*Acanthias vulgaris*), arginine, betaine (12 g.), and choline (0.5 g.) were isolated from the phosphotungstic precipitate, whilst from the filtrate from the latter was isolated about 1 g. of a substance,  $C_{15}H_{22}O_4N_4$ , m. p. 122—124°, for which the name *acanthine* is suggested. It does not give the biuret or tryptophan reactions, but gives Pauly's diazo-reaction.

Betaine and choline were also found in the liver of the dog-fish. The embryos contain 1.2% of betaine and the liver and muscle about 0.07%; similarly, young beetroots contain more betaine than the older plants, indicating that in both plants and animals the substance is formed in the early stages and utilised during growth.

C. T. G.

**Changes in Chemical Composition of the Tissues of the Herring in Relation to Age and Maturity.** J. R. BRUCE (*Biochem. J.*, 1924, **18**, 469—475).—At any given stage of sexual maturity, the water, fat, and protein contents of the fresh muscle substance of the herring are dependent on age, the older fish containing a lower percentage of water and protein and a higher percentage of fat. This variation in composition with age resembles

that previously observed to be associated with the successive stages of sexual maturation. The metabolic demands of the growing gonads are made first on the fatty reserves of the liver. The muscular tissue is depleted only shortly before spawning. There are indications that the developing gonads have a high phosphorus requirement and that phosphatides play a part in the tissue changes and translocation associated with maturation. S. S. Z.

**Culture of the Marine Diatom *Nitzschia closterium* (F.) *minutissima* in Artificial Sea-water.** E. A. PEACH and J. C. DRUMMOND (*Biochem. J.*, 1924, **18**, 464—468).—This organism can grow and thrive in an inorganic culture medium, and does not require an organic substance specific to its growth. S. S. Z.

**Occurrence of Lactase in the Alimentary Tract of the Chicken.** T. S. HAMILTON and H. H. MITCHELL (*J. Agric. Res.*, 1924, **27**, 605—608; cf. following abstract, and Plimmer and Rosedale, A., 1922, i, 485).—Lactase is present in the crop, but absent from the proventriculus, the pancreas, and the intestines of normal chickens. E. M. C.

**Utilisation of Lactose by the Chicken.** T. S. HAMILTON and L. E. CARD (*J. Agric. Res.*, 1924, **27**, 597—604).—The lactose present in the whole or skim milk, whey, or buttermilk consumed by chickens will be completely absorbed. Lactose was utilised fairly completely in amounts up to 8 g. per hen per day, although such amounts invariably produced acute diarrhoea. Large amounts of uric acid interfere with the Munson-Walker-Bertrand method, but not with the Benedict method, for the determination of reducing sugars. E. M. C.

**Reducing and Oxidising Reaction in Milk.** P. HAAS and B. LEE (*Biochem. J.*, 1924, **18**, 614—620).—Itate and peroxydase are not identical, since they can be partly separated. Itate does not oxidise nitrite directly. It forms a peroxide by acting on the acetaldehyde present, which in its turn is utilised by the peroxydase of the milk in oxidising the nitrite. Attempts to effect a similar oxidation of nitrite by a peroxydase of vegetable origin in the presence of hydrogen peroxide have so far been unsuccessful. S. S. Z.

**Fission and Synthesis of Esters by Lipase from the Lacteal Glands and from Milk.** A. I. VIRTANEN (*Z. physiol. Chem.*, 1924, **137**, 1—13).—An investigation of the fission and synthesis of esters by the expressed juice and the glycerol extract of the lacteal glands of cattle. The lipolytic properties of these glands are very feeble. In the quantitative experiments only the glycerol extract was used, and concordant results were obtained only when  $p_H$  was maintained constant throughout. Under these conditions the hydrolysis of ethyl butyrate at 40° follow the course of a unimolecular reaction. In a series of experiments in which  $p_H$  varied from about 8.7 to about 5, the velocity of hydrolysis decreased with decrease

in  $p_H$ , finally ceasing at a value somewhat below 5. This cessation was not due to the destruction of the lipase by the acidity of the solution. Attempts to esterify butyric acid with glycerol failed, but the synthesis of ethyl butyrate was effected. Synthesis occurs at  $p_H$  values up to about 4, but beyond this value the reaction ceases. Whole milk acted hydrolytically at  $p_H$  8.8. B. F.

**Secretion of Bile. III.** E. NEUBAUER (*Biochem. Z.*, 1924, **146**, 480—485).—In continuation of previous work (*ibid.*, 1922, **130**, 556), it is shown that dehydrodeoxycholic acid is a powerful cholagogue, somewhat more active than deoxycholic acid, whilst in its hæmolytic action it is somewhat weaker than both deoxycholic and cholic acids. In 1.5% aqueous solution sodium dehydrodeoxycholate has a surface tension higher than that of sodium deoxycholate and cholate, and lower than that of sodium dehydrocholate. Dehydrodeoxycholic acid is less toxic in its cardiac effects than deoxycholic acid. It is concluded that hæmolytic and toxic action in the bile acid group increases with surface activity, whilst the latter is not related to cholagogic properties. J. P.

**Blood and Spinal Fluid. II. Calcium, Magnesium, and Phosphorus.** N. G. BARRIO (*J. Lab. Clin. Med.*, 1923, **9**, 54—56).—The spinal fluid contains (in mg. per 100 c.c.) 4.6—6.1 of calcium, 1.5—2.7 of inorganic phosphorus, and 1.4—6.1 of magnesium. The concentrations are, respectively, 50%, 50%, and 125% of those of the blood-serum. CHEMICAL ABSTRACTS.

**Analysis of Liquid Produced in a State of General Oedema.** R. FABRE (*J. Pharm. Chim.*, 1924, **29**, 484—485).—The pale yellow, feebly acid liquid ( $d^{15}$  1.009) contained, per litre, protein 1.2 g., urea 0.92 g., uric acid nitrogen 0.43 g., combined ammonia 0.034 g., ammoniacal nitrogen 0.028 g., total nitrogen 0.66 g., and sodium chloride 5.73 g.; ratio of uric acid nitrogen to (total—protein) nitrogen, 0.85. The blood, at the time of puncturing, contained 0.89 g. of urea per litre. W. T. K. B.

**Excretion of Uric Acid in the Urine of Dogs.** P. MEDERHOFF (*Z. physiol. Chem.*, 1924, **137**, 85—88).—After feeding on potato until the urine was free from uric acid, pure uric acid was mixed with the diet of a dog; no uric acid was excreted in the urine until the administration of the pure substance reached 2 g. per day. With larger doses, the quantity excreted increases with the dose. When meat was substituted for potato in the diet, the excretion of uric acid was somewhat greater than before; it is shown that this is not due to the purine content of meat. It is concluded that the power of dogs to decompose uric acid is quite low, and hence that the amount of purine derivatives which may be formed intermediately in the course of the metabolism of the dog is not very large. B. F.

**Significance of Determinations of Uric Acid in Urine, Particularly in Gout, Related Diseases, and Uric Acid Diathesis.** M. WEINTRAUT (*Arch. Pharm.*, 1924, **262**, 48—52).—The results obtained in the determination of uric acid in the urine

are mainly of significance when compared with the amount of acid phosphates present (Zerner's coefficient) and with the urea (coefficient of uric acid diathesis); their clinical significance is discussed.

G. M. B.

**Fat Excretion. II. Quantitative Relations of the Fæcal Lipoids.** W. M. SPERRY and W. R. BLOOR (*J. Biol. Chem.*, 1924, **60**, 261—287).—An exhaustive fractionation of the lipid content of the fæces of cats and dogs under various dietary conditions showed that the total lipid excretion is almost as great on a fat-free diet as on one rich in fats; it is less on a "sham-feeding" diet of agar and bone-ash. The relationships between the individual fractions and the total lipid are not markedly affected by changes in the diet except that an increase in the intake of fatty acids calls forth an increase in the excretion of fatty acids of the same nature. There is, in general, a close resemblance between the lipid material of the fæces and that found in the blood. The authors suggest that the fat excreted in the fæces does not originate directly from the fat of the food, but represents an excretion of lipid materials from the blood.

C. R. H.

**Presence of Pyruvic Acid in the Contents of the Intestine.** A. BERTHELOT and G. AMOUREUX (*Bull. Soc. Chim. biol.*, 1924, **6**, 338—339).—Pyruvic acid was found in the fæces of a subject whose intestinal flora was rich in *Bacillus aminophilus* and whose food for several years had consisted solely of fruit, vegetables, starchy materials, sugar, butter, and a little milk. Before the experiment, a quantity of potatoes was taken in addition to the usual ration and, in the evening, 8 g. of precipitated chalk. Pyruvic acid was also detected in the contents of the small intestine of a guinea-pig fed for 4 days on bread and potatoes treated with a rich culture of *B. aminophilus*, but not in the large intestine, where it is no doubt utilised by bacteria, thus accounting for its absence from normal fæces.

C. T. G.

**Minimal Lethal Doses of Lead Salts Intravenously Injected.** L. SCREMIN (*Arch. expt. Path. Pharm.*, 1924, **101**, 207—217).—From experiments on the intravenous injection into rabbits of lead nitrate, chloride, iodide, sulphate, carbonate, sulphide, and phosphate (the first two in true solution, the remainder in colloidal solution), it was found that the toxicity of the salts diminished in the above order, which is also the order of diminishing solubility. The salts fall into three groups, the first consisting of the nitrate, chloride, and iodide (and acetate), all of which are very toxic. Of the remainder, all except the phosphate are in an intermediate group of moderate toxicity; the phosphate is only slightly toxic.

H. J. P.

**Influence of Phosphorus Poisoning on Muscle Creatine and on Creatine-Creatinine Excretion.** A. PALLADIN and A. KUDRJAWZEWA (*Z. physiol. Chem.*, 1924, **136**, 45—56).—Phosphorus-poisoned rabbits show an increase in muscle creatine and an increased creatinine excretion with associated creatinuria. This is correlated

with a diminution in lactacidogen in the muscle, with a hypoglycæmia, and with a general diminution in carbohydrates.

J. P.

**Viscosity and Toxicity of Arsphenamine [Salvarsan] Solutions.** C. VOEGTLIN, J. M. JOHNSON, and H. DYER (*U.S. Public Health Rep.*, 1924, 179—195).—Dilute solutions of salvarsan on keeping undergo a progressive diminution in toxicity; at the same time there is a diminution in the viscosity of the solution. Investigation of a large number of samples, both of the hydrochloride and of the di-sodium salt, showed that this relationship between viscosity and toxicity is a general one.

C. R. H.

**Pharmacology of Benzyl Alcohol and Esters.** I. Effect of Benzyl Alcohol, Acetate, and Benzoate (per os). II. (Intravenously.) C. M. GRUBER (*J. Lab. Clin. Med.*, 1923, 9, 15—33, 92—112).—The action of benzyl acetate and benzoate is not dependent on their hydrolysis to benzyl alcohol.

CHEMICAL ABSTRACTS.

**Hypoglycæmic Action in Bases of the Choline Group.** A. MADINAVEITIA and S. HERNÁNDEZ (*Anal. Fis. Quím.*, 1924, 22, 168—173).—The ethyl ester of betaine produces hyperglycæmia in rabbits.

G. W. R.

**Ethylisoamylbarbituric Acid, an Anæsthetic without Influence on Blood-sugar Regulation.** J. H. PAGE (*J. Lab. Clin. Med.*, 1923, 9, 194—196).—Ethylisoamylbarbituric acid has little or no influence on blood-sugar in amounts sufficient to produce surgical anæsthesia.

CHEMICAL ABSTRACTS.

[Physiological Effect of Iodine Solutions.] E. RUPP.—(See ii, 562.)

**Toxicity of Copper Sulphate to the Spores of *Tilletia tritici* (Bjerk.), Winter.** F. N. BRIGGS (*Univ. Calif. Pub. in Agric. Sciences*, 1923, 4, 407—412).—The germination of spores of *Tilletia tritici* was inhibited by 0.002*N*-copper sulphate but was not affected by solutions more dilute than 0.0004*N*.

E. M. C.

**Organic Mercury Compound with Powerful Germicidal Properties.** G. W. RAIZISS and M. SEVERAC (*J. Lab. Clin. Med.*, 1923, 9, 71—80).—4-Nitro-3:5-diacetoxydimercuri-*o*-cresol is a powerful germicide and has a high mercuric chloride index; it is a non-irritant and has low toxicity when given intramuscularly. It does not precipitate proteins in 1:200 concentration.

CHEMICAL ABSTRACTS.

**Antiseptic Action of Compounds of the *apo*Cyanine, Carbo-cyanine, and *iso*Cyanine Series.** C. H. BROWNING, J. B. COHEN, S. ELLINGWORTH, and R. GULBRANSEN (*Proc. Roy. Soc.*, 1924, B, 96, 317—333).—In general, the compounds tested had a more powerful antiseptic effect on *Staphylococcus aureus* than on *Bacillus coli*, and there appears to be no relation between the chemical nature of the substances and their antiseptic effect. In the *apocyanine* and

isocyanine series, the introduction of amino groups tends to diminish rather than to enhance the antiseptic effect. The addition of side-chains to the quinoline fraction of the molecule in the isocyanine series, in contrast to their presence in the 2-methylquinoline fraction, reduces the antiseptic effect.

O. O.

**Antiseptic Action of Benzoic Acid, Salicylic Acid, Cinnamic Acid, and their Salts.** H. I. WATERMAN and P. KUIPER (*Rec. trav. chim.*, 1924, **43**, 323—325).—The growth of *Penicillium glaucum* in liquid media at room temperature was greatly hindered by 0.05–0.1% of benzoic acid ( $p_H$  4.4–4.0), 0.05–0.06% of cinnamic acid ( $p_H$  4.8–4.4) or 0.04–0.06% of salicylic acid ( $p_H$  4.8–3.4). Much larger concentrations of the sodium salts ( $p_H$  6.5–6.4) were without much influence. The inhibiting action is not due to hydrogen-ion concentration, but is explained by the Meyer-Overton lipid theory, which attributes antiseptic action to undissociated molecules of the organic acid (cf. Vermast, A., 1922, i, 406). The checking of growth by borax at a concentration (on anhydrous salt) of 0.2–0.3% ( $p_H$  8.2–8.4) is, however, undoubtedly due to hydroxyl ions, since it occurred at the same  $p_H$  with sodium hydroxide or carbonate.

E. H. R.

**Influence of Hydrogen-ion Concentration in the Presence of Salts on the Growth of *Gibberella Saubinetii*.** H. LUNDEGÅRDH (*Biochem. Z.*, 1924, **146**, 564–572).—The growth of cultures of *Gibberella*, which is increased at a given hydrogen-ion concentration by the presence of salts, shows a maximum at  $p_H$  6.8 in the presence of phosphate, whilst in the presence of calcium the maximum occurs at  $p_H$  4.7. An antagonism between hydrogen- and calcium-ion concentrations is inferred. Calcium diminishes the inhibiting action of magnesium on the fungus. Ammonium salts give a reaction similar to that of calcium but less well marked, whilst aluminium is very toxic.

J. P.

**Synthesis of Starch from Sugar by Bacteria.** E. C. GREY (*Biochem. J.*, 1924, **18**, 712–715).—Bacteria synthesise starch abundantly from dextrose. This formation of the polysaccharide can only be observed at a very early stage of the fermentation; the synthetic period in this investigation was found to be over in about 40 hours.

S. S. Z.

**Oxygen Uptake of Bacteria.** A. B. CALLOW (*Biochem. J.*, 1924, **18**, 507–518).—The oxygen uptake of spore-forming and non-spore-forming aerobic bacilli, spore-forming anaerobic bacilli, and aerobic cocci was studied. The organisms were washed free from culture medium, emulsified in sterile buffer solution,  $p_H$  7.6, and investigated for the oxygen uptake at 22° in Barcroft's micro-respirometer. Hydrogen-ion concentration had no appreciable effect on the oxygen uptake. Bacteria grown on agar or dextrose tryptic broth gave the same oxygen uptake as when grown on tryptic broth. *Bacillus pyocyaneus*, *B. fluorescens*, *B. prodigiosus*, *B. alcaligenes*, *B. proteus*, *B. coli*, Timothy grass bacillus, *B. megatherium*, *B. subtilis*, *Staphylococcus aureus*, and *Sarcina aurantiaca*, took up large



amounts of oxygen (5—25 c.c. per hour per g. of dry weight) at a steady rate. *B. alcaligenes*, *S. aureus*, and Timothy grass bacillus took up nearly as much oxygen when dried in a vacuum and emulsified in a buffer solution as before drying. *B. pyocyaneus*, on the other hand, took up oxygen after being dried at a much reduced rate. The aërobe *S. acidi lactici*, like the anaërobe *B. sporogenes*, took up only a minute amount of oxygen, at a rapidly decreasing rate. The presence of catalase did not alter the oxygen uptake of *S. acidi lactici* or *B. sporogenes*. S. S. Z.

**Equilibria between Succinic, Fumaric, and Malic Acids in the Presence of Resting Bacteria.** J. H. QUASTEL and M. D. WHETHAM (*Biochem. J.*, 1924, **18**, 519—534).—Resting cells (*i.e.*, a saline emulsion of the organism grown for 2 days) of *Bacillus coli* and *B. pyocyaneus*, possess an enzyme, similar to that present in muscle, which is capable of bringing about a reduction of methylene-blue in presence of sodium succinate with the formation of fumaric acid. This reaction is reversible. The effect of varying  $p_H$  on the times of reduction is a summation of the effect on the physical structure of the organism and the effect on the chemical reaction. Below  $p_H$  5.0 no apparent reduction can be obtained and the organism appears to be coagulated. The velocity of reduction increases rapidly with increase of  $p_H$  from 6.0 to 9.0 but not above this figure. The effect of heat on the reaction at constant  $p_H$  is also a summation of two superimposed effects as mentioned above. The reduction velocity increases with increase of temperature. The temperature coefficient between 30° and 60° is 2.1. The temperature of 45° is very suitable for a high velocity of reduction without risk of injury to the organism. The rate of reduction is roughly directly proportional to the concentration and the organism present. The rate of decolorisation of the methylene-blue and the equilibrium constant of this equation are also worked out. The reversible equilibrium fumaric acid  $\rightleftharpoons$  *l*-malic acid exists in presence of resting organism, fumaric acid in small quantities having been isolated after the action of the resting organism on *l*-malic acid. It has been shown that fumaric acid readily absorbs oxygen in presence of resting organisms although it will not donate hydrogen to methylene-blue.

S. S. Z.

**Effect of Oxygen Supply on the Metabolism of *Bacillus coli communis*.** M. STEPHENSON and M. D. WHETHAM (*Biochem. J.*, 1924, **18**, 498—506).—The carbon dioxide output and oxygen uptake of *B. coli* on a dextrose inorganic medium were studied. The organism is almost anaërobic during the early stages of dextrose breakdown. In an atmosphere of oxygen there is an increase in carbon dioxide output and a larger increase in oxygen uptake, which is not associated in the early stages of the experiment with increased utilisation of dextrose. Metabolism continues longer in oxygen than in air, the limiting hydrogen-ion concentration not being reached so soon. The increase of gaseous exchange with increase of oxygen pressure is attributed to the action on some acid degradation product of dextrose; this is supported by the

observation that the disappearance of lactic acid (as the ammonium salt) with the production of carbon dioxide is greatly increased with increased oxygen tension. The growth of the organism does not take place on lactic acid under anaërobic conditions. Succinic and acetic acids and glycerol are also suitable sources of carbon for *B. coli* in air but not under anaërobic conditions. S. S. Z.

**Use of Clark and Lubs Indicators for the Detection of Acid Production by the Colon-Typhoid Group.** P. A. TETRAULT (*Proc. Indiana Acad. Sci.*, 1922, 247—252).—Complete data are tabulated for the use of bromocresol-purple, bromothymol-blue, and phenol-red as indicators, whereby bacteria of the colon-typhoid group (*Bacillus coli*, *B. typhosus*, *B. dysenteriae*, *B. paratyphosus A* and *B.*, and *B. enteritidis*) can be distinguished in their formation of acid from dextrose, lactose, sucrose, maltose, raffinose, mannose, dulcitol, xylose, rhamnose, arabinose, lævulose, and galactose. The above indicators are mentioned in increasing order of sensitivity. CHEMICAL ABSTRACTS.

**Transformation of Carbon Compounds by *Bacillus pyocyaneus*.** J. SUPNIEWSKI (*Compt. rend. Soc. Biol.*, 1923, 89, 1377—1379; from *Chem. Zentr.*, 1924, i, 1679).—Sodium acetate when added to cultures of *B. pyocyaneus* is rapidly decomposed, probably with formation of formaldehyde and formic acid. Acetaldehyde is oxidised to acetic acid. Acetone gives formic and acetic acids. Ethyl alcohol gives acetaldehyde and acetic acid. Lactic acid gives pyruvic and acetic acids, acetaldehyde, and carbonates. Glycerol is oxidised to carbon dioxide. Dextrose is rapidly attacked. Cultures containing aliphatic compounds with carboxyl groups become alkaline by oxidation of these groups, whilst compounds containing the groups  $-\text{OH}$ ,  $=\text{CO}$ , or  $-\text{CHO}$  become acid through oxidation to acids. The limit on the alkaline side is  $p_{\text{H}}$  8.8 and on the acid side  $p_{\text{H}}$  6.6. G. W. R.

**Transformation of Nitrogen Compounds by *Bacillus pyocyaneus*.** J. SUPNIEWSKI (*Compt. rend. Soc. Biol.*, 1923, 89, 1379—1380; from *Chem. Zentr.*, 1924, i, 1679; cf. preceding abstract).—*B. pyocyaneus* readily assimilates ammoniacal and nitrate nitrogen, the oxygen in the latter case being also utilised. Carbamide is decomposed to ammonium carbonate by means of a urease. Glycine is not readily attacked. Asparagine is first deamidised with formation of ammonium aspartate and, ultimately, ammonium malate. Cyanogen compounds are assimilated after being converted into ammonium compounds. G. W. R.

**Metabolism of Cyclic Compounds by *Bacillus pyocyaneus*.** J. SUPNIEWSKI (*Biochem. Z.*, 1924, 146, 522—535).—*B. pyocyaneus* is unable to utilise most benzene derivatives, nor are aminobenzenes suitable as sources of nitrogen. Salicin is decomposed, the dextrose residue being utilised and the saligenin oxidised to salicylic acid. Aliphatic and cyclic amino-acids are decomposed with destruction of the carboxyl group and liberation of ammonia. Tryptophan is decomposed with, apparently, the intermediate formation of anthranilic

acid. The bacillus acts very slowly on indole itself. Anthranilic acid is decomposed to form ammonium carbonate whilst *p*- and *m*-aminobenzoic acids are not attacked. These two last-mentioned acids together with *o*- and *m*-aminocinnamic acids do not serve as sources of carbon or nitrogen. J. P.

**Oxidation and Reduction by *Pneumococcus*. I. Production of Peroxide by Anaërobic Cultures of *Pneumococcus* on Exposure to Air under Conditions not Permitting Active Growth. II. Production of Peroxide by Sterile Extracts of *Pneumococcus*.** O. T. AVERY and J. M. NEILL (*J. Exp. Med.*, 1924, **39**, 347—355, 357—366).—I. When grown anaërobically, pneumococci form peroxide on exposure to molecular oxygen with a rapidity which varies with the condition of the culture; the effect is not dependent on active cell-growth.

II. At  $p_H$  5—9, sterile extracts of unwashed cells form peroxide on exposure to the air. CHEMICAL ABSTRACTS.

**Growth-inhibitory Substances in *Pneumococcus* Cultures.** H. J. MORGAN and O. T. AVERY (*J. Exp. Med.*, 1924, **39**, 335—346).—A study of the effect of hydrogen peroxide on the growth of *Pneumococcus* and *Staphylococcus aureus*, and of the latter in filtrates from cultures of the former. CHEMICAL ABSTRACTS.

**Chemical Evidence on the Phylogenetic Classification of the Tubercle Bacillus.** E. R. LONG (*Amer. Rev. Tuberculosis*, 1923, **8**, 195—213).—The fairly definite animal tendencies of the tubercle bacillus are: a nucleic acid probably identical with that of the thymus, pancreas, sperm, and spleen. The basis, therefore, lies in the established presence of the pyrimidines, thymine, and cytosine, in tubercle bacillus nucleic acid, and the presence of a hexose, and the established absence of uracil. The fairly definite plant tendencies are: a marked chemosynthetic power in nitrogen metabolism; synthesising such complex substances as amino-acids and purine bases with no source of nitrogen other than ammonia. The less definite animal tendencies are: the said possession of lipins of the diamino-monophosphatide type, which so far have been described convincingly only in animals. The less definite plant tendencies are: the said content of hemicellulose or pentosans, made up of pentose units, which are typical plant substances, and an appreciable content of lauric acid, which has a wide plant distribution. CHEMICAL ABSTRACTS.

**Enzymic Studies on Lactic Acid Bacilli.** A. I. VIRTANEN (*Z. physiol. Chem.*, 1924, **134**, 300—319).—Lactic acid fermentation is a unimolecular reaction. Attempts to demonstrate a synthesis of hexose phosphate from mixtures of inorganic phosphate and dextrose or lactose were entirely negative, both with the living organisms and with dried preparations. Lævulose diphosphate was not affected by lactic acid bacilli. Catalase was entirely absent from the organisms. The living bacteria, but not the dried preparations, have the power of reducing methylene-blue; it is suggested

that the reducing power of milk towards methylene-blue is due partly to the presence of bacteria. C. R. H.

**Production of Formaldehyde by Intestinal Bacteria.** B. H. SHAW (*Brit. Med. J.*, 1924, I, 461—463).—From 0.0001 to 0.0015% of formaldehyde was produced by the action of various intestinal bacteria on peptone alone and admixed with lactose, dextrose, mannitol, or inulin. Bacteria do not appear to be capable of producing formaldehyde when oxygen is excluded. A. A. E.

**Influence of Sodium Pyruvate on Phosphorescent Bacteria.** A. BERTHELOT and G. AMOUREUX (*Bull. Soc. Chim. biol.*, 1924, 6, 336—337).—The luminosity of cultures of a species of phosphorescent bacterium (isolated from a marine fish) in a liquid medium was first depressed and afterwards much increased by the addition of sodium pyruvate at the rate of 4 g. per litre. Urea acted similarly, and a still greater effect was obtained with a mixture of urea and pyruvate. It is not yet known whether the pyruvate acts directly on the phenomenon of phosphorescence or whether it simply causes a greater development of the organism. C. T. G.

**Culture of Spirochaetes in Media containing Sodium Pyruvate.** A. BERTHELOT and P. SÉGUIN (*Bull. Soc. Chim. biol.*, 1924, 6, 341).—Two species of spirochaete from the mouth—*Sp. dentium* and *Sp. tenuis*—which do not develop on ordinary serum-bouillon, grew and remained alive for more than a month in this medium with the addition of 2 to 10 drops of a 20% solution of sodium or potassium pyruvate to each tube. Such a medium is suitable for the maintenance of pure cultures of these organisms and is much more simple to prepare than Noguchi's medium. C. T. G.

**Variations in Hydrogen-ion Concentration during the Assimilation of Ammoniacal Salts of Strong Acids by *Aspergillus repens*, de Bary.** D. BACH (*Compt. rend.*, 1924, 178, 2194—2195).—The growth of this mould is inhibited by high hydrogen-ion concentration, and for this reason a medium containing ammonium chloride is deleterious, since it results in the liberation of hydrochloric acid. Any cause capable of retarding this increase of acidity increases value of the salt as a nutrient for the mould. A. COUSEN.

**Preparation of Organic Acids by Biological Methods with the Help of Hyphenated Moulds.** R. FALCK and VAN BEYMA THOE KINGMA (*Ber.*, 1924, 57, [B], 915—920).—A general account is given of the experimental technique necessary for the production of uniform results in the investigation of the production of acids from carbohydrates with the aid of moulds. An approximately 1% agar jelly is used as substrate into which the mould hyphae do not penetrate more than a few millimetres. Dextrose is generally used as source of carbon, but may be replaced by other sugars, glycerol, starch, wood, or cellulose; the best concentration varies greatly with the particular type of mould. Ammonium nitrate

(0.16—0.32%) is the most suitable source of nitrogen; other nutrient salts are required in such small amount that their special provision is unnecessary if technical glucose is employed. For a given solution, the amount of acid formed in the unit of time is proportional within certain limits to the surface of the agar jelly. The production of acids by various types of *Aspergillus*, *Penicillium*, and *Citromyces* has been investigated. The black, brown, or pale brown types of *Aspergillus* yield acid freely, the yellow and greenish-yellow varieties moderately, whereas the pale or colourless types give little acid. The ultimate product is oxalic acid; the intermediate formation of citric acid is nearly always observed.

H. W.

#### Production of Gluconic Acid by Hyphenated Moulds.

R. FALCK and S. N. KAPUR (*Ber.*, 1924, **57**, [B], 920—923; cf. preceding abstract).—Gluconic acid is produced by the action of four varieties of *Aspergillus niger*, *A. cinnamomens*, *A. fuscus*, and *Citromyces lactis* on solutions of glucose in the presence of calcium carbonate. The best conditions are secured by using relatively concentrated sugar and very dilute ammonium nitrate solutions, working at a low temperature, and interrupting the action when the calcium carbonate is dissolved, but previous to the separation of calcium citrate. The yield of acid is 50% of the sugar. The production of glycuronic acid could not be observed.

H. W.

#### Presence of Pyruvic acid in Cultures of certain *Mucors*.

A. BERTHELOT and R. POUISOT (*Bull. Soc. Chim. biol.*, 1924, **6**, 343—344).—Pyruvic acid was detected in cultures of three species of *Mucor* in media containing sugars, after incubation for 15 days. In older cultures, pyruvic acid was not found. The production of this acid is no doubt one of the factors accounting for the favourable action of *Mucor* on the growth of yeast.

C. T. G.

**Formation of Pyruvic Acid and Ethyl Alcohol from Calcium Lactate by Yeasts.** E. KAYSER (*Bull. Soc. Chim. biol.*, 1924, **6**, 345—351).—Further details are given of work already published (cf. A., 1923, i, 986). The formation of the ethyl and amyl esters of acetic and valeric acids by various yeasts in media containing calcium lactate and mineral salts is confirmed. The alcohols were determined after saponification of the distillate from the cultures by a combination of the methods of Duclaux and Nieloux.

C. T. G.

**Rôle of the Reaction of the Medium in Selective Fermentation.** A. FERNBACH and N. SCHILLER (*Compt. rend.*, 1924, **178**, 2196—2197).—The fermentation of sugar solutions by 8 types of yeast has been studied, and in each case it has been found that lævulose is at first attacked more readily than dextrose, until a point is reached, varying with the yeast employed and not occurring in the case of Sauternes yeast, at which the relative rate of attack is

reversed. It was found possible to modify the course of the fermentation in other cases than that of the Sauternes yeast by decreasing the acidity of the solution.

A. COUSEN.

**Enzymic Equilibria. I.** H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **136**, 39—44).—From a mathematical treatment of the results obtained in a study of the equilibria in aqueous systems of the type, methyl alcohol-dextrose-emulsin, and fatty acid-alcohol-lipase, it is concluded that a more satisfactory interpretation results from the assumption that an affinity exists between enzyme and reaction products as well as between enzyme and substrate. This applies even in the case of invertase showing a hydrolytic action only.

J. P.

**Co-zymase of Yeast. III.** H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **136**, 107—129).—The concentration, purification, and characterisation of co-zymase are described. A method has been devised for determining co-zymase, based on the measurement of the carbon dioxide evolved with zymase and dextrose under standard conditions at  $p_H=6.2-6.6$ . The fermentative power of dried yeast preparations is increased by the addition of co-zymase and also by the addition of washed inactive yeast free from the co-enzyme. The rate of fermentation therefore depends on the relative quantities of zymase and co-zymase, and it is assumed that the two together form a dissociable compound which constitutes the active enzyme. By the addition of either zymase or co-zymase the dissociation of this active compound is suppressed, resulting in an increase in the activity of the mixture. The results on the thermostability of co-zymase are similar to those arrived at by Tholin (A., 1922, i, 305). Co-zymase is decomposed rapidly in solutions more alkaline than  $p_H$  10, shows maximum stability at  $p_H$  7, and is still active in 0.5*N*-hydrochloric acid ( $p_H$  0.6). Contrary to the view hitherto accepted, it was found that lead acetate is capable of precipitating the co-zymase to a greater or less extent according to the  $p_H$  of the solution. The co-zymase is not affected by hydrogen sulphide, but is inactivated by traces of lead. When lead acetate was added to yeast juice containing the co-zymase at  $p_H$  6, the free phosphate and the hexosephosphate were precipitated and the co-zymase was found mainly in the filtrate. When the latter was brought to  $p_H$  8.3—10.0 the co-zymase was almost completely precipitated. It could be recovered from the lead precipitate by suitable means and such fractional precipitation may be employed for purification. It can also be purified in a solution free from phosphate, by adsorption on alumina, which is almost quantitative at  $p_H$  10, whilst in acid solutions no adsorption occurs. The alumina adsorbate is strongly active and the co-enzyme is not eluted therefrom by water or very dilute acids although it can be readily eluted quantitatively with 1% phosphate solution at  $p_H$  6.3.

D. R. N.

**Nitrogen Content of Invertase.** K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **136**, 224—231).—In reply to Willstätter and Schneider

(this vol., i, 692), it is urged that proportionality between enzyme activity and nitrogen content is possible only when due regard is paid to the inactivation of part of the enzyme during the processes used for its purification. It is shown that, when the same yeast is used and experimental conditions are standardised, an approximate constancy exists for the ratio  $I/f/N$ . With simple assumptions, ratios for two of Willstätter's preparations show reasonable agreement.

O. O.

**Affinity of Invertase for Different Sugars. III. Identity of Invertase and Raffinase.** K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **136**, 62—74; cf. Euler and Josephson, this vol., i, 467; Josephson, this vol., i, 801).—Invertase and raffinase show the same affinity constants to  $\alpha$ - and  $\beta$ -dextrose, to lævulose, and to  $\beta$ -galactose, and these sugars inhibit the action of the two enzymes on sucrose and on raffinose to the same extent. It is concluded that invertase and raffinase are identical. Melibiose shows no affinity for invertase.

J. P.

**Relative Specificity of Yeast Maltase.** R. WILLSTÄTTER, R. KUHN, and H. SOBOTKA (*Z. physiol. Chem.*, 1924, **134**, 224—242).—The hydrolysis of  $\alpha$ -methyl-,  $\alpha$ -ethyl-, and  $\alpha$ -phenyl-glucosides and of amygdalin by the maltase of yeasts from various sources was studied. The hydrolysis of  $\alpha$ -ethylglucoside in some cases obeyed the law of a unimolecular reaction; in others the rate of reaction fell off more rapidly. In the case of  $\alpha$ -phenylglucoside, the curve representing the course of the reaction corresponds with that already described for the hydrolysis of  $\alpha$ -methylglucoside (A., 1921, i, 282). The power of different yeast-extracts to hydrolyse the  $\alpha$ -glucosides is parallel with their rate of hydrolysis of amygdalin. All the specimens of maltase examined showed less affinity for the aliphatic glucosides than for  $\alpha$ -phenylglucoside.

C. R. H.

**Lipase of the Castor Oil Bean.** R. WILLSTÄTTER and E. WALDSCHMIDT-LEITZ (*Z. physiol. Chem.*, 1924, **134**, 161—223).—The enzyme was most active at a  $p_H$  of 4.7 to 5.0; its activity was unaffected by the addition of manganese salts and was inhibited by sodium chloride; the optimum temperature was 35°. An investigation of the kinetics of the reaction under constant physical conditions showed that its course was not regular.

The removal by means of organic solvents of the oil contained in the beans resulted in all cases in a serious loss of enzymic activity; moreover, the preparations so obtained were very unstable. This method of purification was therefore abandoned in favour of the separation, and drying in a vacuum desiccator or in an air current, of the "cream" obtained by centrifuging an aqueous emulsion of the pulverised beans. In this way there was far less loss, especially if the cream were mixed with a quantity of kieselguhr before drying. Further purification was effected by washing the "cream" with dilute alkali. The dried preparation finally obtained retained its activity for a fairly long period; it contained much protein but

no carbohydrate. The only marked difference in its elementary composition from that of the crude powdered beans was an increase in the phosphorus content.

The apparent increase in lipolytic activity during germination observed by previous authors (cf. A., 1903, i, 218; 1904, ii, 433) is due to a change in the character of the enzyme by which its optimum hydrogen-ion concentration is shifted to the alkaline side. (For distinction, the original enzyme is termed *spermatolipase*, and the altered one *blastolipase*.) The formation of blastolipase from the spermatolipase can also be brought about by the action of pepsin and by hydrolysis with acids. Dried preparations of blastolipase were much more stable than those of spermatolipase, and their synthetic action, on a mixture of glycerol and oleic acid, was considerably stronger. C. R. H.

**Animal Carboxylase.** A. GOTTSCHALK (*Biochem. Z.*, 1924, **146**, 582—588).—Rabbit liver pulp to which pyruvic acid is added shows after incubation, both in the presence and in the absence of oxygen, more acetaldehyde formation than controls containing no added pyruvic acid. The presence of a carboxylase is inferred (cf. also Neuberg and Gottschalk, this vol., i, 785). J. P.

**Methylated Proteins. I. Action of Proteolytic Enzymes on Methylated Proteins.** T. IMAI (*Z. physiol. Chem.*, 1924, **136**, 173—187).—When casein or edestin is methylated with methyl sulphate and sodium hydroxide at 20°, the methyl derivative, which is insoluble in alcohol and in ether, is obtained as an amorphous white powder easily soluble in water. These derivatives are hydrolysed by pepsin, trypsin, and erepsin, although to a much lesser extent compared with the unmethylated protein. D. R. N.

**Methylated Proteins. II. Hydrolysis of Methylated Casein.** T. IMAI (*Z. physiol. Chem.*, 1924, **136**, 188—191).—A certain relation exists between the lysin content of a protein and the free amino groups in the protein molecule (cf. A., 1912, i, 1041; 1920, i, 687). If, therefore, methylated amino-acids could be isolated from the products of hydrolysis of a methylated protein, it could be readily ascertained which amino groups are free in the original molecule. Edlbacher (A., 1921, i, 199) obtained in the lysin fraction a considerable quantity of a syrupy mass from which he was not able to isolate any well-defined compound. This fraction has now been further examined. When a methylated protein is hydrolysed with proteolytic enzymes, from the products of hydrolysis histidine is obtained in traces, arginine in a small quantity, whilst a considerable amount is obtained as a syrupy mass in the lysin fraction, from which a crystalline platinum chloride double salt has been isolated. It is very easily soluble in water, and in methyl and ethyl alcohol. D. R. N.

**Methylated Proteins. III. Action of Erepsin on Methylated Polypeptides.** T. IMAI (*Z. physiol. Chem.*, 1924, **136**, 192—204).—It is supposed that in methylated proteins the free amino groups are methylated whilst the imino groups are not



affected (A., 1920, i, 825). Owing to the relative difficulty of hydrolysis of methylated proteins by enzymes, it appeared probable that the ease of hydrolysis of the peptide linkings by proteolytic enzymes depended on their distance from the methylated amino groups. To establish this view the behaviour of the betaines of glycylglycine, diglycylglycine, and triglycylglycine towards erepsin has been studied. The first two are not attacked, whilst the latter is hydrolysed to a slight extent. D. R. N.

**Action of Erepsin on Benzoylated Polypeptides.** T. IMAI (*Z. physiol. Chem.*, 1924, **136**, 205—213).—As the methylated polypeptides of glycine are only crystallisable with difficulty, the behaviour of the more easily crystallisable benzoylated polypeptides of glycine towards erepsin has been studied. Benzoylglycylglycine, in common with the methylated dipeptide, is not attacked whilst the benzoyl-di-, -tri-, and -tetra-glycylglycines are hydrolysed to different extents. It is uncertain which peptide linkings in these derivatives are attacked. D. R. N.

**Comparison of certain Oxidising Enzymes of the Higher and Lower Plants.** M. E. ROBINSON (*Biochem. J.*, 1924, **18**, 543—548).—The oxydases of the higher plants consist of three components, a pyrocatechol derivative and two enzymes—oxygenase and peroxydase. Those of the *Basidiomycetes* consists only of an enzyme-like peroxide and peroxydase. The experiments of Onslow on certain phanerogam oxydases and those of Gallagher on extractable plant phosphatides have been repeated and confirmed. Gallagher's interpretation of his results is criticised. S. S. Z.

**Oxidising Enzymes. VII. Oxygenase of Higher Plants.** M. W. ONSLOW (*Biochem. J.*, 1924, **18**, 549).—Polemical. It is reasserted that oxygenase catalyses the formation of peroxide; Gallagher's assertion that the blueing of guaiacum is due to the presence of an autoxidisable lecithin-like substance is criticised. S. S. Z.

**Use of Guaiacol for Measuring the Activity of Oxydase Preparations.** P. FLEURY (*J. Pharm. Chim.*, 1924, [vii], **29**, 402—414).—Tetraguaiacoquinone,  $[C_6H_3(OMe)O]_4$ , to which the red coloration given by the action of laccase on guaiacol is due, separates as a precipitate when the solution is kept and forms colloidal solutions, which readily coagulate, with water. It can be used for the purposes of colorimetric analysis, however, by extracting it with chloroform and comparing the colour of the solution with that of a 0.01*N*-solution of iodine. A solution of 46.5 mg. of guaiacoquinone in 1 litre of chloroform, obtained by extraction from aqueous solution, has the same colour as 0.01*N*-iodine solution, the thickness of the layer viewed in each case being 10 mm. The oxidation of guaiacol by air in the presence of laccase proceeds quantitatively, but the yield of guaiacoquinone varies between 72 and 95%, being influenced adversely by allowing the reaction to be prolonged, by the presence of an excess of guaiacol, by the alkalinity of the medium, and by raising the temperature. These

influences are negligible, however, under the conditions of the experiments described. The activity of the laccase remains practically unchanged at the end of the reaction.

W. T. K. B.

**Influence of X-Rays on Leucocytic Oxydases.** P. LEMAY, C. GUILBERT, R. PETIT, and L. JALOUSTRE (*Compt. rend.*, 1924, **178**, 1711—1713; cf. Maubert and others, *A.*, 1923, i, 723; this vol., i, 808).—The activity of both direct and indirect leucocytic oxydases is increased by weak doses of X-rays, but whilst the direct oxydases remain stable and unchanged under the action of more powerful doses, the indirect oxydases are inactivated. The latter are not, however, destroyed, and they recover again a certain time after the cessation of radiation.

M. S. B.

**History of Carbon Dioxide Assimilation.** F. WEIGERT (*Z. physikal. Chem.*, 1924, **109**, 79—80; cf. *A.*, 1923, i, 1271).—A question of priority (cf. Warburg and Negelein, this vol., ii, 241).

M. S. B.

**Blackman's Reaction.** O. WARBURG and T. UYESUGI (*Biochem. Z.*, 1924, **146**, 486—492).—Using suspensions of the alga *Chlorella*, the influence of hydrogen cyanide and of various substituted urethanes on the Blackman reaction (rate of decomposition of carbon dioxide and liberation of oxygen in strong light), on the one hand, and on the decomposition of hydrogen peroxide and on respiration on the other, has been investigated. The parallelism between the two sets of results lends support to the views of Willstätter and Stoll ("Untersuchungen über die Assimilation der Kohlensäure," Berlin, 1918).

J. P.

**Influence of Acidity on Plant Growth without regard to other Factors.** A. G. MCCALL (*J. Amer. Soc. Agron.*, 1923, **15**, 290—297).—A general review of recent work on soil reaction and the tolerance of acidity by plants in solution cultures and by bacteria in soils. Measurements of hydrogen-ion concentrations may prove more useful than lime requirement tests, but in practice the application of lime need not necessarily be carried to the point of neutralisation.

E. M. C.

**Effect of Hydroxyl-ion Concentration on the Growth of Walnut Roots.** H. S. REED and A. R. C. HAAS (*Amer. J. Bot.*, 1924, **11**, 78—84).—Walnut seedlings are very sensitive to the absence of calcium from the culture solution. The injury to walnut roots from solutions of high  $p_H$  values is due principally to calcium starvation rather than to the effect of high concentration of hydroxyl ions on the plant.

A. A. E.

**Effect of Salts on the Intake of Inorganic Elements and on the Buffer System of the Plant.** D. R. HOAGLAND and J. C. MARTIN (*California Agr. Expt. Sta., Tech. Paper*, 1923, 8, 26 pp.).—Sodium chloride and sodium sulphate, added to a culture solution, caused marked alteration in the composition of the barley plant, tending to decrease the absorption of calcium, magnesium, and potassium. Sodium and chlorine may be absorbed and stored by the barley

plant in relatively large quantities. The sulphate ion is taken up by several plants less rapidly than the chloride ion. No definite alkali tolerance for different plants can be established because of the important modifying effects of environmental factors. The buffer effects of the expressed sap of stems and leaves was greater than that of roots. Rapid and extreme changes in reaction of the expressed root sap were caused by the addition of sodium hydrogen carbonate to the culture solutions. Calcium chloride produced appreciable changes in the reaction and buffer effects of plant juices. Sodium nitrate increased the alkalinity of the expressed root sap, with a slight accompanying injury resembling that induced by sodium hydrogen carbonate. E. M. C.

**Effect of Sodium Chloride and Calcium Chloride upon Growth and Composition of Young Orange Trees.** H. S. REED and A. R. C. HAAS (*California Agr. Expt. Sta., Tech. Paper*, 1923, 4, 21 pp.).—Orange trees were grown in various nutrient solutions in sand and the distribution throughout the plant of nitrogen, calcium, sodium, and potassium was determined. Physiological disturbances developed in a few months in the trees grown in incomplete nutrient solutions. Omission of calcium caused spotting and shedding of the leaves and the repeated development of new buds. In such trees, the calcium was retained principally in the trunks and roots, and was present only in small amounts in the leaves, shoots, and rootlets, indicating a low mobility of calcium. In plants grown in full nutrient solutions, the percentage of calcium in the ash was fairly constant throughout the plant. The percentage of potash was high in all parts of the trees. In the presence of calcium chloride vigorous growth was made even when considerable amounts of sodium chloride were also present. E. M. C.

**Nutrition of the Potato Plant with Special Reference to Water Cultures.** W. NEWTON (*J. Amer. Soc. Agron.*, 1923, 15, 392—399).—Potato plants were rapidly injured by the omission of calcium salts from the solution, but showed an increased yield of tubers when potassium was omitted. It is suggested that the value of potash fertilisers may be due in part to the indirect effect of increasing the calcium content of the soil solution. E. M. C.

**Plant Colloids. XV. Amylopectins Prepared from Different Starches.** M. SAMEC, M. MINAEFF, and N. RONŽIN (*Koll. Chem. Beihefte*, 1924, 19, 203—212).—Amylopectins of various origin differ in the appearance, conductivity, viscosity, and hydrogen-ion concentration of the aqueous solutions, and in the phosphorus content, titratable acidity, and amount of alkali combined with one g.-atom of phosphorus. The amylopectins from underground storage organs (potato, arrowroot, and tapioca) and from seeds (maize, rice, wheat) form two distinct groups. These differences do not depend on variations in the cations associated with the amylophosphoric acids, since they are maintained in starches washed with dilute hydrochloric acid. Synthetic amylopectins prepared from the different starches are closely analogous.

E. M. C.

**Occurrence of Alkaloids in Nature. I. Common Occurrence of Alkaloids and Tannides.** L. ROSENTHALER and M. MOSEMANN (*Schweiz. Apoth.-Ztg.*, 1924, **62**, 13—15, 29—31, 48—50; from *Chem. Zentr.*, 1924, i, 1678).—In a considerable number of cases alkaloids and tannides occur together in the same cells. It is not, however, always necessary to assume the existence of alkaloid-tannide compounds. Such compounds may be present where the presence of alkaloids is not shown by the usual tests. Many alkaloids and tannides are products of excretion and insoluble alkaloid-tannide compounds may also be regarded as such. They may, however, have some physiological function. G. W. R.

**Phytosterols of the Endosperm of Corn [Maize].** R. J. ANDERSON (*J. Amer. Chem. Soc.*, 1924, **46**, 1450—1460).—Maize gluten (23 kg.) was extracted with ether-alcohol (1:1), and the extract, which contained some free phytosterol, yielded, on hydrolysis with alcoholic potassium hydroxide, crude, crystalline phytosterol (55 g.) and an oil (30 g.). *Dihydrositosterol*,  $C_{27}H_{47}OH \cdot H_2O$ , m. p.  $139^\circ$  (anhydrous, m. p.  $141^\circ$ ),  $[\alpha]_D^{20} + 24.23^\circ$  in chloroform, was obtained from the crude phytosterol by 39 crystallisations from alcohol, and hydrolysis of the purified *acetyl* derivative, which formed large hexagonal plates, m. p.  $138^\circ$ ,  $[\alpha]_D^{20} + 14.41^\circ$ . The accompanying sitosterol could not be completely removed by crystallisation, but was extracted from the chloroform solution of the acetyl derivatives by concentrated sulphuric acid, dihydrositosterol then being obtained of  $[\alpha]_D^{20} + 25.04^\circ$ . The crude phytosterol (15.6 g.) obtained similarly from maize bran (15 kg.) is relatively rich in dihydrositosterol. Dihydrositosterol does not give the Liebermann-Burchard reaction, and does not absorb bromine. F. G. W.

**Aleurone Cells of Cereals.** E. B. BENNION (*Cereal Chem.*, 1924, **1**, 138—148).—The author has separated the aleurone layer from barley and wheat, and made elementary analyses on products obtained by extraction with sodium chloride solution and alcohol. The aleurone cells of barley contain only small quantities of fatty matter, but those of wheat contain an oil and a white, waxy material, probably phytosterol. The residue after extraction with alcohol was rich in nitrogen and ash. E. M. C.

**The Genus *Mentha*. *Mentha piperita*.** F. J. BACON, G. C. JENISON, and R. E. KREMERS (*J. Amer. Pharm. Assoc.*, 1923, **12**, 1075—1077).—Methylcyclohexanone is not constantly present and it is possible that its reported occurrence is due to the treatment to which the oil was subjected. Its precursor, pulegone (and possibly piperitone) is constantly present. It is suggested that menthenone is first formed and that menthol and menthone are formed from it by reduction. Aldehydes are present in only small proportions in the natural oil and are mostly eliminated in the refining processes. From 5454.5 kg. of oil, 500 g. of isovaleraldehyde were obtained. CHEMICAL ABSTRACTS.

**Constituents of Ragweed Pollen.** F. W. HEYL (*J. Amer. Pharm. Assoc.*, 1923, **12**, 669—676; cf. A., 1922, i, 1224).—The

ethereal extract of ragweed pollen contained formic, acetic, valeric, lauric, oleic, linoleic, palmitic, and myristic acids, and an unsaturated acid,  $C_{10}H_{18}O_2$ : the alcoholic extract contained a mixture of phosphatides. The acetone-insoluble lipin was obtained by recrystallisation. The water-soluble portion of the alcoholic extract contained adenine, betaine, sucrose, lævulose, and a trace of guanosine. With the exception of the colouring matters and possibly a proteose, none of the 27 substances isolated appears to be a chemical specialisation of the pollen cell. CHEMICAL ABSTRACTS.

**Accumulation of Iron and Aluminium Compounds in Maize Plants and its Probable Relation to Root Rots.** II. G. N. HOFFER and J. F. TROST (*J. Amer. Soc. Agron.*, 1923, **15**, 323—331).—The accumulation of iron and aluminium compounds in the nodal tissues of maize plants is affected by soil conditions. The accumulation of aluminium and to a less extent of iron in the plants is associated with retarded growth and increased susceptibility of certain strains to root rots. E. M. C.

**Action of Metabolic End-products on Plants.** III. **Action of Nitrogen-free End-products of Plant Metabolism (Ethereal Oils, Terpenes, etc.) on the Germination of Seeds.** W. SIGMUND (*Biochem. Z.*, 1924, **146**, 389—419).—An investigation of the influence of various ethereal oils and terpenes on the germination of vetch, wheat, and rape seeds. Mustard oil proved most toxic, followed by clove and caraway oil; the oils of aniseed, fennel, geranium, peppermint, rosemary, and thyme, although less active than the first three, also definitely inhibited germination. Oil of garlic was toxic in the form of vapour but much less so in solution, whilst oil of turpentine gave similar results. The oils of bergamot, cedar, citron, eucalyptus, rue, and juniper berry were practically devoid of effect in solution. The results obtained with individual constituents of the oils were as follows: Hydrocarbons:—cymene, *d*- and *l*-limonene, *d*- and *l*-pinene, and styrene, no action. Alcohols:—borneol, linalool, menthol, terpin hydrate, no action; terpineol, toxic. Aldehydes:—benzaldehyde, citral, cinnamaldehyde, very toxic; anisaldehyde, somewhat less toxic; isovaleraldehyde and vanillin least toxic. Ketones:—in order of diminishing toxicity, carvone, camphor, fenchone, cineole. Phenols:—carvacrol, thymol, apiole, safrole, very toxic; anethole, weakly toxic. Acid:—anisic acid, little or no action. Ester:—methyl salicylate, toxic. J. P.

**Action of Formates on the Growth of certain Plants in Pot Cultures.** C. RICHET, junr. (*Compt. rend.*, 1924, **178**, 1922—1923).—The addition of small amounts of sodium or calcium formate to soil, either at the time of sowing or at the commencement of germination, increased the germinating power of wheat and barley by 10—20%. There was no significant increase in the weight of the shoots. E. M. C.

**Influence of Temperature of the Soil on the Relation of Roots to Oxygen.** CANNON (*Science*, 1923, **58**, 331).—The maximum, optimum, and minimum temperatures for the growth

of roots in normally aerated soil are altered under conditions of diminished oxygen supply. The rate of root growth with a given oxygen supply as compared with the rate under normal aeration decreases with increase of temperature of the soil.

Typical results are given with regard to several species of plants, and it is suggested that investigations on the oxygen relation of roots would give results of considerable value from an ecological point of view. C. T. G.

**Action of Salt Solutions on the Soil. II.** O. NOLTE and E. SANDER (*Landw. Versuchs-Stat.*, 1924, **102**, 219—225).—On theoretical grounds and as the result of earlier work (cf. A., 1921, i, 914), it was expected that the rate of percolation of a salt solution through a column of soil, *i.e.*, the permeability of the soil, would bear a definite relation to the reaction of the solution. Tables and graphs are presented showing the changes in the  $p_H$  values (determined electrometrically), week by week, of the percolate from a column of soil, treated for 4 weeks with water, followed by a 1% salt solution for 4 weeks and then by water again for a final period. Uni-, bi-, and ter-valent salts (chlorides) are included. A close connexion between the hydrogen-ion concentration and the permeability is indicated. Similar changes in reaction were recorded on percolating powdered quartz with potassium chloride solution. C. T. G.

**Formation of Sodium Carbonate in Soils.** A. B. CUMMINS and W. P. KELLEY (*California Agr. Expt. Sta., Tech. Paper*, 1923, 3, 35 pp.).—An explanation is suggested for the observation that semi-arid soils, on treatment with sodium chloride solutions and subsequent leaching, swell and become impervious, yielding a dark, alkaline percolate. The sodium silicate complexes ("absorbates") formed by the displacement of calcium and other bases by sodium are less stable, more soluble, and more readily hydrolysed than the corresponding calcium complexes. The alkalinity results from the hydrolysis of these "absorbates" on the reduction of the salt concentration by leaching and an interaction with the carbon dioxide of the soil solution. Some of the products of hydrolysis tend to assume the colloidal state. The presence of calcium carbonate is not essential for the formation of sodium carbonate in soils. Certain soils from humid regions react similarly to, but not so markedly as, the semi-arid soils. Alkalinity was also developed by granite and pure mineral silicates after similar treatment. Sodium chloride solutions more concentrated than 0.01N were able to form hydrolysable compounds in soil, and the concentration of sodium chloride needed to be reduced to about one-half by leaching before alkalinity developed. Calcium salts in sufficient concentration prevented the formation of hydrolysable sodium "absorbates," and tended to prevent the hydrolysis of such compounds when already formed. E. M. C.

**Removal of Sodium Carbonate from Soils.** W. P. KELLEY and E. E. THOMAS (*California Agr. Expt. Sta., Tech. Paper*, 1923, 1, 23 pp.).—Active oxidation of added sulphur took place in

alkali soils containing relatively high concentrations of sodium salts and ultimately removed the soluble carbonates in all but one of the soils studied. Calcium sulphate reduced the soluble carbonates, but failed to remove the alkalinity except when it was used in conjunction with leaching. Sulphuric acid was somewhat more effective than the sulphur oxidation products and considerably more so than calcium sulphate. The amounts of these materials needed is considerably greater than the soluble carbonate content, indicating that they interact with silicates and other alkaline compounds. In view of the importance of the subsoil, treatment with calcium sulphate followed by leaching seems to be the most successful for black alkali soils. Preliminary experiments indicated that ferrous sulphate and alum might also prove useful. E. M. C.

#### **Alkali Soil Investigations. I. Colloidal Phenomena.**

J. S. JOFFE and H. C. MCLEAN (*Soil Sci.*, 1924, **17**, 395—409).—The oxidation of sulphur added to an alkali soil resulted in an increased surface tension of the aqueous extracts, and increased rates of capillary rise of water and percolation of water through the soil. E. M. C.

**Importance of Hydrogen-ion Concentration Control in Physico-chemical Studies of Heavy Soils.** R. BRADFELD (*Soil Sci.*, 1924, **17**, 411—422).—The amount of electrolyte required to flocculate a colloidal clay solution can only be defined with reference to a definite  $p_H$  value. The initial reaction of the clay is an important factor in determining its behaviour at other  $p_H$  values; with alkaline flocculants, a part is utilised in neutralising an acid clay and the concentration of the clay thus becomes important. Different acids flocculate colloidal clay solutions at about the same concentration of hydrogen ions, but the amounts of acid needed may vary widely if expressed in terms of the titratable acidity. The hydrogen-ion concentration at equilibrium plays an important part in determining the absorption and exchange of bases between clay and salts. A colloidal clay was treated with various mixtures of potassium chloride and hydroxide, such that the potassium was 0.1N. The amount of potassium absorbed increased steadily with the  $p_H$  value. The amounts of alumina, silica, and ferric oxide liberated decreased with decreasing hydrogen-ion concentration, and became negligible near the neutral point. With increasing alkalinity, silica and alumina were again made soluble. The amounts of calcium and magnesium oxides liberated fell off with decreasing acidity and remained negligible in the more alkaline solutions. The difference between the absorption and liberation of bases, expressed in equivalent amounts, closely followed the equilibrium  $p_H$  value over a wide range and became zero for the value corresponding with that of the original clay solution. E. M. C.

**Active Acidity of Soils.** E. T. WHERRY (*J. Wash. Acad. Sci.*, 1924, **14**, 207—211).—A restatement of the importance of the measurement of the hydrogen-ion concentration or "active acidity" of soil suspensions. E. M. C.

**Methods of Diagnosing [Soil] Toxicity.** P. L. GILE (*J. Amer. Soc. Agron.*, 1923, **15**, 305—312).—The author reviews the experiments on the relationship of aluminium salts to soil acidity. It is suggested that no specific toxicity of aluminium ions has been established and that the importance of the soil reaction is connected with its effect on the availability of different nutrients.

E. M. C.

**Inorganic Substances, especially Aluminium, in Relation to the Activities of Soil Micro-organisms.** WHITING (*J. Amer. Soc. Agron.*, 1923, **15**, 277).—A discussion of recent American work on the part played by aluminium in the occurrence of acidity and toxicity in soils and its influence on the biological activity of soil organisms. A summary of "concordant results" and of "results in need of verification and further investigation" is included.

C. T. G.

**Effect of certain Potassium Fertilisers on Ammonification, Nitrification, and Crop Production.** VAUDECAVEYE (*J. Amer. Soc. Agron.*, 1923, **15**, 415).—An account of pot-culture experiments on the effects of organic manure, lime, kainit, and potassium chloride and sulphate on ammonification, nitrification, and crop yield. Potassium fertilisers caused large increases in nitrification, but had little effect on ammonification. A definite relationship is shown to exist between bacterial activities and the production of soluble potassium in the soil.

C. T. G.

**Microbiological Analysis of Soil as an Index of Soil Fertility. VIII. Decomposition of Cellulose.** S. A. WAKSMAN and O. HEUKELEKIAN (*Soil Sci.*, 1924, **17**, 275—291).—There is a definite relation between the amount of cellulose decomposed in the soil by micro-organisms and the nitrogen assimilated, the available nitrogen becoming the controlling factor. Differences in the amount of cellulose decomposed in soils of different fertility are due to differences in the availability of the nitrogen and not to variations in the micro-flora, since all soils contain organisms able to attack cellulose. In acid soils the fungi are chiefly concerned, whilst in limed and neutral soils bacteria and probably actinomycetes also play an active part.

The cellulose-decomposing power of a soil determined with and without addition of sodium nitrate and with and without addition of calcium carbonate and mineral salts can be used to assist in the differentiation of soil fertility. The breaking down of cellulose (finely-divided filter-paper) may be followed by measuring the carbon dioxide evolved during a given time; or, the residual cellulose in the soil after incubation may be determined by the use of Schweitzer's reagent according to the method of Charpentier (*Diss.*, Helsingfors, 1921). Detailed procedures are suggested.

C. T. G.

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## Organic Chemistry.

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**Photolysis of Organic Iodides: The Photochemical Threshold and Energy of Linking.** A. JOB and G. EMSCHWILLER (*Compt. rend.*, 1924, **179**, 52—54).—The action of light on ethyl iodide in a closed system and in complete absence of oxygen results in the liberation of iodine and of a large quantity of gas composed principally of ethylene and ethane, together with small amounts of butane and hydrogen. The presence of butane is readily explained by the assumption of a unimolecular decomposition, and that of ethylene and ethane, which is often observed when an ethyl radical is set free, is attributed by Schlubach and Goes (A., 1922, i, 1204) to a lack of equilibrium in the ethyl radical which causes migration of one of its hydrogen atoms to a neighbouring radical. Since, however, ethylenic hydrocarbons are never found in the gas resulting from the photochemical decomposition of alcohols, aldehydes, acids, or ketones, the iodine from the ethyl iodide probably acts as acceptor towards a hydrogen atom of the ethyl radical, ethylene and hydrogen iodide being first formed and the latter then being decomposed under the influence of light. Results similar to the above are observed with methyl iodide.

If the iodine in ethyl iodide is represented as united to the carbon by means of a co-valence, the quantum of luminous energy which detaches the iodine from the molecule must bring the latter to an energy level at least equal to the critical level. If it touches and just suffices to bring to the critical level an average molecule, this quantum,  $h\nu$ , will by definition be the critical complement and measures the energy of linking of the co-valence, C—I. When a tube containing ethyl iodide is placed in the spectrum of the carbon arc, the reaction appears distinctly as soon as wave-lengths shorter than  $0.41\ \mu$  are reached and increases in intensity as the frequency increases (cf. Crymble, Stewart, and Wright, A., 1910, ii, 470). The energy quantum corresponding with this wave-length is 69,300 cal. per g.-mol., which is thus approximately the energy of the carbon-iodine co-valence in ethyl iodide. T. H. P.

**Oxonium Compounds. Researches on the Relative Strength of the Higher Valencies of Oxygen in different Classes of Organic Compounds.** M. W. TSCHELINZEFF (*Bull. Soc. chim.*, 1924, [iv], **35**, 741—753).—The relative strength of the higher valencies of oxygen has been determined by measurements of the heats of formation of a large number of additive compounds of magnesium ethoxy iodide,  $\text{EtO}\cdot\text{MgI}$ , with different classes of organic compounds. Among oxonium compounds of the hydrone type,  $\text{R}_2\text{O}^{\leftarrow}$ , such as those obtained from alcohols, phenols, and ethers, the strength of the additional oxygen valencies depends closely on the radicals attached to the oxygen, but with the

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carbonyl oxonium compounds,  $R_2CO^{\leftarrow}$ , formed by ketones and aldehydes this influence is less marked, and the thermal effects of the addition of magnesium ethoxy iodide are more constant, maintaining their value even with aromatic radicals. The number of molecules of the organic compound combining with 1 mol. of magnesium ethoxy iodide varies from one to three, the thermal effects of the addition of the second and third molecules being smaller than that produced by the first. With the aliphatic radicals, the largest thermal effects are produced by the first members of the series. Aromatic radicals usually produced a marked lowering of the heats of formation. Among the alcohols, the strongest thermal effects were produced with the primary alcohols and the smallest by the tertiary alcohols, the effects produced by phenols being of the same magnitude as in the case of tertiary alcohols. With oxonium compounds of a mixed hydrone-carbonyl type, such as those formed by esters, the thermal effects are produced by the carbonyl oxygen, and correspond with those observed with the compounds produced from ketones. No thermal effect was observed with furan, pyrrole, or thiophen compounds, the higher valencies in these compounds falling to zero. The formation of oxonium compounds from dimethylpyrone is due to the carbonyl oxygen, as is shown by a comparison of the thermal effects produced with magnesium ethoxy iodide and dimethylpyrone, furan, and quinone. Oxygen in a ring compound shows very little higher valency. In some cases, the molecules attached to magnesium ethoxy iodide can be displaced either partly or completely by other molecules. Thus ethyl alcohol replaces phenol:  $ROMgI, 3PhOH + 3EtOH = ROMgI, 3EtOH + 3PhOH$ . The course of the reaction depends partly on the nature of the original oxonium complex and partly on the radicals bound to it. The displacements always follow the relative value of the heats of formation of the respective complexes.

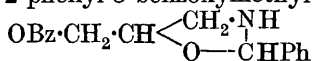
R. B.

**Physical-Chemical Properties of Mixtures of Ethyl and *n*-Propyl Alcohols.** G. S. PARKS and J. R. SCHWENCK (*J. Physical Chem.*, 1924, **28**, 720—729).—Mixtures of ethyl and *n*-propyl alcohols form an almost "ideal" system. The heat evolution on mixing is very small (<5 cal. per mol. of mixture); the densities and refractive indices agree well with those calculated on the assumption of ideal solution. The vapour pressures of the mixtures are slightly higher than those calculated from Raoult's law, and the viscosities deviate about 2% from the values found by Kendall's equation (A., 1920, ii, 670). The entropy change due to mixing is almost identical with that calculated on the assumption of ideal solution.

S. K. T.

**Synthesis and Structure of Glycerides.** M. BERGMANN (*Z. physiol. Chem.*, 1924, **137**, 27—46; cf. A., 1921, i, 444; Fischer, Bergmann, and Bärwind, A., 1920, i, 805).—A method is described for the synthesis and determination of structure of  $\alpha$ -monoglycerides, and incidentally of  $\alpha\beta$ -diglycerides. The initial material,  $\gamma$ -chloro- $\beta$ -hydroxypropylamine, may be condensed with benzaldehyde,

yielding 2-phenyl-5-chloromethylloxazolidine. The imino group of the latter is then acylated (for example, with benzoyl chloride) and on removal of the benzaldehyde residue by acid hydrolysis, there is obtained a compound of the type of  $\gamma$ -chloro- $\beta$ -hydroxy- $\alpha$ -benzoylaminopropane. On boiling the latter with water, a replacement of the chlorine by hydroxyl occurs, simultaneously with an intramolecular change, giving  $\gamma$ -aminopropylene glycol  $\alpha$ -benzoate hydrochloride, which is converted into glycerol  $\alpha$ -benzoate. The structure of the latter is proved by *p*-nitrobenzoylation of its free hydroxyl groups, and its identity with that prepared by Fischer, Bergmann, and Bärwind (*loc. cit.*) from isopropylidene glycerol. The intermediate compounds of the type of  $\gamma$ -aminopropylene glycol  $\alpha$ -benzoate may be used for a new synthesis of  $\alpha\beta$ -diglycerides. For this purpose, the initial substance is condensed with benzaldehyde, resulting, in this particular instance, in the formation of 2-phenyl-5-benzoxymethylloxazolidine,



This, on benzoylation or *p*-nitrobenzoylation and subsequent hydrolysis as before to remove the benzaldehyde residue, gives a substance of the type of  $\gamma$ -benzoylaminopropylene glycol  $\alpha$ -benzoate. This yields, on treatment with phosphorus pentachloride and subsequently with water, by intramolecular change,  $\gamma$ -aminopropylene glycol  $\alpha\beta$ -dibenzoate, whence glycerol  $\alpha\beta$ -dibenzoate is obtained as usual.

*Glycerol  $\alpha\beta$ -dibenzoate*, previously known only as an oil, has been obtained as a colourless solid, m. p. 57—58°. *2-Phenyl-5-benzoxymethylloxazolidine* (preparation above), m. p. 76°, yields a *p*-nitrobenzoyl derivative, m. p. 95—96°. The resolution of  $\gamma$ -aminopropylene glycol  $\alpha\beta$ -dibenzoate, previously effected through the quinate, has been carried out anew, by condensation of the base with helicin. There crystallises out a yellow *Schiff's base*, m. p. 175—176°,  $[\alpha]_D -46^\circ$  (in glacial acetic acid). From this compound, the *l*-amine hydrochloride is obtained in an almost pure form. In anticipation of future syntheses of glycerides, a number of other substances were prepared. *2-Phenyl-5-chloromethylloxazoline*, m. p. 25°, b. p. 120—123°/1 mm., is obtained by the action of sodium acetate on its *hydrochloride*, which results from the action of thionyl chloride on  $\gamma$ -chloro- $\beta$ -hydroxy- $\alpha$ -benzoylaminopropane.

[With F. WEINMANN.]— $\gamma$ -Iodo- $\beta$ -hydroxy- $\alpha$ -benzoylaminopropane, m. p. 138—139°, is obtained from the corresponding chloro compound by the action of sodium iodide; it gives, on boiling with water,  $\gamma$ -aminopropylene glycol  $\alpha$ -benzoate hydriodide, and on treatment with stearyl chloride,  $\gamma$ -iodo- $\beta$ -stearoxy- $\alpha$ -benzoylaminopropane. The latter on successive treatment with phosphorus pentachloride, alcohol, and hydrochloric acid, gives  $\gamma$ -iodo- $\beta$ -stearoxypropylamine hydrochloride, needles, m. p. 90—93°.

[With P. ECKWALL.]— $\gamma$ -Iodo- $\beta$ -lauroxy- $\alpha$ -benzoylaminopropane, m. p. 50—51°, gives, on boiling with silver nitrite, a  $\gamma$ -benzoylaminopropylene glycol monolaurate, m. p. 79—80°.

[With E. BRAND and F. DREYER.]— $\gamma$ -*Laurylaminopropylene-glycol*  $\alpha$ -*laurate*, m. p. 82—83°, is obtained by the action of lauryl chloride on 2-phenyl-5-hydroxymethyloxazolidine, and the usual hydrolysis; with palmityl chloride it yields  $\gamma$ -*laurylaminopropylene-glycol*  $\alpha$ -*laurate*  $\beta$ -*palmitate*, m. p. 55—56°.  $\gamma$ -*Laurylaminopropylene-glycol*  $\alpha\beta$ -*dilaurate*, m. p. 47—49°, is prepared from  $\gamma$ -aminopropylene-glycol and lauryl chloride. It yields, on treatment with phosphorus pentachloride and subsequently alcohol and oxalic acid,  $\gamma$ -*aminopropylene-glycol*  $\alpha\beta$ -*dilaurate* *hydrogen oxalate*, m. p. 134° after softening at 104°. The corresponding *hydrochloride* is described.  $\gamma$ -*Aminopropylene-glycol*  $\alpha$ -*laurate*  $\beta$ -*palmitate* *hydrogen oxalate*, no definite m. p., may be obtained from  $\gamma$ -*laurylaminopropylene-glycol*  $\alpha$ -*laurate*  $\beta$ -*palmitate* in the usual manner.  $\gamma$ -*Palmitylaminopropylene-glycol*  $\alpha$ -*palmitate*, m. p. 90—91°, is prepared from 2-phenyl-5-hydroxymethyloxazolidine in the usual way.  $\gamma$ -*Palmitylaminopropylene-glycol*  $\alpha$ -*palmitate*  $\beta$ -*laurate*, needles, m. p. 56—59°, is converted into  $\gamma$ -*aminopropylene-glycol*  $\alpha$ -*palmitate*  $\beta$ -*laurate* *hydrogen oxalate*.  
B. F.

#### $\alpha$ -Monoglycerides of Fatty Acids of High Molecular Weight.

M. BERGMANN and S. SABETAY (*Z. physiol. Chem.*, 1924, **137**, 47—61; cf. preceding abstract).—Attempts are described to establish further the constitution of certain glycerides containing an asymmetric carbon atom by isolating their optically active forms. It is found that the optical activity is somehow masked by the presence of hydroxyl groups and becomes evident only when these are more or less replaced, for instance, by solution in thionyl chloride. A similar masking effect is observed with complex fatty acyl groups.

$\gamma$ -*Chloro- $\beta$ -hydroxy- $\alpha$ -laurylaminopropane*, m. p. 54—55°, is prepared from 2-phenyl-5-chloromethyloxazolidine by the usual method (see preceding abstract). On treatment with thionyl chloride, it yields the *hydrochloride* of 2-undecyl-5-chloromethyl-oxazoline,  $\text{CH}(\text{CH}_2\text{Cl})\cdot\text{CH}_2\cdot\text{N}\begin{array}{c} \text{O} \\ \text{C}_{11}\text{H}_{23} \end{array}$ , m. p. 96—98°, which on hydro-

lysis gives the free oxazoline. The oxazoline hydrochloride is easily soluble in mineral acids, which, especially on warming, give rise to an intramolecular change, yielding  $\gamma$ -*chloro- $\beta$ -lauroxypropylamine hydrochloride*, m. p. 86—87°.  $\gamma$ -*Iodo- $\beta$ -hydroxy- $\alpha$ -laurylaminopropane*, m. p. 55—56°, is prepared by boiling the corresponding chloro compound with sodium iodide.  $\gamma$ -*Aminopropylene-glycol*  $\alpha$ -*laurate* *hydrochloride* is prepared by heating  $\gamma$ -chloro- $\beta$ -hydroxy-*N*-laurylpropylamine with excess of water; if the reaction is carried out in the presence of 1 mol. of potassium hydroxide, to neutralise the acid formed, a compound,  $\text{C}_{15}\text{H}_{29}\text{O}_2\text{N}$ , of m. p. 75—76° is isolated.  $\gamma$ -Aminopropylene-glycol  $\alpha$ -*laurate* condenses with benzaldehyde to give 2-phenyl-5-lauroxymethyloxazolidine, m. p. 62°. This may be stearylized, and on fission in the usual way gives  $\gamma$ -*stearylaminopropylene-glycol*  $\alpha$ -*laurate*, m. p. 98°.  $\gamma$ -Aminopropylene-glycol  $\alpha$ -*laurate*, on treatment with alkali, yields by intramolecular rearrangement  $\gamma$ -*laurylaminopropylene-glycol*, m. p.

99—100°. The resolution of inactive  $\gamma$ -aminopropylene glycol  $\alpha$ -laurate into its active components is effected by fractionally crystallising its acid saccharate, whereby *d*- $\gamma$ -aminopropylene glycol  $\alpha$ -laurate hydrochloride,  $[\alpha]_D^{25} +12.4^\circ$  in absolute alcohol, is obtained. By the usual means, an attempt was made to convert the *d*-amine into an optically active  $\alpha$ -monolaurin, the product had m. p. 62—63°, and showed no optical rotatory power in indifferent media, but was lævorotatory in thionyl chloride. *dl*- $\alpha$ -Monolaurin under similar conditions gave an inactive product.

$\gamma$ -Chloro- $\beta$ -hydroxy- $\alpha$ -stearylaminopropane, rhombic plates, m. p. 77—77.5°, is prepared like its lauryl analogue, and on boiling with water gives  $\gamma$ -aminopropylene glycol  $\alpha$ -stearate hydrochloride, which shows remarkable colloidal properties on treatment with water. The benzaldehyde condensation product of the above amine is 2-phenyl-5-stearylloxymethyloxazolidine, m. p. 80°, whilst the hydrochloride of the amine, on treatment with 1 mol. of very dilute alkali, gives, by internal rearrangement,  $\gamma$ -stearylaminopropylene glycol, m. p. 105°. The fission of  $\gamma$ -aminopropylene glycol  $\alpha$ -stearate into its optically active components is carried out as in the case of its lauryl analogue, and there is finally obtained a *d*- $\gamma$ -aminopropylene glycol  $\alpha$ -stearate hydrochloride,  $[\alpha]_D^{25} +10.5^\circ$ . This was converted into an  $\alpha$ -monostearin, which showed no optical activity in the usual solvents, but was lævorotatory in thionyl chloride.

B. F.

**Trimyristin, a Glyceride present in Milk.** M. PIETRE and C. ROÉLAND (*Compt. rend.*, 1924, 178, 2283—2285).—The cream from 500 c.c. of milk is stirred with 200 c.c. of a mixture of alcohol (1000 parts by vol.) and ether (1100 parts by vol.), and a further 50—60 c.c. of ether are added subsequently. The ether-alcohol extract is filtered and allowed to evaporate slowly at 8—10°. Trimyristin crystallises from the solution in long plates, m. p. 52—54°. It gives myristic acid, m. p. 50—52°, when hydrolysed with alcoholic potassium hydroxide. The calculated content of the glyceride is 2—2.4 g. per litre of milk. It is less easy to obtain a pure product from butter.

W. T. K. B.

**Dependence of Rotatory Power on Chemical Constitution.**  
**XXII. Some Compounds containing the Secondary Octyl Radical Linked to Oxygen.** H. HUNTER (*J. Chem. Soc.*, 1924, 125, 1389—1395).—The complex rotatory dispersion associated with the carboxyl group or its equivalents is considered to be due to the presence in one molecule of both a singly- and a doubly-linked oxygen atom, arranged unsymmetrically. Exceptions in the case of the  $\beta$ -octyl compounds are the carbonates and sulphite. It is suggested that in these cases the unsaturated oxygen atoms are distributed symmetrically about the unsaturated one, and that this is sufficient to suppress any obvious complexity of rotatory dispersion. The following compounds are described: *Di-d*- $\beta$ -octylformal,  $\text{CH}_2(\text{OC}_8\text{H}_{17})_2$ , mobile liquid with fragrant odour, b. p. 175—177°/16 mm.,  $d_4^{25}$  0.8523,  $n_D^{20}$  1.4314; *d*- $\beta$ -octyl chloroformate,  $\text{C}_8\text{H}_{17}\cdot\text{O}\cdot\text{COCl}$ , made by the action of carbonyl chloride

on *d*- $\beta$ -octanol in pyridine, b. p.  $92^{\circ}/13$  mm.,  $d_4^{19}$  0.9748,  $n_D^{20}$  1.4282; *ethyl d*- $\beta$ -octyl carbonate,  $\text{EtO}\cdot\text{CO}\cdot\text{OC}_8\text{H}_{17}$ , made by the action of ethyl alcohol on the above chloroformate, a fragrant, limpid liquid, b. p.  $110^{\circ}/14$  mm.,  $d_4^{18}$  0.9136,  $n_D^{20}$  1.4175; *di*-*d*- $\beta$ -octyl carbonate, b. p.  $168^{\circ}/13$  mm.,  $d_4^{19}$  0.8828,  $n_D^{20}$  1.4305; *tri*-*l*- $\beta$ -octyl orthoformate,  $(\text{C}_8\text{H}_{17}\cdot\text{O})_3\text{CH}$ , a nearly odourless liquid, b. p.  $202$ — $203^{\circ}/\text{ca. } 1$  mm.,  $d_4^{15}$  0.8592,  $n_D^{15}$  1.4376, made by heating ethyl orthoformate with *l*- $\beta$ -octanol for 30 hours at  $140^{\circ}\pm 5^{\circ}$ ; *di*-*d*- $\beta$ -octyl sulphite, b. p.  $133$ — $134^{\circ}/1$  mm.,  $d_4^{17}$  0.9264,  $n_D^{20}$  1.4429, made by the slow addition of thionyl chloride to *d*- $\beta$ -octanol in light petroleum, at  $-10^{\circ}$  to  $-5^{\circ}$ , with vigorous shaking. The optical rotations of the compounds are given fully in the original.

A. C.

**Dependence of Rotatory Power on Chemical Constitution. XXIII. The Normal Aliphatic Ethers of *d*- $\gamma$ -Nonanol.** J. KENYON and J. W. BARNES (*J. Chem. Soc.*, 1924, 125, 1395—1400).—With the possible exception of the methyl member, the rotatory dispersions of the ethers of this series cannot be represented by a one-term Drude equation and cases of optical heterogeneity, unaccompanied by chemical heterogeneity, appear to be presented. It is pointed out that the values for  $[\alpha]_{5461}^{20}$  for this series of ethers plotted against the number of carbon atoms in the growing alkyl group attached to the ethereal oxygen atom give a smooth curve with, however, a characteristic depression at the *n*-propyl member and a similar, but much smaller, depression at the *n*-octyl member, where the group contains five more carbon atoms. A number of active ethers were prepared by treating the potassium compound of *d*- $\gamma$ -nonanol in dry ether with the requisite alkyl halide. After freeing the product from uncombined *d*- $\gamma$ -nonanol by heating with excess of phthalic anhydride, the ether was redistilled until its rotatory power and refractive index were constant. The following individuals are described: *methyl ether*, b. p.  $74^{\circ}/15$  mm.,  $n_D^{20}$  1.4154,  $d_4^{23}$  0.7926; *ethyl ether*, b. p.  $88^{\circ}/21$  mm.,  $n_D^{20}$  1.4164,  $d_4^{22}$  0.7901; *n*-*propyl ether*, b. p.  $103^{\circ}/23$  mm.,  $n_D^{20}$  1.4193,  $d_4^{21}$  0.7961; *n*-*butyl ether*, b. p.  $114^{\circ}/19$  mm.,  $n_D^{20}$  1.4226,  $d_4^{21}$  0.7978; *n*-*amyl ether*, b. p.  $123^{\circ}/15$  mm.,  $n_D^{20}$  1.4257,  $d_4^{21}$  0.8017; *n*-*hexyl ether*, b. p.  $138^{\circ}/17$  mm.,  $n_D^{20}$  1.4283,  $d_4^{22}$  0.8048; *n*-*heptyl ether*, b. p.  $155^{\circ}/18$  mm.,  $n_D^{20}$  1.4310,  $d_4^{17}$  0.8101; *n*-*octyl ether*, b. p.  $166^{\circ}/17$  mm.,  $n_D^{20}$  1.4335,  $d_4^{24}$  0.8085; *n*-*nonyl ether*, b. p.  $176^{\circ}/17$  mm.,  $n_D^{20}$  1.4356,  $d_4^{24}$  0.8082. For all the ethers, values for the densities over a range of temperatures are given, also a range of rotation values for different wave-lengths and temperatures. A table of the rotatory powers of the ethers in (a) carbon disulphide and (b) ethyl alcohol at room temperature, is given.

A. C.

**Conductivity of some Compounds of Platinum with Thioethers. VIII.** L. TSCHUGAEV and W. MALZSCHEWSKY [compiled by E. FRITZMANN] (*Z. anorg. Chem.*, 1924, 135, 385—391).—The electrolytic conductivities of the  $\alpha$  and  $\beta$  forms of the compound  $\text{PtCl}_2\cdot 2\text{Et}_2\text{S}$  have been determined in solution in dry methyl and

ethyl alcohols and in aqueous ethyl alcohol, the experiments being carried out at a dilution of 1 g.-mol. in 300 litres. In all cases, the molecular conductivity of the  $\beta$  form was the greater. In dry alcohols, the conductivities of both forms are slight, indicating that the halogen is present in a co-ordination complex. The molecular conductivity of the  $\alpha$  variety increases greatly if the solutions are kept for some time, whilst in the case of the  $\beta$  variety the conductivity decreases very slightly on keeping. In aqueous alcoholic solutions, the conductivities are higher owing to slight hydrolysis. The experiments in general confirm the results of Klason (A., 1895, i, 488). When increasing quantities of thioether are added to a solution of either the  $\alpha$  or  $\beta$  compound in dry methyl alcohol, the molecular conductivity increases rapidly to a limiting value of about 74. This is regarded as due to a change from a non-conducting complex compound,  $[\text{Pt}, 2\text{Et}_2\text{S}, \text{Cl}_2]$ , to a conducting form,  $[\text{Pt}, 4\text{Et}_2\text{S}]\text{Cl}_2$ . The sulphate compound,  $\text{PtSO}_4, 2\text{Et}_2\text{S}$ , resembles the  $\alpha$  chloride when in solution in dry alcohols, but is readily soluble in water with a great increase in molecular conductivity.

W. H.-R.

**Conductivity of Platinum Monosulphide Compounds in Solution in Methyl Alcohol. IX.** L. TSCHUGAEV and N. WLADIMIROFF [compiled by E. FRITZMANN] (*Z. anorg. Chem.*, 1924, **135**, 392—400).—The electrolytic conductivities of the  $\alpha$  and  $\beta$  forms of the compound  $\text{PtCl}_2, 2\text{Et}_2\text{S}$ , and of the corresponding propyl compound, have been determined in solution in dry methyl alcohol at a dilution of 1 g.-mol. in 500 litres. The results confirm those obtained previously for the ethyl compound at a dilution of 300 litres (cf. preceding abstract). The experiments in solution in methyl alcohol furnish a proof of the co-ordination theory in a case where hydrolysis cannot occur. The sulphide complexes are analogous to the corresponding ammonia complexes; a new series of complex compounds exists of the general form  $[\text{Pt}4\text{S}]\text{X}_2$ , where S is a monosulphide compound and X a halogen, nitrite, or nitrate ion. These are unstable in the case of monosulphide compounds, but are stable in the case of the corresponding disulphide compounds prepared from dithioethers; these compounds are strictly analogous to the diammine compounds. W. H.-R.

**Electrical Conductivity of Complex Compounds of Platinum and Palladium with Organic Monoselenides. III.** E. FRITZMANN (*Z. anorg. Chem.*, 1924, **133**, 133—152).—The molecular electrical conductivity of various platinum and palladium halide complexes with monoalkyl selenides in methyl alcohol solution at 25° is measured, and the effects of different halogens, concentration, the presence of an excess of alkyl selenide, and time on the conductivity are fully worked out and explained. Compounds of the types  $\text{PtX}_2, 2\text{R}_2\text{S}$  and  $\text{PdX}_2, 2\text{R}_2\text{S}$  show very slight electrical conductivity, that of the chlorine compound being the greatest and of the iodine complex the smallest. With the compound  $\text{PtCl}_2, 2\text{Et}_2\text{S}$ , increasing dilution causes a very slight increase in  $\mu$  for the  $\alpha$ -com-

pound, but with the  $\beta$  form,  $\mu$  rapidly increases. The addition of increasing quantities of alkyl selenide to the solution causes, in the case of the  $\beta$  compound, a rapid increase in  $\mu$  to a constant value, showing that ionisation has occurred by the formation of the higher type of compound  $\text{PtCl}_2\cdot 4\text{Et}_2\text{Se}$ , due to the passage of two chlorine atoms from the inner co-ordination sphere to the outer. Since  $\mu$  has a much smaller value than that for the ternary electrolyte thus formed (236), the equilibrium  $\text{PtCl}_2\cdot 4\text{Et}_2\text{Se} \rightleftharpoons \text{PtCl}_2\cdot 2\text{R}_2\text{Se} + \text{R}_2\text{Se}$  must exist in solution. With the  $\alpha$  compound, the rate of increase in  $\mu$  is much smaller, and is incomplete at the proportion of 8 mols. of added alkyl selenide, owing to the greater stability and consequent smaller lability of the *cis* modification ( $\alpha$ ) compared with the *trans* ( $\beta$ ). In the presence of alkyl selenide, the value of  $\mu$  for the  $\alpha$  compound increases rapidly during the first half hour to a definite constant value (for each concentration), whilst for the  $\beta$  compound,  $\mu$  decreases at the same rate to the same constant value, showing that equilibrium between the two isomerides exists in solution. Since similar constant values are not attained in the absence of alkyl selenide, equilibrium must be established by solvation with the excess of alkyl selenide. The bromine and iodine compounds of platinum and all the palladium complexes show a very slight conductivity which is practically unaffected by varying conditions, since these compounds have the *cis* configuration and hence show no characteristic phenomena of dissociation and no tendency to isomerism. The results are generally analogous to those obtained for the corresponding sulphur compounds (preceding abstracts), but with important differences in detail, due to the greater mobility of the selenium atom compared with the sulphur atom.

J. W. B.

### Complex Compounds of Palladium with Organic Selenides.

II. E. FRITZMANN (*Z. anorg. Chem.*, 1924, **133**, 119–132; cf. A., 1912, i, 71).—The greater mobility of the selenium atom compared with the sulphur atom prevents the existence of isomerism and causes the complexes to be less stable than the corresponding sulphur compounds. Compounds of the types  $\text{PdX}_2\cdot 2\text{R}_2\text{Se}$  and  $\text{PdX}_2\cdot \text{R}\cdot\text{Se}\cdot[\text{CH}_2]_n\cdot\text{Se}\cdot\text{R}$  are produced by methods similar to those employed in the preparation of the corresponding bivalent platinum compounds (*loc. cit.*), which, in reactions, they resemble, but are monomeric and show no isomerism. They are less stable than the corresponding palladium-sulphur and platinum-selenium complexes, and the stability of the compounds formed with palladium chloride, bromide, and iodide decreases in this order.

*Methyl selenium palladium chloride*,  $\text{PdCl}_2\cdot 2\text{Me}_2\text{Se}$ , orange-red crystals, has m. p. 127–128°. Ethyl selenide forms the compound  $\text{PdCl}_2\cdot 2\text{Et}_2\text{Se}$ , orange-red crystals, m. p. 45°; *n*-propyl selenide the compound  $\text{PdCl}_2\cdot 2\text{Pr}_2\text{Se}$ , m. p. 62–62.5°; *isobutyl* selenide the compound  $\text{PdCl}_2\cdot 2\text{Bu}_2\text{Se}$ , orange-red crystals, m. p. 79°; *isoamyl* selenide the compound  $\text{PdCl}_2\cdot 2(\text{C}_5\text{H}_{11})_2\text{Se}$ , m. p. 76°, and phenyl selenide yields the compound  $\text{PdCl}_2\cdot 2\text{Ph}_2\text{Se}$ , orange-red needle clusters, m. p. 181–182°. Diethyltrimethylene diselenide



yields the compound  $\text{PdCl}_2 \cdot \text{EtSe}[\text{CH}_2]_3\text{SeEt}$ , softening at  $181^\circ$  (decomp.). The corresponding bromine derivatives, obtained by an analogous method or by the action of excess of potassium bromide on the chlorine derivatives in alcoholic solution, are similar to the chlorine compounds, but are slightly darker in colour and form good crystals; compound  $\text{PdBr}_2 \cdot 2\text{Me}_2\text{Se}$ , m. p.  $129^\circ$ ; compound  $\text{PdBr}_2 \cdot 2\text{Et}_2\text{Se}$ , m. p.  $167^\circ$ ; compound  $\text{PdBr}_2 \cdot 2\text{Pr}_2\text{Se}$ , m. p.  $165^\circ$ ; compound  $\text{PdBr}_2 \cdot 2\text{Bu}_2\text{Se}$ , m. p.  $17^\circ$ ; compound  $\text{PdBr}_2 \cdot 2(\text{C}_5\text{H}_{11})_2\text{Se}$ , m. p.  $04^\circ$  (?); compound  $\text{PdBr}_2 \cdot 2\text{Ph}_2\text{Se}$ , m. p.  $197^\circ$ ; compound  $\text{PdBr}_2 \cdot \text{EtSe}[\text{CH}_2]_3\text{SeEt}$ , m. p.  $162^\circ$ . The corresponding iodine compounds are nearly black, and are very slightly soluble in organic solvents; compound  $\text{PdI}_2 \cdot 2\text{Me}_2\text{Se}$ , m. p.  $123.5^\circ$ ; compound  $\text{PdI}_2 \cdot 2\text{Et}_2\text{Se}$ , m. p.  $60^\circ$ ; compound  $\text{PdI}_2 \cdot 2\text{Pr}_2\text{Se}$ , m. p.  $74^\circ$ ; compound  $\text{PdI}_2 \cdot 2\text{Bu}_2\text{Se}$ , m. p.  $147^\circ$ ; compound  $\text{PdI}_2 \cdot 2(\text{C}_5\text{H}_{11})_2\text{Se}$ , m. p.  $121^\circ$ .

Gold also forms complexes with alkyl selenides which cannot be obtained except in solution, whereas the corresponding sulphur compound is stable. The corresponding bismuth complexes are prepared from potassium bismuth iodide,  $\text{BiI}_3 \cdot 3\text{KI}$ , and are raspberry-red in colour, are much more stable than the gold compounds, and can be obtained in the solid state.

Benzyl telluride forms the compound  $\text{PtCl}_2 \cdot 2(\text{C}_7\text{H}_7)_2\text{Te}$ , an orange powder which decomposes in solution with the separation of tellurium, platinum, and dibenzyl, but by rapid crystallisation from chloroform is obtained as a microcrystalline shimmering powder of greenish-gold colour which darkens and softens at  $115\text{--}120^\circ$ . J. W. B.

**Alcoholysis. V. Alcoholysis of Esters of  $\alpha\beta$ -Unsaturated Acids and of the Corresponding Saturated Esters.** B. DASANNACHARYA (*J. Indian Inst. Sci.*, 1924, 7, 1—28).—The rates of alcoholysis of menthyl butyrate, crotonate, hydrocinnamate, and cinnamate with methyl alcohol, and of methyl butyrate, methyl crotonate, and ethyl butyrate with menthol, respectively, were measured at  $30^\circ$ , using excess of the alcohol in each case, and dry hydrogen chloride ( $0.2238\text{--}1.050N$ ) as catalyst, by observing the rate of change of the optical rotation of the reaction mixture. An  $\alpha\beta$ -olefinic linking in the acyl group of an ester exerts a strong retarding influence on the alcoholysis of the ester, the mean ratio, in the cases examined, of the alcoholysis constant of the saturated to that of the unsaturated compound being 14.2. The retardation effect is less marked with menthol and menthyl esters than when methyl or ethyl alcohols and esters are alone involved. Replacement of a  $\beta$ -methyl group by phenyl increases the retardation, the influence of the  $\beta$ -group being more pronounced in the unsaturated compounds. The ratio of the constants for the direct and reverse reaction is independent of the nature of the acids (cf. A., 1921, i, 667). F. G. W.

**Movement in an Electrical Field. Migration, Electrophoresis, and Electro-osmose of Sodium Oleate.** M. E. LAING (*J. Physical Chem.*, 1924, 28, 673—705).—The following  
*kk\**

general formula (in which the conductivities of the free outer ions of the "double layer" are taken into account):  $n \times (\text{total conductivity of all constituents of a system}) = (\text{effective conductivity of any one constituent})$ , where  $n$  is the transport number of the selected constituent, is shown to hold for all the three cases in which transport of matter accompanies conduction of electricity. Velocity of cataphoresis is not identical with mobility except when there is one electric charge per chemical equivalent. From this point of view, the only distinction between colloids and crystalloids lies in the number of chemical equivalents per unit charge.

Transport number experiments show that the movement of the various constituents of the soap (sodium oleate) system relative to the solvent is the same for the sol and gel, and in the case of gels and curds is independent of whether the solvent moves through the particles of the latter or *vice versa*. In concentrated solutions, rather more sodium is moved towards the anode than the cathode; in a curd, this is greatly accentuated. This change with concentration is attributed to hydration, the extent of which, assuming the ionic micelle to contain very little soap, is calculated to be 10 mols. of water per equivalent of total soap. This assumption is justified, since it enables the migration data for oleate and laurate of potassium (cf. T., 1923, 123, 2417) to be quantitatively predicted; these salts are hydrated to the extent of 13 and 17 (max.) mols. of water, respectively. The migration data for curds are predicted from a knowledge of the concentration of the mother-liquor surrounding the curd fibres.

Neither hydration nor frictional drag of the individual ion suffices to explain electro-osmosis.

The experimental evidence shows that the colloid particles in a sol are identical in number and nature with those in a gel.

S. K. T.

**Tautomerism of the Mesoxalic Acid and Pyruvic Acid Phenylhydrazones. Evidence for the Hydrazone Structure of the Tautomerides.** R. H. STEVENS and F. W. WARD (*J. Chem. Soc.*, 1924, 125, 1324—1329; cf. Pechmann, A., 1893, i, 82; Dimroth, A., 1909, i, 66).—Comparison of the absorption curves of the phenyl- and phenylmethyl-hydrazones of mesoxalamide and pyruvic acid, and the phenylhydrazone of mesoxalic acid with those of azobenzene, benzeneazofornamide, benzeneazoethane, and the phenyl- and phenylmethyl-hydrazones of benzaldehyde and acetaldehyde indicates that the phenylhydrazones of mesoxalic and pyruvic acids are in truth phenylhydrazones. The following compounds are described incidentally: *Acetaldehydephenylmethylhydrazone*, a colourless oil, b. p.  $136^{\circ}/25$  mm. The *additive product*,  $\text{NHPh}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CH}(\text{CO}_2\text{Et})_2\cdot\text{HCl}$ , m. p.  $130^{\circ}$ , formed by the interaction of ethylidenemalonic ester and phenylhydrazine. *s-Trichlorophenylhydrazones* of ethyl mesoxalate and of mesoxalic acid, m. p.  $75^{\circ}$  and  $170^{\circ}$ , respectively. *Bromomethylmalonamide*, white solid, m. p.  $172^{\circ}$ . *Bromoethylmalonamide*, m. p.  $161.5^{\circ}$ .

A. C.

**Keto-enol Equilibrium of Ethyl Acetoacetate. Accelerators and Stabilisers.** G. RUMEAU (*Bull. Soc. chim.*, 1924, [iv], 35, 762—771).—The velocity with which a specimen of ethyl acetoacetate rich in the enolic form (up to 85%) reverts to the equilibrium proportion (7% enol) at 20° is greatly influenced by the presence of other substances. Alkalis such as potassium hydroxide, sodium ethoxide, and ammonia, produce the largest increase in the velocity with which equilibrium is attained, but traces of bromine, either alone or in solution, and mineral acids are also powerful accelerators. Organic acids, such as acetic and chloroacetic acids, ferric chloride, carbon dioxide, borax, and some phenols (resorcinol, *m*-cresol), produce a smaller accelerating effect. Iodine, neutral salts, and many organic substances, including benzoic and phthalic acids, have no influence on the rapidity with which equilibrium is attained, whilst other substances, such as (in decreasing order of importance) ethyl oxalacetate, methyl *p*-hydroxybenzenesulphonate and *p*-methoxybenzenesulphonate, *p*-benzoquinone, oxalic acid, pyrocatechol, methyl salicylate, and *isophthalic* acid decrease the velocity and act as stabilisers. With oxalacetic ester, a sample of ethyl acetoacetate kept for 4 days at 25° without special precautions was found to contain 60% of the enolic form. Solvents generally exert little influence, but benzene and carbon disulphide are weak stabilisers. Iodine bromide is a much weaker accelerator than bromine, but attempts to substitute this reagent for bromine in K. Meyer's method of determining the enolic form gave unsatisfactory results. With ethyl oxalacetate containing more than the equilibrium proportion of the keto-form, traces of bromine, potassium hydroxide, and hydrochloric acid act as accelerators, and equilibrium is at once established. R. B.

**Photochemical Decomposition of Oxalic Acid in the Presence of Uranium Salts.** W. C. HOLMES (*Amer. Dyestuff Rep.*, 1924, 13, 188, 197—198; cf. Freer and Gibbs, *Eighth Int. Cong. Appl. Chem.*, 1912, 20, 153; A., 1913, ii, 88).—The photochemical decomposition of oxalic acid in the presence of uranium salts is quantitative, and might be employed in determining the light-fastness of dyes. CHEMICAL ABSTRACTS.

**Action between Bromine and Malonic Acid in Aqueous Solution.** R. W. WEST (*J. Chem. Soc.*, 1924, 125, 1277—1282).—Colorimetric investigation of the action of bromine on malonic acid suggests that the change consists in (i) the unimolecular formation of bromomalonic acid and (ii) the bimolecular production of dibromomalonic acid. The unimolecular nature of the first stage indicates that the measured velocity is the slow transformation of the keto into the enolic form of the acid, and that the subsequent bromination is very rapid. The mechanism of the second stage cannot be deduced with certainty. A. C.

**Rotatory Dispersion of Tartaric Acid.** W. T. ASTBURY (*Nature*, 1924, 114, 122).—The results of Longchambon (this vol., ii, 373) support the conclusion (A., 1923, i, 178) that the lævoro-rotatory component in solution is substantially the same system

as that which produces the strong lævorotation in the crystalline form. It follows (cf. Lowry and Austin, following abstract) that in infinitely dilute solutions the rotatory dispersion will still be anomalous, and that the dispersion in the crystal is also probably not truly normal.

A. A. E.

**Anomalous Rotatory Dispersion of Tartaric Acid.** T. M. LOWRY and P. C. AUSTIN (*Compt. rend.*, 1924, **178**, 1902—1904).—The authors accept the theory revived by Longchambon (this vol., ii, 373) that the anomalous rotatory dispersion of tartaric acid is due to the presence of two forms in equilibrium, one lævo- and the other dextro-rotatory. Whilst the lævorotatory constituent can be obtained in crystalline form, the dextrorotatory acid can only be isolated as a derivative, and not by great dilution of the solution, as has been suggested.

S. B.

**Tartrates.** K. P. CHATTERJEE (*J. Proc. Asiatic Soc. Bengal*, 1922, **18**, 77).—The accepted molecular volume of water of crystallisation is confirmed by observations on the following anhydrous and hydrated tartrates: *cobalt* ( $2.5\text{H}_2\text{O}$ ), *magnesium* ( $2.5\text{H}_2\text{O}$ ), *manganese* ( $2\text{H}_2\text{O}$ ), *strontium* ( $\text{H}_2\text{O}$ ), and the salt  
 $2\text{Cu}(\text{C}_4\text{H}_4\text{O}_6), \text{K}_2(\text{C}_4\text{H}_4\text{O}_6), 3\text{H}_2\text{O}$ .

CHEMICAL ABSTRACTS.

**Walden Inversion.** P. A. LEVENE and L. A. MIKESKA (*J. Biol. Chem.*, 1924, **59**, 473—478).—A change in the sign of the rotation of the compounds is observed when  $\beta$ -thiioctane is oxidised to the corresponding sulphonic acid. In this instance, the change of the polarity of one group brought about without substitution results in a change of the direction of rotation.

D. R. N.

**Walden Inversion. II. The Optical Rotation of  $\alpha$ -Thiolpropionic and Corresponding  $\alpha$ -Sulphopropionic Acids.** P. A. LEVENE and L. A. MIKESKA (*J. Biol. Chem.*, 1924, **60**, 1—3).—In a previous communication (preceding abstract) it was suggested that the oxidation of thiol derivatives, in which the radicals attached to the asymmetric carbon atom were of a different polarity from the corresponding sulphonic acid derivatives, might leave the direction of rotation unchanged. This has been confirmed. *d*-Thiolpropionic acid was oxidised to  $\alpha$ -sulphopropionic acid, which rotated in the same direction as the parent substance.

C. T. G.

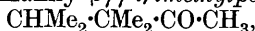
**Absorption of Ultra-violet Rays by Acraldehyde.** V. HENRI.—(See ii, 513.)

**Compounds of Magnesium Alkyl Halides with Carbonyl Compounds and the Reducing Action of Grignard Reagents.** K. HESS and W. WUSTROW.—(See i, 859.)

**Production of Acetone from Acetates and Acetic Acid.** M. G. KEKRE, J. J. SUDBOROUGH, and H. E. WATSON (*J. Proc. Asiatic Soc. Bengal*, 1922, **18**, 77).—By distillation, barium acetate yields more acetone than calcium or magnesium acetate. Yields of 80—90% are obtained in the continuous production of acetone

from acetic acid, using magnesium, calcium, and barium acetates and pumice as catalysts. CHEMICAL ABSTRACTS.

**Some New Pinacolines.** R. LOCQUIN and L. LEERS (*Compt. rend.*, 1924, **179**, 55—57).—The dehydration of trimethylisopropylglycol yields: (1) mainly  $\beta\gamma$ -trimethylpentan- $\delta$ -one,

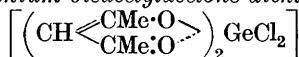


b. p. 150—151°/750 mm.,  $d_4^{20}$  0.856, which forms a semicarbazone, m. p. 150°, and an oxime, b. p. 104—105°/14 mm., m. p. 41°, and (2) a small proportion of the isomeric  $\beta\beta\delta$ -trimethylpentan- $\gamma$ -one (cf. Nef, A., 1900, i, 349; Haller and Bauer, A., 1909, i, 108; 1913, i, 829). Dehydration of trimethylisobutylglycol gives only  $\beta\delta\delta$ -trimethylhexan- $\epsilon$ -one,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CH}_3$ , b. p. 164—165°/750 mm.,  $d_4^{20}$  0.845, which forms a semicarbazone, m. p. 133°, and an oxime, b. p. 110—111°/14 mm., m. p. 61°, and is isomeric with  $\beta\beta\epsilon$ -trimethylhexan- $\gamma$ -one (cf. Haller and Bauer, *loc. cit.*).

From these results and those previously published, it follows that dehydration of pinacones of the form  $\text{OH}\cdot\text{CMeR}\cdot\text{CMe}_2\cdot\text{OH}$ , where R represents ethyl, *n*-propyl, *n*-butyl, *n*-amyl, isopropyl, isobutyl, or *tert*-amyl, yields in preponderating proportion the pinacolone  $\text{CMe}_2\text{R}\cdot\text{CO}\cdot\text{CH}_3$ . With trimethylisopropylglycol and still more so with the higher glycols, small proportions of the isomeric pinacolines are also formed.

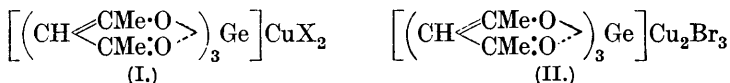
Pinacolines containing the group  $\text{CO}\cdot\text{CH}_3$  may be obtained perfectly pure by means of their oximes or semicarbazones, which crystallise well and are readily decomposed when boiled with concentrated oxalic acid solution. T. H. P.

**Researches on Residual Affinity and Co-ordination. XIX. Interactions of Germanium Tetrahalides and  $\beta$ -Diketones.** G. T. MORGAN and H. D. K. DREW (*J. Chem. Soc.*, 1924, **125**, 1261—1269).—With the exception of germanium, the members of both families of the fourth vertical series of the periodic classification have yielded characteristic compounds with acetylacetone and other  $\beta$ -diketones. Germanium tetrachloride was found to react energetically with acetylacetone in anhydrous solvents (chloroform) forming *germanium bisacetylacetone dichloride*,



colourless prisms, m. p. 240°, in 76% of the theoretical yield. *Germanium bisacetylacetone dibromide*, a colourless, microcrystalline powder, m. p. 226° (intumescence), and *germanium bispropionylacetone dichloride*, a white, crystalline powder, m. p. 128—129°, are also described. Germanium tetrachloride, allowed to interact with copper acetylacetone in cold chloroform solution for 24 hours, formed an insoluble greenish-white additive product which yielded an olive-brown solution when boiled with acetylacetone and left a residue of cuprous chloride. On cooling, the solution deposited successively (i) colourless germanium bisacetylacetone dichloride; (ii) dark blue needles,  $\text{Ge}_2(\text{C}_5\text{H}_7\text{O}_2)_6\text{Cl}_7\text{Cu}_3$ , m. p. (generally) 137—139°. When the latter was treated with cold chloroform, copper

chlorides were deposited and the solution yielded colourless *germanium trisacetylacetone cuprochloride* (I), m. p. 147—148°;



(iii) a green powder decomposed by aqueous chloroform into cupric chloride and copper acetylacetone; (iv) transparent orange to yellow crystals,  $(\text{C}_5\text{H}_7\text{O}_2)_7\text{Cl}_5\text{Cu}_2\text{Ge}_2$ , m. p. 128—129°; (v) colourless prisms, m. p. 147—148° (I) above. Germanium tetrabromide (3 mols.) reacts with copper acetylacetone in chloroform to form a blue solution and a dark precipitate which yielded cuprous bromide and a small quantity of germanium trisacetylacetone dicuprobromide on treatment with boiling acetylacetone; the blue solution gave bromoacetylacetone and a mixture of germanium trisacetylacetone cupri- and dicupri-bromides from which *germanium trisacetylacetone cuprobromide*, m. p. 165—166°, was isolated by addition of copper acetylacetone dissolved in chloroform. *Germanium trisacetylacetone dicuprobromide* (II), m. p. 195°, and *germanium trisacetylacetone cupribromide*,  $\text{C}_{15}\text{H}_{21}\text{O}_6\text{Br}_3\text{CuGe}$ , m. p. 139°, are also described.

A. C.

**Light Absorption of the Pigment formed in the Orcinol Reaction for Pentoses.** G. SCHEFF (*Biochem. Z.*, 1924, 147, 90—93).—A comparison of the absorption spectrum of an amylic-alcoholic solution of the blue pigment formed on applying the orcinol reaction to arabinose and xylose with the data previously obtained by Bergell and Pschorr (*Z. physiol. Chem.*, 1903, 38, 16) in a less accurate form.

J. P.

**Thermal Fractionation of Gaseous Products from the Pyrogenic Decomposition of certain Definite Compounds.** P. LEBEAU (*Compt. rend.*, 1924, 178, 2256—2259).—Curves are plotted showing the volume of gas evolved at various temperatures up to 1000° during the pyrogenic decomposition of various non-volatile organic compounds (*e.g.*, starch, casein, dextrose, sucrose). The form of the curves is related to the constitution of the substance carbonised, *e.g.*, the curves for sucrose and dextrose show a close similarity. The method may thus afford information as to the constitution of organic compounds of high molecular weight.

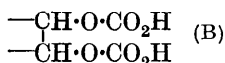
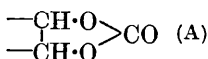
W. T. K. B.

**Optical Inactivity of Active Sugars in the Adsorbed State.**

I. S. S. BHATNAGAR and D. L. SHRIVASTAVA (*J. Physical Chem.*, 1924, 28, 730—743).—The rotatory powers of optically active sugars in presence of adsorbing colloids (*e.g.*, arsenic and antimony sulphides) are always less than those calculated from Beer's law; the discrepancy decreases with increasing dilution and increases with increasing excess of sol over sugar. The sugar adsorbed by the colloid loses its optical activity, which supports the chemical affinity theory of protective action.

S. K. T.

**Sugar Carbonates and their Derivatives. I.** C. F. ALLPRESS and W. N. HAWORTH (*J. Chem. Soc.*, 1924, **125**, 1223—1233).—Sugar carbonates corresponding with normal (A) and acid carbonates (B) have been prepared by acting on the sugars with chloroformic



esters in the presence of (i) sodium hydroxide or (ii) pyridine.

The normal carbonates of the sugars resemble the acetone sugar derivatives in their tendency to crystallise and ease of hydrolysis with dilute acids, but the carbonates are readily hydrolysed to the free sugars on gentle warming with dilute alkalis.

*Monocarbomethoxyfructose dicarbonate* (I), prepared by method (i), has m. p.  $192^\circ$ ,  $[\alpha]_D -78.5^\circ$  in acetone ( $c=0.82$ ) and  $-72.2^\circ$  in ethyl acetate ( $c=0.24$ ). The alcohol washings from (I) deposited needles of a strongly laevorotatory difructose derivative,  $\text{C}_{17}\text{H}_{18}\text{O}_{16}$ , m. p.  $196^\circ$ . *Tetracarbomethoxyfructose*, prisms, m. p.  $126-127^\circ$ , resulted from the condensation of fructose in chloroform with dry pyridine and methyl chloroformate (method ii),  $[\alpha]_D -75.1^\circ$  ( $c=2.47$ ),  $-77.6^\circ$  ( $c=2.04$ ) in acetone and  $-98.1^\circ$  ( $c=1.44$ ) in chloroform. On keeping the solutions, in sunlight or in the dark at a

constant temperature, anomalous variations in the rotation values were observed. *Tetracarbomethoxyfructose*, also by method (ii), formed crystals, m. p.  $118^\circ$ ,  $[\alpha]_D -97.0^\circ$  to  $95.3^\circ$  in chloroform ( $c=1.6$ ), and  $-72^\circ$  in acetone ( $c=0.6$ ); an *isomeride*, a yellow syrup,  $[\alpha]_D -19^\circ$  in acetone ( $c=2.4$ ), accompanied the last compound. Galactose by method (i) gave rise to *tricarbomethoxygalactose carbonate*, needles, m. p.  $170.5-171^\circ$ ,  $[\alpha]_D -88.9^\circ$  in acetone ( $c=0.53$ ). The later deposits contained an *isomeride*, a colourless, amorphous powder, m. p.  $126^\circ$ ,  $[\alpha]_D$  from  $-29.8^\circ$  to  $-45^\circ$  in acetone ( $c=0.40$ ), and  $-34.9^\circ$  in chloroform ( $c=1.1$ ); the rotations showed variations according as the solutions were kept in the light or in the dark. With pyridine as condensing medium, the reaction proceeded with extreme difficulty. *Tetracarbomethoxygalactose* with  $[\alpha]_D +92.6^\circ$  in acetone ( $c=1.86$ ), was obtained as a yellow glass, accompanied by much unaltered galactose. Dextrose by method (i) yielded *tetracarbomethoxyglucose*, an amber-coloured glass having  $[\alpha]_D +34.6^\circ$  ( $c=1.56$ ) and  $+34.1^\circ$  ( $c=0.73$ ) in ethyl alcohol,  $[\alpha]_D +34.8^\circ$  ( $c=0.52$ ) and  $+51.3^\circ$  ( $c=2.2$ ) in acetone. On methylating with Purdie's reagent, vitreous *tetracarbomethoxymethylglucose* was obtained. Using method (ii) a *tetracarbomethoxyglucose*,  $[\alpha]_D +87.1^\circ$  (in acetone), different from the above, was obtained. Mannitol [method (i)] yielded *dicarbomethoxymannitol dicarbonate*, a yellow gum,  $[\alpha]_D +29.6^\circ$  in acetone ( $c=1.2$ ). Sucrose reacted with difficulty in pyridine and yielded a hepta (or octa) *carbomethoxy* derivative,  $[\alpha]_D +53.8^\circ$  in acetone ( $c=1.0$ ), as a pale yellow glass. This product showed unexpected stability towards 1% hydrochloric acid at  $100^\circ$ .

A. C.

**Structure of Diacetone [Diisopropylidene] Glucose. II.  $\gamma$ -Methylglucuronic Acid and  $\delta$ -Methylglucoheptonolactone.** P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1924, **60**, 173—178).—On reduction of the monomethylsaccharolactone, obtained by oxidation of monomethylglucose, *d*- (and not *l*-) $\gamma$ -methylglucuronic acid is formed. This indicates that the methyl group in monomethylglucose is in the  $\gamma$  position. The position of the new substance in the *d*-series was shown by the properties of the *p*-bromophenyldiazine derivative, which has the same character of mutarotation as the corresponding derivative of glucuronic acid, *i.e.*, a decrease in numerical value and direction to the left. It is further shown that the methylglucoheptonolactone obtained from the methylglucose was dextrorotatory, which agrees with the  $\gamma$ -position for the methyl group;  $\delta$ -methylglucose should give a levorotatory heptonolactone.

*d*- $\gamma$ -Methyl- $\alpha$ -glucoheptonolactone was also prepared by the action of hydrocyanic acid on methylglucose and was found to form a  $\gamma$ -methyl sugar acid. C. T. G.

**Derivatives of a New Form of Mannose.** J. C. IRVINE and W. BURT (*J. Chem. Soc.*, 1924, **125**, 1343—1348).—Conditions are given for the preparation of a mixture of two new mannosides which displays properties similar to Fischer's  $\gamma$ -methylglucoside. The name " $\gamma$ -methylmannoside," as used here, refers to a preparation containing two stereoisomeric forms of the compound which differ from each other in the position of the methyl group and from  $\alpha$ -methylmannoside in the linking of the internal ring.

$\gamma$ -Methylmannoside is a very viscous syrup,  $[\alpha]_D^{20} + 80.2^\circ$  in ethyl alcohol, which immediately reduces neutral permanganate. It is converted successively by means of silver oxide and methyl iodide into mixtures of *trimethyl- $\gamma$ -mannosides* and *tetramethyl- $\gamma$ -mannosides*, b. p.  $141^\circ/13$  mm.,  $n_D$  1.4482,  $[\alpha]_D^{20} + 24.9^\circ$  in ethyl alcohol. The tetramethyl derivatives are hydrolysed to *tetramethyl- $\gamma$ -mannose*, a crystalline solid, b. p.  $190^\circ/10$  mm.,  $n_D$  1.4647,  $[\alpha]_D^{20} + 47.4^\circ$  in ethyl alcohol. During methylation, particularly by the methyl sulphate method, a partial conversion of  $\gamma$ - into  $\alpha$ -forms occurs. In preparing  $\gamma$ -methylmannoside by the method involving concentrated hydrochloric acid, auto-condensation of  $\gamma$ -mannose derivatives appears sometimes to take place. A. C.

**Two Isomeric Tetramethylmannonolactones.** P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1924, **60**, 167—171).—The  $\alpha$ - and  $\beta$ -isomerides in sugars with different oxidic structures may be determined by the position of the hydroxyls with respect to the oxidic ring. In mannose, both the butylene and amylen oxide rings have the same direction and possibly some of the abnormalities in the behaviour of mannose may be due to a peculiarity in the oxidic ring, although it is also possible that in solution the two oxidic forms reach an equilibrium. In view of these considerations, the lactones obtained by oxidation of tetramethylmannose and by methylation of mannonolactone were compared. The former, prepared by oxidation of tetramethylmannose with bromine, is a



liquid and is dextrorotatory ( $[\alpha]_D^{20} +105^\circ$ ) as are also the free acid ( $[\alpha]_D +17.5^\circ$ ) and its sodium salt ( $[\alpha]_D +41.6^\circ$ ). The latter, prepared by methylation of mannonolactone by Purdie's method, is crystalline, m. p.  $107^\circ$ ; it is dextrorotatory ( $[\alpha]_D$ , in water,  $+65.2^\circ$ ), whilst the free acid,  $[\alpha]_D -25.3^\circ$ , and its sodium salt,  $[\alpha]_D -22.5^\circ$ , are lævorotatory. The rotation of the two tetramethyl-lactones in opposite directions requires elucidation. C. T. G.

**Relation between Hexosemonophosphoric Acid and Hexosediphosphoric Acid.** C. NEUBERG and E. REINFURTH (*Biochem. Z.*, 1924, **146**, 589—593).—The acid phenylhydrazine salt of hexosemonophosphoric acid osazone is identical with that prepared from hexosediphosphoric acid by the elimination of one phosphoric acid residue. It is concluded that by subjecting hexosediphosphoric acid to gentle hydrolysis the  $\alpha$ -phosphoric acid residue is removed. J. P.

**Action of Ultra-violet Light on Lævulose. Production of Carbon Monoxide and Formaldehyde.** H. BERRY and A. RANC (*Bull. Soc. chim.*, 1924, [iv], **35**, 771—772).—The decomposition of lævulose by ultra-violet light, yielding carbon monoxide, carbon dioxide, and formaldehyde, described by D. Berthelot (this vol., ii, 320), has been previously observed by the authors (A., 1910, i, 652). The decomposition takes place at  $10$ – $20^\circ$ , more rapidly at  $60$ – $70^\circ$ . R. B.

**Posidonia Fibre. II. The Cellulose.** J. C. EARL (*J. Chem. Soc.*, 1924, **125**, 1322—1323; cf. T., 1923, **123**, 3223).—The cellulose of *Posidonia australis* is converted by Irvine and Hirst's method (T., 1922, **121**, 1585) into the *tri-acetate*,  $[\alpha]_D -39.8^\circ$  in chloroform, which is converted by methyl-alcoholic hydrogen chloride to the extent of 95% into a mixture of  $\alpha$ - and  $\beta$ -methylglucosides. *Posidonia*, like cotton, cellulose appears to belong to the poly-anhydroglucose type, but the great difference in optical rotation of the triacetates of the celluloses indicates a difference in their chemical structure. A. C.

**Preparation of Acetone-soluble Cellulose Acetate.** G. KITA, K. ASAMI, J. KATO, and R. TOMIHISA (*Z. angew. Chem.*, 1924, **37**, 414—418).—Dry cellulose (cotton paper) is added to a mixture of glacial acetic acid, acetic anhydride, and a little sulphuric acid cooled with ice water. The mixture is then transferred to a thermostat and the reaction temperature carefully controlled. Hydration is effected by a mixture of equal weights of glacial acetic acid and water. If the hydration temperature is too high, the viscosity of the product does not increase and the copper value increases with the time of hydration, whilst the reverse is the case with a suitably low temperature. The influence of temperature is more marked during acetylation than during hydration. Acetylation at a relatively high temperature (e.g.,  $25^\circ$ ) gives an inferior acetone-soluble acetate even if hydration is effected at a low temperature, whilst the temperature of hydration has comparatively little influence with a product of low-temperature acetylation.

The most suitable temperature depends on the quantity of sulphuric acid added as catalyst, a smaller quantity of the latter being required at higher temperatures, although with too small a quantity a good acetate is unobtainable. If the quantity of catalyst and the time of acetylation are suitably limited, good results may be obtained even at higher temperatures. There is no advantage in neutralising the sulphuric acid on hydration. W. T. K. B.

**Gelatinisation by Heat of Wheat and Maize Starch.** C. L. ALSBERG and O. S. RASK (*Cereal Chem.*, 1924, 1, 107—116).—Suspensions of wheat and maize starch, on slow heating, showed constant viscosities up to about 65° and then steady increases in viscosity to maxima at 91° for maize starch and 95° for wheat starch. Gelatinisation does not take place at a sharply defined transition point, but is a long and gradual process, which does not necessarily commence at the so-called gelatinisation temperature. The disappearance of anisotropy marks an early stage in the gelatinisation process, but not its completion. E. M. C.

**Lignin Hydrochloride.** E. HÄGGLUND and C. B. BJÖRKMAN (*Biochem. Z.*, 1924, 147, 74—88).—The preparation is described of a lignin hydrochloride by treatment of finely-powdered pine wood with highly concentrated hydrochloric acid in the cold. The yield is 22—26% of the weight of the wood after extraction with acetone and ether. The lignin is partly dissolved by further treatment with concentrated acid in the cold, with the liberation of reducing sugars. A similar result is achieved by boiling with dilute acids, and by a combination of the hot and cold treatments more than 50% of the lignin is dissolved. The sugar formed is partly fermentable—the non-fermentable part consisting of arabinose. No methylpentose is present. The lignin hydrochloride yields an alcohol-insoluble furfuraldehyde phloroglucide indicating the presence of pentosans, and a phloroglucide soluble in alcohol which is not a methylfurfuraldehyde phloroglucide. Previous determinations of methylpentoses in lignins are therefore not trustworthy. The green colour of the solution and residue of wood treated with strong hydrochloric acid is regarded as indicative of a lignin-carbohydrate complex, since the similar colour produced by lignins freed from carbohydrate is brown, whilst the solution is violet. More trustworthy quantitative determinations of lignin are obtained by prolonged treatment with highly concentrated acid than by short treatment. Lignin hydrochloride gives rise to oxalic acid on alkali fusion, and to succinic acid on oxidation with hydrogen peroxide (cf. Holmberg, A., 1923, i, 1067; Fischer, A., 1923, i, 185). J. P.

**Condensation of Ethyl Diethylammonium Malonate with Formaldehyde.** C. MANNICH and K. RITSERT (*Ber.*, 1924, 57, [B], 1116—1118).—The condensation of ethyl diethylammonium malonate with formaldehyde at a low temperature gives rise to a mixture of ethyl  $\beta$ -diethylaminopropionate and ethyl  $\beta\beta$ -bisdiethylaminoisobutyrate,  $\text{CO}_2\text{Et}\cdot\text{CH}\cdot[\text{CH}_2\cdot\text{NEt}_2]_2$ , which could not be

separated completely from one another by fractional distillation. The former substance is identified as the *hydrochloride*, the latter as the *chloroplatinate*, m. p. 210° (decomp.). With similar mono-alkylated derivatives of malonic acid, analogous condensation products are doubtless formed primarily which immediately decompose into esters of  $\alpha$ -substituted acrylic acids, diethylamine, carbon dioxide, and water. Thus ethyl diethylammonium ethylmalonate and formaldehyde yield *ethyl  $\alpha$ -ethylacrylate* [ *$\alpha$ -methylenebutyrat*], b. p. 138°. *Ethyl  $\alpha$ -methylacrylate*, b. p. 118°, *ethyl  $\alpha$ -benzylacrylate*, b. p. 134°/15 mm. ( *$\alpha$ -benzylacrylic acid*, m. p. 68°), and *ethyl  $\alpha$ -allylacrylate*, b. p. 60°/16 mm. ( *$\alpha$ -allylacrylic acid*, b. p. 159—161°) are prepared similarly. H. W.

**Synthesis of Aminoketonic Acids.** C. MANNICH and M. BAUROTH (*Ber.*, 1924, 57, [B], 1108—1115).—The synthesis of ketonic bases from formaldehyde, ketones, and amine salts (cf. A., 1922, i, 351, and previous abstracts) has been extended to  $\alpha$ -,  $\beta$ -, and  $\gamma$ -keto-acids.

The action of formaldehyde (35%) on a mixture of pyruvic acid and dimethylamine hydrochloride leads to the production of the *hydrochloride* of  $\alpha$ -keto- $\beta$ -dimethylaminomethyl-*n*-butyrolactone,  $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CH} < \begin{smallmatrix} \text{CO} - \text{CO} \\ \text{CH}_2 - \text{O} \end{smallmatrix}$ , m. p. 168° (decomp.) when rapidly heated (*picrate*, decomp. 147°), which is reduced by tin and concentrated hydrochloric acid to  *$\alpha$ -hydroxy- $\beta$ -dimethylaminomethylbutyrolactone hydrochloride*, m. p. 190°. Similarly, pyruvic acid, formaldehyde, and piperidine hydrochloride yield  *$\alpha$ -keto- $\beta$ -piperidinomethyl-*n*-butyrolactone hydrochloride*, m. p. 180° (decomp.) [*picrate*, m. p. 147° (decomp.)], which is reduced to  *$\alpha$ -hydroxy- $\beta$ -piperidinomethyl-*n*-butyrolactone hydrochloride monohydrate*, m. p. 135° (decomp.) after softening at 100°.  $\alpha$ -Ethylacetoacetic acid, formaldehyde, and dimethylamine appear to yield primarily the expected amino-acid which, however, readily evolves carbon dioxide and passes into  *$\gamma$ -dimethylaminomethylpentan- $\beta$ -one*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CHEt} \cdot \text{CH}_2 \cdot \text{NMe}_2$ , b. p. 62—64°/14 mm.; the hygroscopic *hydrochloride*, m. p. 131°, the *picrate*, the *oxime hydrochloride*, m. p. 178° (decomp.), and the *methiodide*, m. p. 146°, are described.  *$\gamma$ -Piperidinomethylpentan- $\beta$ -one*, prepared in a similar manner, has b. p. 108—110°/15 mm.; it yields a *hydrochloride*, m. p. 136°; *picrate*, m. p. 134°; *oxime hydrochloride*, m. p. about 200° when rapidly heated, and *methiodide*, m. p. 119—120°. Lævulic acid is transformed by formaldehyde and dimethylamine hydrochloride at 110° into  *$\gamma$ -keto- $\epsilon$ -dimethylaminohexoic acid hydrochloride*,

$\text{NMe}_2 \cdot [\text{CH}_2]_2 \cdot \text{CO} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H} \cdot \text{HCl}$ , m. p. 119—120°; the corresponding *picrate*, m. p. 140—143°, and the *hydrochloride* of the *semicarbazone*, decomp. about 165° when rapidly heated, are described. The substance is converted by phenylhydrazine at 100° into the *phenylhydrazide* of 1-*phenylpyrazoline-3-propionic acid*, m. p. 150°.  *$\gamma$ -Keto-1-piperidino-*n*-hexoic acid hydrochloride* crystallises in leaflets, m. p. 145—146°, and yields a *semicarbazone hydrochloride*, decomp. about 190°; it

is converted by phenylhydrazine into 1-phenylpyrazoline-3-propionphenylhydrazide and piperidine. H. W.

**Influence of Acids and Alkalis on Amino-acids.** E. ABDERHALDEN and E. SCHWAB (*Z. physiol. Chem.*, 1924, **136**, 219—223).—Using pure glycine, leucine, alanine, and glutamic acid, the authors were unable to confirm the results of Zelinski and Sadikov (A., 1923, i, 1185), who found that glycine loses nitrogen as ammonia under the influence of *N*/10-sodium hydroxide. It is suggested that the changes observed are due to impurities and possibly to faulty technique in the formol titration. The conversion of glutamic acid into glutimic acid by heat was confirmed.

O. O.

**Do Creatine and Creatinine give the Diazo Reaction?** H. REINWEIN (*Z. Biol.*, 1924, **81**, 49—50).—Various preparations of creatinine and creatine that gave the diazo reaction (Pauly, A., 1904, i, 1068) no longer did so when purified by repeated recrystallisation. It is suggested that the reaction before purification was due to traces of iminazole derivatives such as histidine, which is a normal constituent of mammalian muscle and might be precipitated with creatine and creatinine in their preparation from muscle and from urine.

C. T. G.

**Methylethylmaleinimide.** WILLIAM KÜSTER (*Z. physiol. Chem.*, 1924, **137**, 78—84; cf. A., 1901, i, 298; 1906, i, 337; 1917, i, 443).—Methylethylmaleinimide is prepared in 80% yield by boiling methylethylmaleic anhydride with alcoholic ammonia. The action of boiling aqueous potassium hydroxide solution on methylethylmaleic anhydride yields two acids, m. p. 184° (decomp.) and 126—130°, respectively. The copper salts have the composition  $C_7H_8O_4Cu, \frac{1}{2}H_2O$ .

B. F.

**The Equilibrium between Thiocarbamide and Ammonium Thiocyanate.** G. H. BURROWS (*J. Amer. Chem. Soc.*, 1924, **46**, 1623—1627).—The equilibrium between thiocarbamide and ammonium thiocyanate has been investigated when the substances are melted together at temperatures from 132° to 182°. Side reactions occur with the formation of hydrogen sulphide and ammonia. The percentages of ammonium thiocyanate in the equilibrium mixtures were 66.5, 73.4, and 77.8 at 132°, 156°, and 182°, respectively. The equilibria in *n*-propyl and *n*-butyl alcohols varied with the nature of the solvent, whilst the temperature coefficient in the presence of these solvents was of opposite sign to that in the case of the fused mixture. These effects are ascribed to a change in equilibrium, as the specimens were chilled before analysis. The heat of transformation of 1 mol. of ammonium thiocyanate into 1 mol. of thiocarbamide is calculated to be 4600 cal.

W. H.-R.

**Preparation of Thiocarbonylhydrazide: Mono- and Di-thio-*p*-urazine.** P. C. GUHA and S. C. DE (*J. Chem. Soc.*, 1924, **125**, 1215—1218).—Thiocarbonylhydrazide was prepared in 70% yield by heating alcoholic solutions of hydrazine hydrate (2 mols.)

and diethyl xanthate under reflux. The *diacetyl* derivative had m. p. 180—181°. *Dimethylenethiocarbohydrazide*, obtained by heating thiocarbohydrazide with excess of formaldehyde, had m. p. 204—205° (decomp.). Thiocarbohydrazide and carbohydrazide react with thiocarbimides, forming bithiocarbamyl derivatives:  $\text{XC}(\text{NH}\cdot\text{NH}_2)_2 + 2\text{RCNS} = \text{XC}(\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHR})_2$  ( $\text{X} = \text{S}$  or  $\text{O}$ ;  $\text{R} = \text{Ph}$  or  $p\text{-C}_7\text{H}_7$ ). *Thiocarbohydrazide-dicarbonthiophenylamide* has m. p. 199°. The compound for which  $\text{X} = \text{S}$ ,  $\text{R} = p\text{-C}_7\text{H}_7$ , melts at 201°;  $\text{X} = \text{O}$ ,  $\text{R} = \text{Ph}$ , has m. p. 208—209°;  $\text{X} = \text{O}$ ,  $\text{R} = p\text{-C}_7\text{H}_7$ , m. p. 215—216°. Potassium ethyl xanthate reacts with thiocarbohydrazide in a sealed tube at 100°, giving *dithio-p-urazine*,  $\text{CS} \begin{smallmatrix} \text{NH}\cdot\text{NH} \\ \text{NH}\cdot\text{NH} \end{smallmatrix} \text{CS}$ , m. p. 202—203°, which forms a *disilver* salt and a *dibenzyl ether*, m. p. 142°, but no benzylidene derivative.

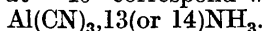
Purgotti and Vigano's "dithio-*p*-urazine," m. p. 198—199° (A., 1902, i, 323), probably has the constitution  $\begin{smallmatrix} \text{CS} & \text{—S} \\ | & \diagup \\ \text{NH}\cdot\text{NH} & \end{smallmatrix} \text{C}\cdot\text{N}\cdot\text{NH}_2$ .

*Dithio-p-urazine disulphide*, obtained by the action of iodine on dithio-*p*-urazine, has m. p. 218° (decomp.). *Monothio-p-urazine*,  $\text{CO} \begin{smallmatrix} \text{NH}\cdot\text{NH} \\ \text{NH}\cdot\text{NH} \end{smallmatrix} \text{CS}$ , m. p. 238° (decomp.), was prepared by heating thiocarbohydrazide with carbamide at 130°, or by heating carbohydrazide with potassium ethyl xanthate in a sealed tube at 100°. *p-Urazine*, m. p. 264—265°, was obtained by heating carbohydrazide with carbamide at 120°. A. C.

**Mustard Oils.** L. ROSENTHALER (*Arch. Pharm.*, 1924, **262**, 126—127).—Allyl isothiocyanate forms a compound with potassium hydrogen sulphite. Although *a priori* the allyl group might have as much claim to be considered the active agent as the isothiocyanate group, yet the instability of the compound, among other evidence, suggests that the latter is really responsible. The compound should therefore be formulated  $\text{C}_3\text{H}_5\cdot\text{NH}\cdot\text{CS}\cdot\text{SO}_2\cdot\text{OK}$ .

W. A. S.

**Reaction between Mercuric Cyanide and certain Metals in Liquid Ammonia.** F. W. BERGSTROM (*J. Amer. Chem. Soc.*, 1924, **46**, 1559—1568).—Aluminium reacts with a solution of mercuric cyanide in liquid ammonia with the initial formation of two liquid phases, the denser of which contains one or more double cyanides of mercury and aluminium, which cannot, however, be crystallised. By further action with excess of aluminium, a solution of aluminium cyanide in liquid ammonia is formed, which shows a transition temperature between 0° and −33°. Crystals deposited at room temperature have the composition  $\text{Al}(\text{CN})_3\cdot 5\text{NH}_3$ , whilst those obtained at −40° correspond with



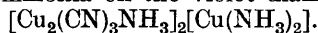
In addition, products with  $1\frac{1}{2}$  (?), 6, and 9 mols. of ammonia have been obtained.

The compound  $\text{Hg}(\text{CN})_2\cdot\text{Mn}(\text{CN})_2\cdot 2\text{—}3\text{NH}_3$  is obtained by the

action of manganese on a solution of mercuric cyanide in liquid ammonia. Two liquid phases are again formed, but the action then stops and manganous cyanide is not produced. Mercuric cyanide and metallic magnesium react in liquid ammonia to form two liquid phases, the denser of which disappears, leaving a grey precipitate of ammoniated magnesium cyanide. Zinc, iron, and tin also react with mercuric cyanide in liquid ammonia.

W. H.-R.

**Cuprous-Cupric Cyanide Ammine Compounds.** A. BEN-RATH and W. SCHRÖDER (*Z. anorg. Chem.*, 1924, **135**, 205—225).—The conditions for the inter-transformation of compounds of the tetra- and tri-cyanogen series of copper amines are considered. A new blue salt,  $[\text{Cu}_2(\text{CN})_3\text{NH}_3]_2[\text{Cu}(\text{NH}_3)_4]$ , is prepared by the action of gaseous ammonia on the violet diammine,



The compound  $[\text{Cu}_2(\text{CN})_4][\text{Cu}(\text{NH}_3)_6]$  is made from the corresponding triammine by the action of ammonia (cf. *Compt. rend.*, 1853, **36**, 1099); Malmberg (A., 1898, i, 547) and Treadwell (A., 1904, i, 479) denied its existence. Treadwell's formulæ for these compounds are adversely criticised; new ones are proposed, based on the assumption that the dark blue, easily soluble salts with the smallest ammonia content are tetrammine copper salts. The solubility curve (in ammonia solution at 10°) of the green salt,  $[\text{Cu}_2(\text{CN})_4][\text{Cu}(\text{NH}_3)_3]$ , of the tetracyanogen series, is discontinuous at an ammonia concentration of 3.614 g. per 100 g. of water, and the curve thereafter represents the solubility of the blue tetrammine,  $[\text{Cu}_2(\text{CN})_4][\text{Cu}(\text{NH}_3)_4]$ . It falls to a minimum and then rapidly increases, indicating the formation of a higher complex (hexammine). At 40°, the solution deposits a brown substance, or, if the ammonia content is high, the violet salt of the tri-cyanogen series appears. At these temperatures, the curve becomes continuous. The violet salt of the tricyanogen series, when shaken with ammonia, forms the green salt of the tetracyanogen series. At low temperatures this is reversed; the reverse reaction is slow unless the solution is "seeded" with a crystal of the green salt. In presence of small quantities of ammonia, the green salt is converted completely into the violet at 70°; cuprous cyanide must be produced first, its formation being assisted by increasing the temperature and hindered by raising the ammonia concentration. Tetrammine salts of the tricyanogen series are readily converted into members of the tetracyanogen series in presence of moisture. Previous work is criticised.

S. K. T.

**Hydrolysis of Potassium Ferricyanide and Potassium Cobalticyanide by Sulphuric Acid.** H. BASSETT and A. S. CORBET (*J. Chem. Soc.*, 1924, **125**, 1358—1366).—Boiling sulphuric acid (80%) hydrolyses potassium ferricyanide according to the equation:  $2\text{K}_3\text{Fe}(\text{CN})_6 + 11\text{H}_2\text{SO}_4 + 13\text{H}_2\text{O} = 3\text{K}_2\text{SO}_4 + 6(\text{NH}_4)_2\text{SO}_4 + 2\text{FeSO}_4 + 11\text{CO} + \text{CO}_2$ . On progressive dilution of the acid, the

reaction tends more and more towards the equation  $2K_3Fe(CN)_6 + 6H_2SO_4 = 3K_2SO_4 + Fe_2(SO_4)_3 + 12HCN$ .

Potassium cobalticyanide is hydrolysed by the concentrated acid in the same way as above. Prolonged boiling, in a reflux apparatus, with 30% acid causes the reaction  $2K_3Co(CN)_6 + 6H_2SO_4 + 2H_2O = 3K_2SO_4 + 2CoSO_4 + NH_4HSO_4 + 11HCN + CO_2$ . A white, crystalline, intermediate product, probably potassium aquopentacyanocobaltate, was isolated in this case; a similar compound was obtained by the action of bromine on potassium cobalticyanide. S. K. T.

**Mixed Organo-aluminium Compounds. Aluminium Monoethyl Di-iodide and Aluminium Diethyl Iodide.** V. GRIGNARD and R. JENKINS (*Compt. rend.*, 1924, 179, 89—92).—Aluminium powder and ethyl iodide (dry and free from alcohol) react readily in an atmosphere of dry nitrogen to give a mixture of *aluminium diethyl iodide*,  $AlEt_2I$ , a clear, mobile liquid, b. p. 118—120°/4—5 mm.,  $d_{25}^{25}$  1.609, and *aluminium ethyl di-iodide*,  $AlEtI_2$ , a solid, m. p. 35—37°, b. p. 158—160°/4 mm. Both compounds ignite spontaneously when exposed to air; the corresponding etherates do not exhibit this property. W. T. K. B.

**The Decomposition of Lead Tetra-ethyl and its Application to Explosion Motors.** P. JOLIBOIS and G. NORMAND (*Compt. rend.*, 1924, 179, 27—28).—Lead tetraethyl, prepared in a pure state by the action of lead chloride on magnesium ethyl iodide, is completely decomposed at 400° with the production of finely-divided metallic lead. It is suggested that this affords an explanation of the observed action of lead tetraethyl, which, when mixed with the fuel of explosion motors, allows greater compression without the danger of self-ignition. By increasing the radius of curvature of the sharp-edged particles by the deposition thereon of the lead, the tendency to self-ignition is reduced in accordance with the observations of Reboul (A., 1913, ii, 303, 489). [Cf. B., 1924, 700.] J. W. B.

**Mercury Ethylmercapto-salts.** G. SACHS (*Z. anorg. Chem.*, 1924, 135, 273—282).—Mercuric ethylmercaptoacetate,  $EtSHgOAc$ ,

is obtained when mercury mercaptide is shaken with mercuric acetate solution. By precipitating an aqueous solution of the mercaptoacetate with alkali-metal salts of the appropriate acids, the corresponding chloride, bromide (which was not crystalline; cf. A., 1898, i, 458), nitrate (crystalline), *normal carbonate* (m. p. 140°), and *benzoate* are obtained. The phosphate appears to be soluble.

The benzoate melts at 130° to 140°, solidifies at 160°, and remelts at 170° (decomp.), yielding benzoic acid, ethyl benzoate, *o*-hydroxy-mercuribenzoic anhydride, diethyl mono- and di-sulphides, mercuric sulphide, and mercury. The mercaptoacetate solution can also absorb further quantities of mercury mercaptide. S. K. T.

**Mercury Ethylmercapto-hydroxides.** G. SACHS (*Z. anorg. Chem.*, 1924, **135**, 283—288; cf. preceding abstract).—Dilute mercuric ethylmercaptoacetate solution yields, with potassium hydroxide or with ammonia in ammonium acetate solution, the unstable free base, which immediately decomposes into mercury mercaptide and mercuric hydroxide:  $2\text{EtS}\cdot\text{Hg}\cdot\text{OH}=\text{Hg}(\text{SEt})_2+\text{Hg}(\text{OH})_2$ . Part of the former is precipitated and part is held in solution with the hydroxide, probably in the form of at least two mercapto-hydroxides, the assumption of which is necessary in order to account theoretically for the amount of mercaptide precipitated decreasing with increasing dilution. These mercapto-hydroxides are exceedingly weak bases and their formation appears to be quantitative. S. K. T.

**Reversible Catalysis of Unsaturated Hydrocarbons.** I. N. ZELINSKY and G. PAVLOV (*Ber.*, 1924, **57**, [B], 1066—1070).—The kinetics of the dehydrogenation of *cyclohexene* under the influence of palladium-asbestos have been examined (cf. A., 1923, i, 767; this vol., i, 665) between 160° and 320°. Dehydrogenation is perceptible at 164° and the product consists of benzene and *cyclohexane* in the proportion required by the equation  $3\text{C}_6\text{H}_{10}=\text{C}_6\text{H}_6+2\text{C}_6\text{H}_{12}$ . Unchanged *cyclohexene* was not present in the distillate (cf. Böeseken and Sillevis, A., 1914, i, 254). This decomposition proceeds at temperatures as low as 92°, even in an atmosphere of carbon dioxide, and at temperatures below 130° hydrogen is not given off. In the absence of palladium, *cyclohexene* is unchanged at 200°. The dehydrogenation curve of *cyclohexene* between 220° and 300° accordingly corresponds closely with that of a mixture of *cyclohexane* (2 mols.) and benzene (1 mol.). A similar process of simultaneous oxidation and reduction (cf. Zelinsky and Glinka, A., 1911, i, 870) takes place with *cyclohexadiene* at 91° in a slow stream of carbon dioxide. In the presence of palladium, no hydrogen is liberated, but benzene and *cyclohexane* are formed thus:  $3\text{C}_6\text{H}_8=2\text{C}_6\text{H}_6+\text{C}_6\text{H}_{12}$ . 1:4-Dimethyl*cyclohexene* similarly decomposes at 140° into xylene and dimethyl*cyclohexane* according to the equation  $3\text{C}_8\text{H}_{14}=\text{C}_8\text{H}_{10}+2\text{C}_8\text{H}_{16}$ , whilst at 175—180° under similar conditions menthene is converted into menthane and cymene.  $\Delta^2$ -Dihydronaphthalene at 130° similarly yields a mixture of naphthalene and tetrahydronaphthalene. This reversible catalysis appears to be characteristic of unsaturated aromatic hydrocarbons containing the double linking in the ring system, but not when the double bond is present in the side-chain. R. B.

**Action of Aluminium Sulphide on certain Organic Compounds.** G. R. LEVI and G. NATTA (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 350—353).—Aluminium sulphide exerts a dehydrating action on aliphatic compounds and also tends to replace their oxygen by sulphur; with aromatic compounds the former effect predominates. In no case has any marked condensing action been observed.

When passed over aluminium sulphide, benzene vapour at 800—900° yields condensation products such as diphenyl, phen-



anthrene, and triphenylene; the same products are obtained in about similar yields when benzene vapour at a similar temperature is passed over pumice. At a temperature somewhat below the boiling point of phenol, aluminium sulphide converts the latter completely into phenyl ether. If alcohol vapour is passed at a suitable rate over aluminium sulphide at  $330^{\circ}$ , ethyl mercaptan is obtained in 46% yield free from ethyl sulphide, the non-reacting alcohol being almost entirely recoverable. Under similar conditions, ether is converted into ethyl sulphide. T. H. P.

**Irregularities in the Specific Heats of certain Organic Liquids [Benzene, Ethylbenzene].** J. W. WILLIAMS and F. DANIELS.—(See ii, 589.)

**Decomposition of Phenylazoimide in Benzene and in *p*-Xylene.** A. BERTHO (*Ber.*, 1924, 57, [B], 1138—1142).—Phenylazoimide is not decomposed by boiling benzene, but is converted by the hydrocarbon at  $150$ — $160^{\circ}$  into azobenzene and a little aniline, which owes its origin to traces of moisture which could not be entirely excluded. Boiling *p*-xylene decomposes phenylazoimide with formation of *s*-*pp'*-ditolylethane, m. p.  $82^{\circ}$ , aniline, and traces of azobenzene. At  $150$ — $160^{\circ}$ , the yields of these products are considerably increased, but the proportion of hydrocarbon still remains below that expected from the yield of the base. H. W.

**Orienting Influence of the Thiocyno Group in Aromatic Compounds.** F. CHALLENGER and A. D. COLLINS (*J. Chem. Soc.*, 1924, 125, 1377—1381).—In accordance with the theory of induced alternate polarities, the thiocyno group has been found, from a study of the nitration of phenyl thiocyanate and its *p*-chloro-, *p*-bromo-, *p*-iodo-, and *p*-methyl derivatives, to possess ortho-para directing influence. The predominating, if not exclusive, formation of 2-nitro derivatives of the chloro and bromo compounds shows that the directing influence of the thiocyanate group is more powerful than that of chlorine or bromine. Nitration of *p*-tolyl thiocyanate, however, gives mainly the 3-nitro derivative. Phenyl thiocyanate with nitric and sulphuric acids at  $5$ — $10^{\circ}$  gives 94% of the theoretical yield of *p*-nitrophenyl thiocyanate, m. p.  $133^{\circ}$ , which on further nitration at  $90^{\circ}$  yields 2:4-dinitrophenyl thiocyanate. *p*-Tolyl thiocyanate similarly yields at  $20^{\circ}$  a mixture of 3-nitro-*p*-tolyl thiocyanate and 2-nitro-*p*-tolyl thiocyanate, yellow needles, m. p.  $40^{\circ}$ . *p*-Bromophenyl thiocyanate, m. p.  $56^{\circ}$ , obtained, together with 4:4'-dibromodiphenyl sulphide, from *p*-bromoaniline, yields *p*-bromophenyl mercaptan with alcoholic potassium hydrosulphide, and on nitration at  $5$ — $10^{\circ}$ , 4-bromo-2-nitrophenyl thiocyanate, long, yellow needles, m. p.  $131^{\circ}$ , also prepared from 4-bromo-2-nitroaniline, which with potassium hydrosulphide gives potassium thiocyanate and 4-bromo-2-nitrophenyl mercaptan, oxidised to 4:4'-dibromo-2:2'-dinitrodiphenyl disulphide. The crude nitration product yields traces of a solid bromothiocyanate, m. p. about  $95^{\circ}$ . *p*-Chlorophenyl thiocyanate, obtained with 4:4'-dichlorodiphenyl disulphide from diazotised *p*-chloroaniline,

on nitration yields 4-chloro-2-nitrophenyl thiocyanate. *p*-Iodo-phenyl thiocyanate, m. p. 51—52°, prepared from diazotised thiocyananiline (Söderbäck, A., 1920, i, 219) and potassium iodide, with potassium hydrosulphide followed by oxidation, yields 4:4'-di-iododiphenyl disulphide and on nitration *p*-nitrophenyl thiocyanate, iodine being displaced by the nitro group. 2:4-Dinitrophenyl thiocyanate (or selenocyanate) is also obtained by boiling 1:2:4-trinitrobenzene with alcoholic potassium thiocyanate (or selenocyanate). 2:4-Dinitrophenyl thiocyanate is also obtained, together with 2:4:2':4'-tetranitrodiphenyl sulphide and disulphide, from 1-chloro-2:4-dinitrobenzene. When boiled with alcoholic aniline, the dinitrophenyl thiocyanate is converted into 2:4-dinitrodiphenylamine, 2:4:2':4'-tetranitrodiphenyl sulphide, and a trace of a product, m. p. above 280°, probably the disulphide. Some phenylthiocarbamide was also formed. *p*-Toluidine and an ethereal solution of thiocyanic acid yield *p*-tolylthiocarbamide.

R. B.

**Aromatic Hydrocarbons of Low-temperature Tar.** O. KOUBER (*Ber.*, 1924, 57, [B], 1008—1015; cf. Schütz, A., 1923, i, 195, 1080; Fischer, *ibid.*, 313, 889).—The lowest-boiling fraction of the so-called "motor-oil" fraction (b. p. 190—300°) of low-temperature tar contains benzene derivatives with long side-chains. By a process of sulphonation, separation of the sulphonic acids, and decomposition of these by the usual methods, 1:2-dimethyl-4-ethylbenzene, 1:2-dimethyl-4-isopropylbenzene, and 4-methylhydrindene (previously unknown), which are not present in coke-oven tar, have been isolated together with durene,  $\psi$ -cumene, hemimellitene, and hydrindene. 1:2-Dimethyl-4-ethylbenzene,  $d_4^{20}$  0.8704, on sulphonation gives a *sulphonic acid*, dense prisms (*sodium salt*,  $+1\frac{1}{2}\text{H}_2\text{O}$ ), yielding a *sulphonamide*, lustrous needles, m. p. 126—127°. The fraction boiling at 199—202°,  $d_4^{15}$  0.88—0.89, was sulphonated and the sulphonic acids were distilled with superheated steam, whereby the benzene hydrocarbons were removed leaving an oil,  $d$  0.93—0.94, which on sulphonation yielded 4-methylhydrindenesulphonic acid, lustrous needles (*sodium salt*,  $+1\text{H}_2\text{O}$ , *sulphonamide*, lustrous, white plates, m. p. 175°). The sodium salt on distilling from 70% sulphuric acid at 160—170° with superheated steam yields 4-methylhydrindene, having a faint characteristic odour, b. p. 203°,  $d_4^{20}$  0.9350 (*tribromo derivative*, lustrous white needles, m. p. 183°), the constitution of which follows from its oxidation with potassium permanganate to 2:6-dicarboxyphenylglyoxylic acid and hemimellitic acid, and its dehydrogenation at 650° to a mixture of indene and methylindene (*benzylidene derivative*,  $\text{C}_{17}\text{H}_{14}$ , golden-yellow plates, m. p. 93°). Hydrindene under the same conditions yields indene and a little chrysene, besides resinous products.  $\psi$ -Cumene yields a *sulphonic acid*, dense prisms, giving a *sulphonamide*, m. p. 179—180°. Hemimellitenesulphonamide has m. p. 194°. 1:2-Dimethyl-4-isopropylbenzene,  $d_4^{20}$  0.8710, yields a *sulphonic acid*, long needles (*sodium salt*; *sulphonamide*, white needles, m. p. 160—161°), and a *trinitro derivative*, lustrous prisms,

m. p. 119°. On oxidation with nitric acid, it yields *o*-xylene-*p*-carboxylic acid, colourless prisms, m. p. 164—165°, the same acid being obtained by oxidation of 1 : 2-dimethyl-4-ethylbenzene.

R. B.

**Low-temperature Tar Oils.** R. WEISSGERBER (*Brennstoff-Chem.*, 1924, 5, 208—214).—Low-temperature tar, obtained in a rotary oven from gas coal, differs from coke-oven tar in comprising mainly homologues, especially methyl homologues, rather than parent types. The homologous aromatic hydrocarbons are separated by washing with sulphuric acid, followed by sulphonation, advantage being taken of differences in the ease with which they are sulphonated and in the stability of the sulphonic derivatives. The following were identified: durene, 1 : 2 : 3-triethylxylene, 4-methylhydrindene, hydrindene,  $\psi$ -cumene, hemimellitene, 2-methyl-*p*-cymene. The fraction b. p. 226—232° gave an aromatic portion having  $d^{15}$  0.962, which was divided into a picrate-forming portion ( $d^{15}$  1.002) and a non-picrate-forming oil ( $d^{15}$  0.930); 2-methylnaphthalene and 4 : 6-dimethylhydrindene were found in these two portions respectively. Acenaphthene was identified in the neutral oils of b. p. 267—280°. Hydroaromatic compounds were converted, for identification, into their aromatic analogues by catalytic dehydrogenation at 320—330° by means of active charcoal impregnated with 5—10% of platinum, the following being found: decahydronaphthalene, methyldecahydronaphthalene (in a fraction boiling essentially at 203—206°), 1 : 6-dimethyldecahydronaphthalene. Indenes were purified by conversion first into potassium and then into sodium derivatives, and the presence of indene, methylindene, and dimethylindenes (b. p. 225—230°) was proved. Coumarones were also found. A series of ketones were isolated from fractions of b. p. 207—240°, by means of phenylhydrazine, as colourless oils of fruity odour, amongst which *p*-tolyl methyl ketone was identified (as semicarbazone) and methyl heptyl ketone was probably present.

W. T. K. B.

**New Preparation of  $\alpha$ -Phenylamino- $\alpha$ -phenyl-ethane, -propane, -butane.** Resolution of  $\alpha$ -Phenylamino- $\alpha$ -phenylethane into its Optical Antipodes and Study of the Rotatory Dispersion of One of These. R. DESCAMPS (*Bull. Soc. chim. Belg.*, 1924, 33, 269—326).—The secondary alcohols  $\text{CHPhR}\cdot\text{OH}$  ( $\text{R} = \text{Me, Et, or Pr}$ ) are converted to the extent of 40—55% into  $\alpha$ -phenylamino- $\alpha$ -phenyl-ethane, -propane, or -butane (cf. A., 1904, i, 663) by mixing with 4 mols. of aniline and 1% of *p*-toluenesulphonic acid and heating for 8—9 hours at 170—190°. Styrene is formed as a by-product to the extent of 14—16%. Reyehler's camphorsulphonic acid may also be used as the catalyst. The following constants are recorded:  $\alpha$ -Phenylethyl alcohol, m. p. 20.1°, b. p. 96°/15 mm., 93.75°/12 mm.,  $d_4^{20}$  1.0290,  $d_4^{15}$  1.0178,  $d_4^{10}$  1.0129,  $n_D^{20}$  1.5232,  $n_D^{20}$  1.5275,  $n_D^{20}$  1.5388,  $n_D^{20}$  1.5485;  $\alpha$ -phenylamino- $\alpha$ -phenylethane,  $\text{CHPhMe}\cdot\text{NHPh}$ , long needles, m. p. 26.4°, b. p. 178°/15 mm., 137°/2 mm.,  $d_4^{20}$  1.0610,  $d_4^{15}$  1.0492,  $d_4^{10}$  1.0453,  $d_4^{100}$  0.9819,  $n_D^{20}$  1.5939,

$n_D^{20}$  1.6004,  $n_B^{20}$  1.6178,  $n_Y^{20}$  1.6332; nitrosoamine, b. p. 168—169°/2 mm. (slight decomp.),  $d_4^{20}$  1.1172,  $d_4^{20}$  1.1010,  $n_a^{20}$  1.5881,  $n_D^{20}$  1.5948,  $n_B^{20}$  1.6118.  $\alpha$ -Phenylamino- $\alpha$ -phenylpropane, CHPhEt·NHPh, pale yellow oil, b. p. 192°/20 mm., 176.6°/10.5 mm., 148°/3 mm.,  $d_4^{20}$  1.0501,  $d_4^{25}$  1.0383,  $d_4^{20}$  1.0343,  $n_a^{20}$  1.5877.  $\alpha$ -Phenylamino- $\alpha$ -phenylbutane, CHPhPr·NHPh, nearly colourless oil, b. p. 209.5°/30 mm., 187.8°/12.5 mm., 167°/3.75 mm.,  $d_4^{20}$  1.0353,  $d_4^{25}$  1.0239,  $d_4^{20}$  1.0190,  $n_a^{20}$  1.5798.  $\alpha$ -Phenylamino- $\alpha$ -phenylethane was resolved by crystallisation of its camphorsulphonate from a mixture of benzene and dry ether, the more sparingly soluble salt being recrystallised from benzene until optically pure. The pure salt had  $[\alpha]_{5893}^{20} + 104.68^\circ$  and  $[\alpha]_{4358}^{20} + 243.02^\circ$  for an 11.73% alcoholic solution. The active base (one antipode only was isolated) had m. p. 49.2°, b. p. 130.2°/1.5 mm., 140°/3 mm., 170.5°/12 mm.,  $d_4^{50}$  1.0253,  $d_4^{50}$  0.9879;  $[\alpha]_D^{50} - 0.12^\circ$  and  $[\alpha]_D^{100} + 5.15^\circ$  (liquid base); its hydrochloride had m. p. 199—200°.

A large number of observations of optical rotatory power of the camphorsulphonate, the hydrochloride, and the free base in different solvents and at different concentrations and temperatures are recorded. The salts are dextrorotatory, but the sign of rotation of the free base depends on the solvent, concentration, and temperature. Between the limits  $\lambda$  5893 and  $\lambda$  4358, the curves for the rotatory dispersion of the camphorsulphonate of the active base in various solvents and for the hydrochloride in ethyl alcohol are all of the simple type; the curves for the base, fused or in solution, are either of the complex normal type or more often of the complex abnormal type; the curve for a 4.09% solution of the base in ethylene dibromide was the only one of these of simple type; the rotatory power of the base in various concentrations in absolute alcohol at 50° is a function of the concentration by weight. The rule of Darmon concerning the rotatory dispersion of mixtures in various proportions of two active substances holds for these solutions.

Two possible explanations of these results are discussed, namely, the presence of an absorption band in some part of the spectrum, or the existence in the liquid of two active substances in equilibrium. The former of these is rejected on account of the simple form of rotatory dispersion shown by the camphorsulphonate, which, having a more complex molecule than the free base, would not be expected to have an absorption band more remote in the ultra-violet. The conception of the presence of two active substances is, on the other hand, supported by all the experimental data. It is suggested that two dynamic isomerides of the base are present, the salts being derived from one of them. G. M. B.

**Absorption Spectrum of Naphthalene Vapour.** V. HENRI and H. DE LAZARÈ.—(See ii, 513.)

**Sulphonation of Fluorene.** C. COURTOT and R. GEOFFROY (*Compt. rend.*, 1924, **178**, 2259—2262).—Fluorene-2-sulphonic acid is obtained as silvery leaflets (m. p. 154—155°) by the action of chlorosulphonic acid on fluorene. It gives a *sulphochloride*,

m. p. 164°, a *sulphonamide*, m. p. 211°, and, when further sulphonated with cold chlorosulphonic acid or 95% sulphuric acid, a single disulphonic acid identical with the  $\alpha$ -compound obtained by Schmidt and others (cf. A., 1912, i, 695). This disulphonic acid gives a *disulphochloride*, m. p. 225–226°, and a *disulphonamide*, m. p. 305°. Various proofs that it is the 2 : 7-derivative are adduced.

W. T. K. B.

**Preparation of Chlorinated Amines.** DURAND et HUGUENIN S.A. (Brit. Pat. 217753).—Highly chlorinated hydro-aromatic compounds containing nitrogen (chloroketimines; cf. Brit. Pats. 193843 and 198676, this vol., i, 631) are reduced (*e.g.*, with zinc and hydrochloric acid, calcined sodium sulphide in methyl or ethyl alcohol, or ethyl alcohol alone), hydrolysis being avoided. The preparation of the following is described: tetrachloro- and pentachloro-aniline, 1 : 3 : 4-trichloro- $\beta$ -naphthylamine, 2 : 3 : 4-trichloro- $\alpha$ -naphthylamine (m. p. 162°), 1 : 3 (or 3 : 4-?)-dichloro- $\beta$ -naphthylamine (m. p. 93.5°), dichloro- and 2 : 3 : 4-trichloro- $\alpha$ -aminoanthraquinone (m. p. 204° and 210°, respectively).

W. T. K. B.

**Action of Mercuric Acetate on *m*-Toluidine and on *p*-Chloro-aniline.** L. VECCHIOTTI (*Gazzetta*, 1924, 54, 411–425; cf. A., 1919, i, 103; 1921, i, 902).—The action of mercuric acetate on *m*-toluidine in aqueous solution yields: (1) *m*-toluidinemercuriacetate, (2) the *m*-toluidinedimercuriacetate [ $\text{Me} : \text{NH}_2 : \text{Hg} : \text{Hg} = 1 : 3 : 4 : 6$ ] obtained in methyl-alcoholic solution by Schrauth and Schoeller (A., 1912, i, 930), and (3) the 1 : 3 : 2 : 5-isomeride of (2).

In the action of mercuric acetate on the three nitroanilines (cf. Jackson and Peakes, A., 1908, i, 523), the mercuriacetoxy group always assumes the para-position with respect to the amino group if such position is free, or alternatively the ortho-position, a second mercuriacetoxy group then also assuming an ortho-position. Similarly, the action of mercuric acetate on *p*-chloroaniline results in the introduction of a mercuriacetoxy group in the ortho-position to the amino group.

*m*-Toluidinedimercuriacetate [1 : 3 : 4 : 6] forms white laminae, m. p. 191°, and its *acetyl* derivative,  $\text{NHAc} \cdot \text{C}_6\text{H}_2\text{Me}(\text{Hg} \cdot \text{OAc})_2$ , tufts of needles, m. p. 250°; the latter gives 4 : 6-dibromoaceto-*m*-toluidide, m. p. 168° (cf. Neville and Winther, T., 1880, 37, 433). *m*-Toluidinedimercuri*hydroxide*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Me}(\text{Hg} \cdot \text{OH})_2$ , forms unstable, white laminae, the *chloride* lamellar crystals, m. p. 195°, and the *bromide*, small, mammillary crystals, m. p. 210°.

*m*-Toluidine-6-mercuriacetate,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{Hg} \cdot \text{OAc}$ , crystallises in small needles, m. p. 176°, and its *acetyl* derivative, m. p. 192° (impure), gives 6-bromoaceto-*m*-toluidide, m. p. 113–114° (cf. Neville and Winther, *loc. cit.*). *m*-Toluidine-2 : 5-dimercuriacetate forms lustrous white needles, m. p. 170°; the corresponding *m*-acetotoluidide, silky, white needles, m. p. 183–184°; the *dimercuri-hydroxide*, a white, lamellar mass, decomposing at 220°; the

*chloride*, acicular crystals, m. p. 239—240° (decomp.), and the *bromide*, white lamellæ, decomposing at 150°.

4-*Chloroaniline-2-mercuriacetate*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{Hg} \cdot \text{OAc}$ , crystallises in long, prismatic needles, m. p. 207°. The corresponding *mercuri-hydroxide* forms a white precipitate, and the *chloride*, minute needles, decomposing at 205°. *p-Chloroacetanilide-2-mercuriacetate* forms long needles, m. p. 200°, and is converted by chlorination into 2:4-dichloroacetanilide.

2-*Mercuridi-p-chloroaniline*,  $\text{Hg}(\text{C}_6\text{H}_3\text{Cl} \cdot \text{NH}_2)_2$ , obtained by the action of sodium thiosulphate on *p-chloroanilinemercuriacetate*, forms regular, white mammillæ, decomposing at 130°. [T. H. P.]

**Amines. IX. Some Chemical Properties of Amino-acetodiphenylamide.** E. B. KELSEY (*J. Amer. Chem. Soc.*, 1924, **46**, 1693—1700; cf. A., 1920, i, 681; 1922, i, 1141).—Attempts have been made, by the methods previously described, to prepare thiocarbimides of acetoethylanilide and acetophenylanilide (acetodiphenylamide), in which intramolecular change to thiohydantoins is precluded, but the carbethoxydithiocarbamate obtained undergoes profound decomposition and no mustard oil could be obtained. *Chloroacetoethylanilide*,  $\text{NPhEt} \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$ , white needles, b. p. 188°/35 mm., from ethylaniline and chloroacetyl chloride, with aqueous or alcoholic ammonia yields only the *tri-phenylethylamide* of triglycolamidic acid,  $(\text{NPhEt} \cdot \text{CO} \cdot \text{CH}_2)_3\text{N}$ , colourless crystals, m. p. 119°. *Chloroacetodiphenylamide*, colourless plates, with alcoholic ammonia after 4 days yields, on evaporation of the alcohol and pouring into water, a viscous mass, converted with alcohol and hydrogen chloride into the *hydrochloride* of the *didiphenylamide* of diglycolamidic acid,  $(\text{NPh}_2 \cdot \text{CO} \cdot \text{CH}_2)_2\text{NH} \cdot \text{HCl}$ , white plates, m. p. 240—245° (decomp.) [*benzoyl* derivative,  $(\text{NPh}_2 \cdot \text{CO} \cdot \text{CH}_2)_2\text{NBz}$ , glistening crystals, m. p. 200°], whilst the filtrate on evaporation yields *aminoacetodiphenylamide hydrochloride*,  $\text{NPh}_2 \cdot \text{CO} \cdot \text{CH}_2\text{NH}_2 \cdot \text{HCl}$  [*nitrate*, plates, m. p. 211—214° (decomp.)]. The *hydrated base*, yellow oil (+1H<sub>2</sub>O), after 2 months in a vacuum desiccator, gave the anhydrous *base*, long, silky needles, m. p. 53—55°. The *didiphenylamide* of diglycolamidic acid is also formed by the prolonged action of aqueous ammonia on chloroacetodiphenylamide. The action of ethyl chloroformate on aminoacetodiphenylamide in benzene gives *carbethoxyaminoacetodiphenylamide*,  $\text{NPh}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$ , silky needles, m. p. 64—65°; the *acetyl*, m. p. 157—158°, *chloroacetyl*, m. p. 117—118°, and *benzoyl*, m. p. 152°, derivatives of aminoacetodiphenylamide are prepared similarly. Carbon disulphide in alcoholic solution converts aminoacetodiphenylamide into a *dithiocarbamate*, m. p. 150—155° on sudden heating (orange *silver salt*), which in hot alcoholic solution loses hydrogen sulphide and slowly deposits pale yellow crystals of the *thiocarbamide*,  $(\text{NPh}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH})_2\text{CS}$ , m. p. 260° (decomp.), also obtained as white crystals, m. p. 258—260°, by the action of thiocarbonyl chloride on aminoacetodiphenylamide. Treatment with ethyl chloroformate in ether converts the dithiocarbamate into *carbethoxyaminoacetodiphenylamide dithiocarbamate*,

$\text{NPh}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CS} \cdot \text{S} \cdot \text{CO}_2\text{Et}$ , pale yellow needles, sintering at  $101^\circ$ , m. p.  $112\text{--}115^\circ$  (decomp.), which on distillation under reduced pressure decomposes, giving a black tar. Hydrochloric acid decomposes aminoacetodiphenylamide dithiocarbamate, but without liberation of hydrogen sulphide, giving aminoacetodiphenylamide hydrochloride, and the filtrate on treatment with mercuric chloride deposits the *mercuric* salt of the dithiocarbamate. R. B.

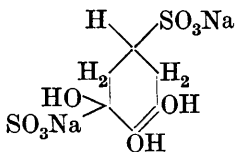
**Nitro Derivatives of *p*-Aminophenol and *p*-Aminophenoxyacetic Acid.** A. GIRARD (*Bull. Soc. chim.*, 1924, [iv], **35**, 772—779).—By nitrating *p*-acetamidophenol with the theoretical amount of nitric acid in sulphuric acid at  $-5^\circ$  with very rapid agitation, a quantitative yield of 2-nitro-4-acetamidophenol is obtained (cf. Reverdin, A., 1905, i, 51, 430; 1906, i, 165). Nitration of *p*-acetamidophenyl acetate at  $-5^\circ$  to  $5^\circ$ , and finally at  $15^\circ$ , by a modification of Hähle's method (A., 1891, 430) gives 3-nitro-4-acetamidophenol in 97% of the theoretical yield; further nitration with sulphuric acid and potassium nitrate at  $0\text{--}10^\circ$  gives a product containing 95% of 2:3-dinitro-4-acetamidophenol and 5% of 3:6-dinitro-4-acetamidophenol, fine lemon-yellow needles, m. p.  $144^\circ$ , which is hydrolysed by sulphuric acid to 3:6-dinitro-4-aminophenol, fine, nearly black needles with coppery lustre, m. p.  $166^\circ$ , subliming at higher temperatures. When diazotised and decomposed with potassium iodide, the dinitroaminophenol yields 4-iodo-3:6-dinitrophenol, lemon-yellow spangles, m. p.  $112^\circ$ . 3:6-Dinitro-4-acetamidophenol, on further nitration, yields 2:3:6-trinitro-4-acetamidophenol, whilst its silver salt with methyl iodide yields 2:5-dinitro-4-acetaniside (Reverdin and Bucky, A., 1906, i, 748). 2-Nitro-4-acetamidophenoxyacetic acid, reddish-yellow needles, m. p.  $205^\circ$ , is obtained by nitration of *p*-acetamidophenoxyacetic acid with sulphuric acid and potassium nitrate at  $-5^\circ$  to  $0^\circ$  (cf. Howard, A., 1898, i, 29), whilst nitration in acetic acid at  $0^\circ$  yields 3-nitro-4-acetamidophenoxyacetic acid, lemon-yellow needles, m. p.  $174^\circ$ , yielding the nitroamino acid of Reverdin (A., 1909, i, 913) on acid hydrolysis. Further nitration with nitric and sulphuric acids gives the dinitro-acid, m. p.  $207^\circ$ , obtained by Howard, which is now shown to be 2:3-dinitro-4-acetamidophenoxyacetic acid by the synthesis of its *ethyl* ester, m. p.  $155^\circ$ , from silver 2:3-dinitro-4-acetamidophenoxide and *ethyl* bromoacetate. R. B.

**Oxidation Induced by Metals.** J. ALOY and A. VALDIGUÉ (*Bull. Soc. chim.*, 1924, [iv], **35**, 792—794; cf. A., 1923, ii, 552).—The oxidation of quinol is catalysed by uranium acetate with production of an intense red coloration (cf. A., 1903, ii, 581; 1905, ii, 616) and precipitation of quinhydrone. Traces of hydrochloric acid do not affect the reaction, but the formation of quinhydrone is prevented by an excess of mineral acid. In the presence of ammonium chloride, the catalytic oxidation of quinol yields a red colouring matter which resembles the quinoneimides in its reactions. Salts of manganese, iron, copper, vanadium, uranium, mercury, lead, and cobalt catalyse the reaction by fixing atmospheric oxygen, whilst magnesium, aluminium, cadmium, zinc, and nickel are

inactive. The alkali salts are also inactive except those possessing a peroxidic structure, such as persulphates, perborates, iodates, and periodates.

R. B.

**Tautomerism of Phenols. VI. Pyrogallol and Hydroxyquinol.** W. FUCHS and B. ELSNER (*Ber.*, 1924, 57, [B], 1225—1231).—Pyrogallol is converted by very protracted heating with an aqueous solution of sodium hydrogen sulphite (2 mols.) into the *sodium hydrogen sulphite* additive compound of *sodium 3:4-dihydroxy-5-keto-1:2:5:6-tetrahydrobenzene-1-sulphonate* (annexed formula). Under similar conditions but with



greater rapidity, hydroxyquinol gives the *sodium hydrogen sulphite* additive compound of *sodium 5:6-dihydroxy-3-keto-1:2:3:4-tetrahydrobenzene-1-sulphonate*. The compounds readily lose a molecule of sodium hydrogen sulphite when acted on by hydrogen peroxide, and yield respectively *sodium 3:4-dihydroxy-5-keto-1:2:5:6-tetrahydrobenzenesulphonate* and *sodium 5:6-dihydroxy-3-keto-1:2:3:4-tetrahydrobenzenesulphonate*, which are isolated by taking advantage of their solubility in acetone. The reaction with ferric chloride is similar to that of pyrocatechol. The action of diazomethane in the presence of acetone yields a *mono-methyl* derivative in each case. The presence of the ketonic group in the compound derived from hydroxyquinol is established by the isolation of a *phenylhydrazone*,  $C_{12}H_{13}O_5N_2SNa$ . Bromine in anhydrous solvents has no action on the mono- or di-products; in aqueous solution, a maximal absorption of one molecular proportion of halogen is observed.

H. W.

**New Catalytic-electrolytic Method of Reduction.** F. ISHIWARA (*Ber.*, 1924, 57, [B], 1125—1126).—The apparatus consists of a round-bottomed vessel which can be suspended so as to permit continuous agitation and through which a current of hydrogen or other gas can be passed. It is pierced near the base by a hole provided with a rubber stopper through which a palladium cathode passes. An opening in the top of the vessel carries a small porous cell containing dilute hydrochloric acid and a nickel anode. During reduction, a current of hydrogen is passed into the vessel. The reducing action of the catalyst appears to be strengthened greatly by the passage of the electric current, but reduction is also effected partly directly at the cathode. 4- $\alpha$ -Methylaminoacetylpyrocatechol hydrochloride is smoothly reduced to 4- $\alpha$ -hydroxy- $\beta$ -methylaminoethylpyrocatechol,  $NHMe \cdot CH_2 \cdot CH(OH) \cdot C_6H_3(OH)_2$ , m. p. 230°, the yield being 96% of the theoretical. 4-*p*-Carbethoxyanilinoacetylpyrocatechol,  $CO_2Et \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CO \cdot C_6H_3(OH)_2$ , m. p. 201°, is prepared by the action of ethyl *p*-aminobenzoate on 4-chloroacetylpyrocatechol in boiling alcoholic solution.

H. W.

**History of Ketopinic Acid and "Norcamphane-1-carboxylic Acid."** P. LIPP (*Ber.*, 1924, 57, [B], 1071).—Since the acid obtained by Wedekind from ketopinic acid (this vol., i, 639) still

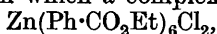


contains two methyl groups, the name *apocamphane-1-carboxylic acid* is preferred, but this name has been assigned by Wedekind to an acid of unknown constitution obtained by Bredt and May (A., 1910, i, 32). The author obtained *apocamphanonitrile* from bromocamphanehydroxamyl bromide (A., 1914, i, 305), and this on hydrolysis yields quantitatively the *apocamphane-1-carboxylic acid*, m. p. 221—222°, described by Wedekind. In Wedekind's papers (this vol., i, 639; 1923, i, 346) Komppa's synthesis of pinophanic acid (A., 1911, i, 642), the acid hydrolysis product of ketopinic acid, has been overlooked.

R. B.

### Action of Metals on Acid Chlorides in presence of Ether.

H. P. KAUFMANN and C. FUCHS (*Arch. Pharm.*, 1924, 262, 119—125).—Zinc, benzoyl chloride, and ether interact to yield ethyl chloride and an oil, from which a complex compound,



crystallises after some time in colourless needles; it is decomposed into its components by water. The oily mother-liquor is ethyl benzoate containing an amorphous compound,  $\text{C}_{16}\text{H}_{12}\text{O}$ , m. p. 125—130°. The relative amount of the latter increases as the proportion of ether used decreases. Two reactions appear to be taking place, in one of which co-ordination compounds containing ether are produced which then undergo a complex change; the zinc chloride formed brings about the formation of ethyl benzoate (cf. Descudé, A., 1903, i, 735; Blaise, A., 1905, i, 255). Aluminium chloride has the same effect but aluminium itself does not behave like zinc. Acetyl chloride, ether, and zinc yield ethyl chloride, ethyl acetate, and an amorphous yellow substance, but no metallic complex compound. Phthalyl chloride treated in the same way (and heated) gives diethyl phthalate, phthalic anhydride (presumably by partial esterification and subsequent scission of ethyl chloride), a little amorphous, yellow substance and a compound,  $\text{C}_7\text{H}_4\text{O}_2$ , m. p. 182°. Anisole, benzoyl chloride, and zinc react vigorously to yield chiefly *p*-methoxybenzophenone; some benzaldehyde is formed by reduction of the benzoyl chloride, the hydrogen chloride formed in the main reaction attacking the unused zinc (cf. Blaise, *loc. cit.*).

W. A. S.

### Application of the Principle of the Schotten-Baumann Benzoylation Process to Acid Anhydrides.

W. AUTENRIETH and G. THOMAE (*Ber.*, 1924, 57, [B], 1002—1008).—The acylation of phenols may be readily effected by acid anhydrides in the presence of sodium hydroxide. The best yields of ester are obtained with double the theoretical quantity of sodium hydroxide; excess of anhydride does not appreciably increase the yield. Acylation of aniline and other bases proceeds best in the absence of sodium hydroxide, and the yields are diminished by excess of this reagent and increased by excess of anhydride. Solid anhydrides must be melted, as the reaction only proceeds in the liquid phase. Anhydrides the melting points of which lie above 100° scarcely react, but *m*-nitrobenzoic anhydride, m. p. 159°, which melts under boiling water, gives 25% of the theoretical yield of *phenyl m*-nitrobenzoate,

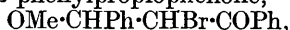
laminæ, m. p. 99°, and 16% of the theoretical yield of *m*-nitrobenzanilide. Alcohols react much less readily than the phenols and only small amounts of the alkyl esters are formed. Although *p*-bromobenzoyl chloride reacts with aqueous methyl alcohol when the concentration of the alcohol is as low as 0.1% (cf. A., 1920, ii, 776), with ethyl alcohol of less than 5% concentration, and sodium hydroxide weaker than 10–15%, *p*-bromobenzoic anhydride is formed almost exclusively. *n*-Propyl and *iso*-amyl alcohols, secondary and tertiary alcohols, borneol, menthol, sabinol, and santalol behave similarly, whilst benzyl alcohol, glycerol, phenol, cresols, and eugenol yield the corresponding *p*-bromobenzoates. Since the anhydride is not formed when *p*-bromobenzoyl chloride and sodium *p*-bromobenzoate are heated with dilute sodium hydroxide at 45°, it is concluded that the formation of *p*-bromobenzoic anhydride under the conditions given is due to the catalytic effect of the alcohols in question. The following esters and anilides were prepared by this method: phenyl benzoate, *p*-tolyl benzoate, resorcinyll benzoate, phloroglucinol tribenzoate, phenyl phenylacetate, phenyl *p*-toluate, *p*-tolyl *p*-toluate, *resorcinyll diphenylacetate*,  $C_6H_4(CO_2 \cdot CH_2Ph)_2$ , needles, m. p. 62–63°, *resorcinyll di-p-toluate*,  $C_6H_4(CO_2 \cdot C_6H_4Me)_2$ , long prisms, m. p. 137–138°, *benzo-piperidide*, dense prisms, m. p. 49°, *p-toluopiperidide*, lustrous plates, m. p. 55–58°, benzanilide,  $\alpha$ -phenylacetanilide, *p*-toluanilide, benzo-*p*-toluidide, and phenylaceto-*p*-toluidide. R. B.

**Compound of "Benzocaine" and Iodine.** L. E. WARREN (*Repts. Lab. Amer. Med. Assoc.*, 1923, 16, 97–99).—"Benzocaine" [ethyl *p*-aminobenzoate] forms a brown compound, probably containing 2 equivalents of iodine per mol., when iodine is added to its solution in dilute hydrochloric acid.

CHEMICAL ABSTRACTS.

**Alcoholysis of Esters of  $\alpha\beta$ -Unsaturated Acids and of the Corresponding Saturated Analogues.** B. DASANNACHARYA.—(See i, 937.)

**Addition of Methyl Hypobromite to certain Ethylene Derivatives.** J. B. CONANT and E. L. JACKSON (*J. Amer. Chem. Soc.*, 1924, 46, 1727–1730).—The action of bromine on a solution of cinnamic acid in methyl alcohol containing 15% of water gives dibromocinnamic acid and  $\alpha$ -bromo- $\beta$ -methoxy- $\beta$ -phenylpropionic acid,  $OMe \cdot CHPh \cdot CHBr \cdot CO_2H$ , m. p. 182–183°, an identical product with this melting point being obtained on repeating Schrauth's work (A., 1922, i, 1125). Similarly, phenyl styryl ketone yields  $\alpha$ -bromo- $\beta$ -methoxy- $\beta$ -phenylpropiophenone,



together with a little dibromide. The reaction apparently involves the formation of methyl hypobromite, and the mechanism of the addition is probably as follows:  $Br_2 + MeOH \rightleftharpoons MeOBr + HBr$ ;  $>C:C < + MeOBr \rightarrow >C(OMe) \cdot CBr <$  (cf. Read and Andrews, T., 1921, 119, 1774).

R. B.

**Unsaturated Compounds. XI. Action of Free Hydroxylamine on Cinnamic Acid and its Nuclear Homologues.** T. POSNER and G. SCHREIBER (*Ber.*, 1924, **57**, [B], 1127—1137).—The action of hydroxylamine on cinnamic acid yields primarily  $\beta$ -hydroxylamino- $\beta$ -phenylpropionic acid, which further undergoes reduction and oxidation to  $\beta$ -amino- $\beta$ -phenylpropionic acid and  $\beta$ -oximino- $\beta$ -phenylpropionic acid; the latter substance is unstable and loses carbon dioxide with formation of acetophenoneoxime or water with production of phenylisooxazolone. Extension of these observations to *o*-, *m*-, and *p*-methylcinnamic acids shows that the additive capacity of the different acids for hydroxylamine is inversely proportional to the strength of the acids and that the hydroxylamino-acid is most readily reduced to the corresponding amino-acid when the former is produced with the greatest difficulty. Differences in the readiness of addition of hydroxylamine are not observed when the acids are replaced by their methyl esters.

The determination of the dissociation constants of the acids is rendered difficult by their very sparing solubility in water. The following data are recorded with reserve: *o*-methylcinnamic acid (2.53), cinnamic acid (2.19), *p*-methylcinnamic acid (1.82), *m*-methylcinnamic acid (1.57).

$\beta$ -Hydroxylamino- $\beta$ -*o*-tolylpropionic acid is oxidised by ammoniacal silver nitrate solution to 3-*o*-tolylisooxazolone, m. p. 89—91°, which yields 4-oximino-3-*o*-tolylisooxazolone,

$$\text{C}_6\text{H}_4\text{Me}\cdot\text{C}\begin{array}{c} \text{---} \text{C} \text{---} \text{NOH} \\ \text{N} \cdot \text{O} \cdot \text{CO} \end{array}$$

m. p. 127—128°.  $\beta$ -Amino- $\beta$ -*o*-tolylpropionic acid, m. p. 242° (decomp.), is converted into the benzoyl derivative, m. p. 197°, and  $\beta$ -carbamido- $\beta$ -*o*-tolylpropionic acid,

$\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 182—183°; the latter substance passes when heated at 230—235° into 4-*o*-tolylidihydrouracil,  $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\begin{array}{c} \text{CH}_2\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array}\text{NH}$ , m. p.

223—225°.  $\beta$ -Amino- $\beta$ -*o*-tolylpropionanilide, m. p. 135—136°, and methyl *o*-tolyl ketoxime, m. p. 61°, are also described. The following compounds are prepared from *m*-methylcinnamic acid:  $\beta$ -Hydroxylamino- $\beta$ -*m*-tolylpropionic acid, m. p. 158°; 3-*m*-tolylisooxazolone, m. p. 82—83°; 4-benzeneazo-3-*m*-tolylisooxazolone, m. p. 142—143°, which is converted by phenylhydrazine into benzeneazo-*m*-tolylphenylpyrazolone, m. p. 141°;  $\beta$ -amino- $\beta$ -*m*-tolylpropionic acid, m. p. about 225° (decomp.), according to the rate of heating;  $\beta$ -benzoylamino- $\beta$ -*m*-tolylpropionic acid, m. p. 154.5°;  $\beta$ -carbamido- $\beta$ -*m*-tolylpropionic acid, m. p. 89°; 4-*m*-tolylidihydrouracil, m. p. 191°;  $\beta$ -amino- $\beta$ -*m*-tolylpropionanilide, m. p. 106—107°; methyl *m*-tolyl ketoxime, m. p. 57°;  $\beta$ -hydroxylamino- $\beta$ -*m*-tolylpropionhydroxamoxime hydrate,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{NH}\cdot\text{OH})\cdot\text{CH}_2\cdot\text{C}(\text{NH}\cdot\text{OH})_2\cdot\text{OH}$ . *p*-Methylcinnamic acid gives rise to the following derivatives: 4-Benzeneazo-3-*p*-tolylisooxazolone, m. p. 176°; benzeneazo-*p*-tolylphenylpyrazolone, m. p. 173°;  $\beta$ -amino- $\beta$ -*p*-tolylpropionanilide, m. p. 127—128°;  $\beta$ -hydroxylamino- $\beta$ -*p*-tolylpropionhydroxamoxime hydrate, m. p. 128—129°.

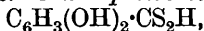
Rapid chlorination of *m*-xylene at its boiling point under the

influence of ultra-violet light until the gain in weight corresponding with the absorption of one atomic proportion of chlorine is attained gives a mixture of unchanged *m*-xylene, *m*-xylyl chloride, and *m*-xylylene dichloride, m. p. 33–34°. H. W.

**Substituted Salicylic Acids. IV.** H. P. KAUFMANN and M. THOMAS (*Arch. Pharm.*, 1924, 262, 117–119; cf. i, 175).—Chloroacetylsalicylic acid interacts in alcohol solution with gaseous ammonia in presence of copper, yielding *glycylsalicylic acid*,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , the *hydrochloride* of which has m. p. 70°; the *ammonium* salt is described. When potassium methyl salicylate and glycyl chloride hydrochloride (Fischer, A., 1905, i, 863, 892) are heated in benzene, the *methyl* ester of the above is obtained, needles, m. p. 195°. *Hippurylsalicylic* (*benzoylglycylsalicylic*) acid, m. p. 119°, is similarly produced from sodium salicylate and hippuryl chloride (Fischer, *loc. cit.*); its *phenyl* ester, from the potassium compound of phenyl salicylate (salol), has m. p. 45°. W. A. S.

**Method of Preparation of Organic Dithio-acids.** G. BRUNI and T. G. LEVI (*Gazzetta*, 1924, 54, 389–395).—Organic dithio-acids of the aromatic series may be readily obtained by the action of yellow ammonium sulphide on the corresponding aldehydes; the presence of alcohol as a solvent of the aldehyde is sometimes advantageous, but is not necessary (cf. Bloch and Höhn, A., 1910, i, 256; White, P., 1914, 37).

Dithiosalicylic acid, its zinc and lead salts, and the corresponding disulphide (Bloch and Höhn, *loc. cit.*) have been prepared in this way, also dithioanisic acid and its zinc and lead salts (the disulphide has m. p. 150°; Bloch and Höhn found 161–163°), and the following compounds. *Dithioprotocatechuic acid*,



forms a violet-red oil, its *zinc* salt being reddish-brown and its *lead* salt forming unstable, reddish-brown crystals. *Dithiovanillic acid*,  $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CS}_2\text{H}$ , forms a red, crystalline mass, its *zinc* and *lead* salts orange-yellow crystals, and the corresponding *disulphide* red crystals. *Dithiopiperonylic acid*,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CS}_2\text{H}$ , prepared from piperonaldehyde, forms a red, crystalline mass, its *zinc* salt orange-red needles, its *lead* salt orange crystals, and the *disulphide* greenish-yellow crystals, m. p. 146°. *Dithiocinnamic acid* forms a red oil and its *zinc* and *lead* salts red crystals. *Dithio-*

*pyromucic acid*,  $\text{CS}_2\text{H}\cdot\text{C}\begin{smallmatrix} \diagup \text{CH}\cdot\text{CH} \\ \diagdown \text{O}-\text{CH} \end{smallmatrix}$ , forms a stable, violet-red oil, its *zinc* and *lead* salts orange crystals, and its *disulphide* purple-red crystals, m. p. 89.5–90.5°.

The zinc salts of the above acids act as accelerators in the vulcanisation of rubber and more pronounced effects are shown by the disulphides, which, if used in large proportion or if vulcanisation is protracted, exhibit an auto-accelerating action.

The action of ammonium polysulphide in excess on aliphatic aldehydes, diluted with a suitable solvent, furnishes an excellent

method for the rapid preparation of the corresponding thioaldines. Formaldehyde, however, behaves differently, the resulting product being a white, crystalline base containing nitrogen and sulphur which is being investigated.

T. H. P.

**Nitro- and Amino-iodohydroxybenzoic Acids.** P. BRENANS and C. PROST (*Compt. rend.*, 1924, 178, 1824—1826).—The action of iodine on 5-nitrosalicylic acid ( $\text{CO}_2\text{H}:\text{OH}:\text{NO}_2=1:2:5$ ) in presence of mercuric oxide yielded 3-iodo-5-nitrosalicylic acid, white needles, m. p.  $228^\circ$  (decomp.), together with 2:6-di-iodo-4-nitrophenol, needles, m. p.  $155^\circ$ ; these compounds were separated by fractional crystallisation of their barium and sodium salts. Reduction of the former substance by stannous chloride yields 3-iodo-5-aminosalicylic acid hydrochloride, white needles, from which the acid, silvery plates, decomp.  $215^\circ$ , is prepared by the action of sodium acetate. The hydrochloride on treatment with amyl nitrite affords 3-iodosalicylic acid (cf. A., 1923, i, 797). 5-Iodo-3-nitrosalicylic acid, pale yellow needles, m. p.  $105^\circ$ , mixed with some 4:6-di-iodo-2-nitrophenol, yellow needles, m. p.  $98^\circ$ , was obtained from 3-nitrosalicylic acid in a similar manner to its isomeride. Its ethyl ester forms pale yellow plates, m. p.  $129^\circ$ ; the acid on reduction yields 5-iodo-3-aminosalicylic acid, brilliant white needles, changing at  $190$ — $200^\circ$  without melting; treatment with amyl nitrite affords 5-iodosalicylic acid (*loc. cit.*). 5-Iodo-3-nitro-4-hydroxybenzoic acid, small lemon-yellow needles, m. p.  $240^\circ$  (decomp.), is formed together with 4:6-di-iodo-2-nitrophenol from iodine and 3-nitro-4-hydroxybenzoic acid; ethyl ester, yellow needles, m. p.  $105^\circ$ ; corresponding amino-acid, needles, decomp.  $155^\circ$ , hydrochloride, white needles.

H. J. E.

**o-Benzoylbenzoic Acids containing Fluorine, Iodine, and Sulphur.** F. C. HAHN and E. E. REID (*J. Amer. Chem. Soc.*, 1924, 46, 1645—1653).—Aromatic fluorine derivatives readily condense with phthalic anhydride in the presence of aluminium chloride, yielding white fluorobenzoyl-o-benzoic acids which on heating with sulphuric acid at  $100$ — $150^\circ$  are converted into pale yellow anthraquinones. Fluorobenzene gives in 90% of the theoretical yield p-fluorobenzoyl-o-benzoic acid, m. p.  $137$ — $137.5^\circ$  (methyl ester, m. p.  $93.5^\circ$ ; ethyl ester, m. p.  $80.5^\circ$ ; propyl ester, b. p.  $200^\circ/8$  mm.; butyl ester, b. p.  $225^\circ/8$  mm.), yielding p-hydroxybenzoyl-o-benzoic acid on hydrolysis with sodium hydroxide, p-fluorobenzoyl-o-benzoic acid, m. p.  $148$ — $149^\circ$ , on reduction by Scholl's method (A., 1911, i, 1007) and  $\beta$ -fluoroanthraquinone, m. p.  $203$ — $204^\circ$ , on treatment with sulphuric acid. From p-fluorotoluene is obtained, in 96% of the theoretical yield, 5-fluoro-2-methylbenzoyl-o-benzoic acid, m. p.  $150^\circ$  (methyl ester, m. p.  $79.5$ — $80^\circ$ ; ethyl ester, oil) condensing to 4-fluoro-1-methylanthraquinone, m. p.  $155$ — $156^\circ$ , which is oxidised by nitric acid to 4-fluoroanthraquinone-1-carboxylic acid, m. p. about  $250^\circ$ , and losing carbon dioxide to give probably  $\alpha$ -fluoroanthraquinone, m. p.  $128$ — $129^\circ$ . Similarly, o-fluorotoluene gives 96% of the theoretical yield of 3-fluoro-4-methylbenzoyl-o-benzoic acid, m. p.

153.5—154° (*methyl* ester, m. p. 108°; *ethyl* ester, m. p. 74°), oxidised by alkaline permanganate to 3-fluorobenzophenone-2':4-dicarboxylic acid, m. p. 183—184° (sintering at 175°), and condensing to 3-fluoro-2-methylanthraquinone, m. p. 172°, oxidised by nitric acid to 3-fluoroanthraquinone-2-carboxylic acid, m. p. 183—185°, which loses carbon dioxide on heating and gives  $\beta$ -fluoroanthraquinone. 4-Fluoro-*m*-xylene yields a mixture of 5-fluoro-2:4-dimethylbenzoyl-*o*-benzoic acid (giving 4-fluoro-1:3-dimethylanthraquinone, m. p. 178°), and 3-fluoro-2:6-dimethylbenzoyl-*o*-benzoic acid, yellow needles, m. p. 126°, which gives no anthraquinone.

Iodobenzene and phthalic anhydride, with aluminium chloride in carbon disulphide, yield chiefly benzoyl-*o*-benzoic acid and iodine, but from the product by treatment with chlorine in chloroform solution *p*-iodobenzoyl-*o*-benzoic acid chloride,  $C_{14}H_9O_3Cl_2I$ , yellow granules, was obtained, melting with loss of chlorine without explosion. On treatment with chloroform, water, and sodium thiosulphate it yields *p*-iodobenzoyl-*o*-benzoic acid, m. p. 200° (*methyl* ester, m. p. 104—104.5°; *ethyl* ester, 81.5—82°; *propyl* ester, m. p. 52°; *butyl* ester, oil), and by solution in sodium hydroxide and acidification with hydrochloric acid is converted into *p*-iodosobenzoyl-*o*-benzoic acid, m. p. 179—180°. Treatment of *p*-iodobenzoyl-*o*-benzoic acid with sulphuric acid at 150—160° yields  $\beta$ -iodoanthraquinone, m. p. 175°. Phenyl methyl sulphide condenses with phthalic anhydride in the presence of aluminium chloride, yielding *p*-methylthiolbenzoyl-*o*-benzoic acid, fine, white needles, m. p. 154°, oxidised by chromic anhydride in acetic acid to *p*-methylsulphonylbenzoyl-*o*-benzoic acid,  $SO_2Me \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot CO_2H$ , white flakes, m. p. 221°, condensing in sulphuric acid to anthraquinone- $\beta$ -methylsulphone. Details are given for the determination of fluorine in organic compounds by fusion with sodium peroxide, calcium fluoride being precipitated and washed under standardised conditions. The following esters have been prepared: *methyl p*-chlorobenzoyl-*o*-benzoate, m. p. 110° (corresponding *ethyl* ester, m. p. 88°; *propyl* ester, m. p. 45°; *butyl* ester, oil); *methyl p*-bromobenzoyl-*o*-benzoate (*ethyl* ester, m. p. 83.5°; *propyl* ester, m. p. 51°; *butyl* ester, oil), and *methyl m*-nitrobenzoyl-*o*-benzoate, m. p. 100° (*ethyl* ester, m. p. 84°).

R. B.

**Sparassol.** E. WEDEKIND and K. FLEISCHER (*Ber.*, 1924, 57, [B], 1121—1123; cf. Wedekind and Fleischer, this vol., i, 174).—The authors agree with the conception of Pfau (this vol., i, 512) and Späth and Jeschki (*ibid.*, i, 513) that sparassol is methyl 4-hydroxy-6-methoxy-*o*-toluate.

4:6-Dimethoxy-*o*-toluic acid is remarkably stable towards alkaline permanganate, whereas 2:6-dimethoxy-*p*-toluic acid is readily oxidised to 2:6-dimethoxyterephthalic acid, m. p. 295°.

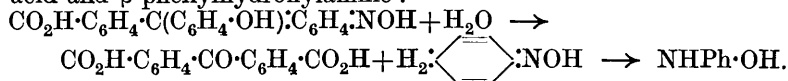
H. W.

**The Oximic and Iminic Compounds of Phenolphthalein.** B. ODDO and D. CURTI (*Atti R. Accad. Lincei*, 1924, [v], 33, i, 354—357).—Previous results having shown that coupling with

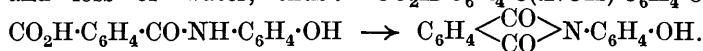
diazo salts serves as a means for determining the structure of the unstable phthaleins (A., 1913, i, 1110; 1916, i, 87), attention has now been directed to the oxime and imide of phenolphthalein. In presence of the amount of alkali hydroxide required by a molecule containing three replaceable hydrogen ions, treatment of the oxime with a diazo salt (1 or 3 mols.) results in the introduction into the molecule of only one azo group, whereas with the imide both mono- and bis-azo compounds are obtainable.

This difference in behaviour is explained on the assumption that, in so far as these coupling reactions are concerned, the oxime exhibits a quinonoid structure and thus gives the monoazo compound,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NOH})\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{N}_2\text{R}$ , whilst the imide is lactoid and thus yields the mono- and bis-azo compounds,  $\text{CO}<\text{C}_6\text{H}_4>\text{C}<\text{C}_6\text{H}_3(\text{OH})\cdot\text{N}_2\text{R}$  and  $\text{CO}<\text{C}_6\text{H}_4>\text{C}[\text{C}_6\text{H}_3(\text{OH})\cdot\text{N}_2\text{R}]_2$ . In correspondence with these formulæ, the azo derivative of the oxime readily furnishes a diacetyl compound, whereas each of the imide derivatives yields a triacetyl compound.

When prepared in the ordinary way, phenolphthaleinoxime is always accompanied by the *p*-hydroxyphthalanil, obtained by Piutti by fusion of phthalic anhydride with *p*-aminophenol (A., 1886, 1026) and by Meyer by treating phenolphthaleinoxime, suspended in alcohol, with concentrated aqueous hydroxylamine hydrochloride solution (A., 1899, i, 707). The authors do not accept Meyer's explanation of the mechanism of formation of this phthalanil. Since phenolphthaleinoxime remains unaltered when treated with a faintly alkaline, absolute or 75% alcoholic solution of free hydroxylamine, the acid of the hydrochloride probably hydrolyses the oxime, giving *p*-hydroxybenzoyl-*o*-benzoic acid and  $\beta$ -phenylhydroxylamine:



The acid then yields the oxime, which undergoes isomerisation and loss of water, thus:  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NOH})\cdot\text{C}_6\text{H}_4\cdot\text{OH} \rightarrow$



The fact that only one azo group can be introduced into the molecule of dichlorophenolphthalein (cf. Consonno and Apostolo, A., 1921, i, 346) may be explained by the presence of the two chlorine atoms.

*p*-Hydroxyphthalanil forms pale yellow, lamellar crystals, m. p. 286°, and its *acetyl* derivative, white crystals, m. p. 235–236°. *Benzeneazophenolphthaleinoxime*,  $\text{C}_{26}\text{H}_{19}\text{O}_4\text{N}_3$ , forms dark green crystals, m. p. 202°, and its *diacetyl* compound, acicular crystals, m. p. 231–232°. *Benzeneazophenolphthaleinimide*,  $\text{C}_{26}\text{H}_{19}\text{O}_3\text{N}_3$ , forms minute, pale yellow crystals, m. p. 248–250°; its *triacetyl* derivative has m. p. 183°. *Bisbenzeneazophenolphthaleinimide*,  $\text{C}_{32}\text{H}_{23}\text{O}_3\text{N}_5$ , forms small, brownish-yellow crystals, m. p. 270–272°, and its *triacetyl* compound, brown, microscopic crystals, m. p. 207–208°.

T. H. P.

**Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. V. Preparation of Primary Alcohols by the Catalytic Hydrogenation of Aldehydes.** W. H. CAROTHERS and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, **46**, 1675—1683; cf. A., 1923, ii, 310).—The platinum oxide catalyst of Voorhees and Adams (A., 1922, ii, 558; cf. Adams and Shriner, A., 1923, ii, 773) has now been used for the reduction of a number of aldehydes, both aromatic and aliphatic. No promoter more powerful or satisfactory than ferrous chloride has been found, and the reductions were carried out in the presence of 0.1 millimol. of ferrous chloride and 0.1725 g. of platinum oxide catalyst per 0.2 g.-mol. of aldehyde. Absorption of hydrogen is very slow in the absence of a solvent, and the most satisfactory general solvent is 95% ethyl alcohol. The effect of the solvent is to some extent specific, and solvents such as acetone or glacial acetic acid which give satisfactory results with benzaldehyde may give much slower reductions or undesirable secondary effects with other aldehydes. With technical methyl alcohol, benzaldehyde showed incomplete reduction (70%) owing to the formation of the dimethylacetal, but in the presence of 0.00034 mol. of sodium hydroxide or sodium methoxide the reduction was rapid and normal. The addition of alkali prevents acetal formation with the aliphatic aldehydes and also prevents the polymerisation of certain phenolic aldehydes which are very sensitive to traces of acid. The total reduction time may be decreased or increased by the addition of alkali, and the use of alkali is dependent on the specific case. By this method salicylaldehyde, vanillin, anisaldehyde, and piperonaldehyde give 92—96% of the theoretical yield of the corresponding alcohol in periods up to 1 hour, alkali being used in the first three cases. *p*-Chloro-, *p*-bromo-, and *o*-chloro-benzaldehyde are rapidly reduced to the corresponding alcohols in 92—96% of the theoretical yield, and the formation of appreciable amounts of halogen acid was not observed. Aldol gives an 86% yield of butan-1:3-diol in 2 hours, and in the same period butyraldehyde is completely reduced to the alcohol, the addition of alkali in the latter case (as with heptaldehyde) preventing acetal formation. With dextrose and other aldoses, the reduction by this method is too slow to be practicable. Resorcyaldehyde and *p*-dimethylaminobenzaldehyde were reduced readily, but only viscous products could be isolated. R. B.

**Action of Nitroso Derivatives on Unsaturated Compounds. II. Synthesis of  $\alpha$ -Ketodinitrones.** L. ALESSANDRI (*Gazzetta*, 1924, **54**, 426—450; cf. A., 1915, i, 555; 1921, i, 730).—The action of nitrosobenzene on styrene is analogous to that on asarone the products being the *N*-phenyl derivative of benzaldoxime (phenyl-*N*-phenylnitron),  $\text{CHPh}\cdot\text{NPh}\cdot\text{O}$ , azoxybenzene, formic acid, benzaldehyde, and benzoic acid. Miescher ("Nitron and Nitrene," Dissertation, Zurich, 1918) found that nitrosobenzene and benzophenone hydrazone react to form the ketonitron, diphenyl-*N*-phenylnitron, and azoxybenzene. The author now finds that towards the *N*-phenyl ether of piperonaldoxime, which



is an aldonitrone with the same C:N grouping as this hydrazone but with the nitrogen quinquivalent and oxygenated, nitroso-benzene exhibits a more profound oxidising action, piperonaldehyde and azoxybenzene being formed in good yields.

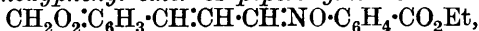
In acetic acid solution, the action of ethyl *p*-nitrosobenzoate on toluene (cf. A., 1922, i, 558) results in the addition of this nitroso compound to the multiple linking of the toluene with formation of the *NN*-di-*p*:*p*'-carbethoxyphenyl ether of benzildioxime,  $[\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{NO}\cdot\text{CPh}]_2$ , together with traces of benzoic acid and a small proportion of ethyl azoxybenzene-*p*:*p*'-dicarboxylate; the latter is also formed, together with benzil as principal product, and traces of benzoic acid, when the reaction occurs in chloroform solution. In this solvent, the action of nitrosobenzene on toluene yields the ketodinitrone,  $(\text{O}\cdot\text{NPh}\cdot\text{CPh})_2$ , the diversity in the behaviour of these two nitroso compounds being possibly dependent on the nature of the substituent in the para-position with respect to the nitroso group.

The action of nitrosobenzene on safrole yields the aldonitrone,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NPh}\cdot\text{O}$ , obtained by the condensation of piperonylacrolein with phenylhydroxylamine, together with azoxybenzene as secondary product. The interaction of ethyl *p*-nitrosobenzoate and safrole in ethereal solution gives ethyl azoxybenzene-*p*:*p*'-dicarboxylate and a small proportion of the *N*-*p*-carbethoxyphenyl ether of piperonylacroleinoxime.

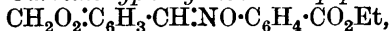
The action of hydrazine sulphate on the *N*-phenyl ether of benzaldoxime yields benzaldazine and *p*-aminophenol.

The *NN*-di-*p*:*p*'-carbethoxyphenyl ether of benzildioxime (see above) forms masses of short, dull, sulphur-yellow crystals, m. p. 182—183° (decomp.) when heated rapidly, decomposing at about 178° when heated slowly, and resinifying rapidly in direct sunlight. When hydrolysed by means of dilute sulphuric acid in presence of alcohol, it yields benzil, ethyl azoxybenzene-*p*:*p*'-dicarboxylate, and the corresponding acid.

*N*-*p*-Carbethoxyphenyl ether of piperonylacroleinoxime,



forms short, orange crystals or minute needles, decomposing at 197—198°. *N*-*p*-Carbethoxyphenyl ether of piperonaldoxime,



prepared by the action of ethyl β-phenylhydroxylamine-*p*-carboxylate on piperonaldehyde, forms minute, flat, straw-yellow crystals, m. p. 145.5°. The last two compounds resinify rapidly with an odour of piperonaldehyde when exposed to direct sunlight.

T. H. P.

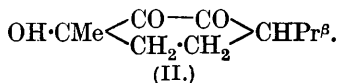
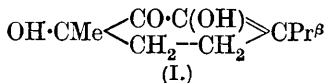
**Preparation of Phenylcarbamyldhydrazones of cyclo-Hexenones.** H. MAZOUREWITCH (*Bull. Soc. chim.*, 1924, [iv], 35, 779—784).—The action of aniline on the semicarbazones and semicarbazidesemicarbazones of αβ-unsaturated cyclic ketones is analogous to that observed by Borsche (A., 1902, i, 486; 1904, i, 945; 1905, i, 305), ammonia being evolved with production of the phenylsemicarbazones (phenylcarbamyldhydrazones). Mesityl

oxide is an exception, the action of aniline on its semicarbazide-semicarbazone yielding hydrazodicarbonamide,  $C_2H_6O_2N_4$ , yellowish crystals, m. p. 228—230° (decomp.), and *s*-diphenylcarbamide, m. p. 234—236°. The semicarbazidesemicarbazone of 3-methyl- $\Delta^2$ -cyclohexenone yields the *phenylsemicarbazone*,  $C_{14}H_{17}ON_3$ , yellowish needles, m. p. 173—174° (decomp.), the same product being obtained from the semicarbazone, together with a small quantity of a by-product, m. p. 195—198° (decomp.). The semicarbazidesemicarbazone and semicarbazone of 3:5-dimethyl- $\Delta^2$ -cyclohexenone, yield 3:5-dimethyl- $\Delta^2$ -cyclohexenone *phenylsemicarbazone*,  $C_{15}H_{19}ON_3$ , white needles, m. p. 191—192° (decomp.), together with, in the latter case, hydrazodicarbonamide, m. p. 233—234° (decomp.). Similarly, 3-methyl-5-ethyl- $\Delta^2$ -cyclohexenone semicarbazone yields 3-methyl-5-ethyl- $\Delta^2$ -cyclohexenone *phenylsemicarbazone*, m. p. 169—170°, the semicarbazidesemicarbazone yielding in addition *s*-diphenylcarbamide and an insoluble substance, m. p. 210—211° (decomp.). The semicarbazidesemicarbazone of 3-methyl-5-isopropyl- $\Delta^2$ -cyclohexenone on warming with aniline yields 3-methyl-5-isopropyl- $\Delta^2$ -cyclohexenone *phenylsemicarbazone*, m. p. 152—153° (decomp.), with an unidentified insoluble substance. R. B.

**Constitution of Diosphenol [Buchu-camphor].** K. VON AUWERS (*Ber.*, 1924, 57, [B], 1106—1108).—Comparison of the spectroscopic constants of diosphenol with those of its methyl and ethyl ethers and acetate confirms the constitution assigned to it by Wallach (this vol., i, 156, 862) on purely chemical grounds. The following constants are recorded: Diosphenol,  $d_4^{20}$  0.9524,  $n_D^{20}$  1.46079;  $n_{He}^{99.8}$  1.46473;  $n_{\beta}^{99.8}$  1.47513. Diosphenol methyl ether, b. p. 240—242°/750 mm., 118—119°/10 mm.,  $d_4^{20}$  0.9930;  $n_D^{20}$  1.48405,  $n_{He}^{19.2}$  1.48783,  $n_{\beta}^{19.2}$  1.49744,  $n_{\gamma}^{19.2}$  1.50601,  $n_{He}^{20}$  1.4852. Diosphenol ethyl ether, b. p. 242—246°/750 mm., 123—125°/10 mm.,  $d_4^{20}$  0.9825,  $d_4^{20}$  0.977,  $n_D^{19.0}$  1.48405,  $n_{He}^{19.0}$  1.48788,  $n_{\beta}^{19.0}$  1.49743,  $n_{\gamma}^{19.0}$  1.50601,  $n_{He}^{20}$  1.4852. Diosphenol acetate, b. p. 140—142°/12 mm.,  $d_4^{14.6}$  1.0415,  $d_4^{20}$  1.036,  $n_D^{14.6}$  1.48027,  $n_{He}^{14.6}$  1.48378,  $n_{\beta}^{14.6}$  1.49233,  $n_{\gamma}^{14.6}$  1.49996,  $n_{He}^{20}$  1.4814. H. W.

**Catalytic Oxidation in presence of Platinum Black. Oxidation of Buchu-camphor. II.** G. CUSMANO and E. CATTINI (*Gazzetta*, 1924, 54, 377—388).—The compound,  $C_{10}H_{16}O_3$ , obtained when an ethereal solution of buchu-camphor containing platinum black is left exposed to the air (A., 1923, i, 586), retains some of the properties of the buchu-camphor, and is converted into monobromobuchu-camphor (A., 1914, i, 303) when treated with hydrobromic acid. It is hence a hydroxybuchu-camphor, and since it is readily transformed by alkali hydroxide into two monobasic acids,  $C_{10}H_{18}O_4$ , which yield iodoform when treated with iodine and potassium hydroxide and consequently contain a methyl group joined to an alcoholic or carbonyl group, the hydroxyl group is situated at the carbon atom in the 1-position of the cymene skeleton.

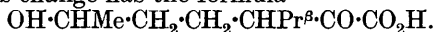
Three tautomeric formulæ are admissible for buchu-camphor, and the solubility of hydroxybuchu-camphor and the fact that, like phenols, it gives a coloration with ferric chloride suggest for it structure (I), whereas its ability to react with two molecules of phenylhydrazine indicates for it also the tautomeric formula (II) :



A hydroxybuchu-camphor of the structure



could also, on hydrolysis, yield acids capable of giving the iodoform reaction, but that this occurs is excluded by the fact that monobromobuchu-camphor is readily convertible into 3-methyl-6-isopropylpyrocatechol. Moreover, one of the acids  $\text{C}_{10}\text{H}_{18}\text{O}_4$  (III; cf. A., 1923, i, 586) obtained by hydrolysis of hydroxybuchu-camphor is formed also by the catalytic oxidation of buchu-camphor and is transformed, by oxidation and subsequent intramolecular condensation, into the acid,  $\text{CHMe}_2 \cdot \text{CH} \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \text{C}(\text{CO}_2\text{H}) : \text{CH} \end{array} \text{CO}$  (cf. Semmler and Mackenzie, A., 1906, i, 373); the only such acid capable of undergoing this change has the formula



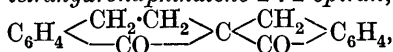
The other compound of the formula  $\text{C}_{10}\text{H}_{18}\text{O}_4$  (cf. A., 1923, i, 586) is neutral, gives no coloration with ferric chloride, and is readily converted, by withdrawal of water, into hydroxybuchu-camphor. It appears to be the first product of the oxidation of buchu-camphor and to have the structure  $\text{OH} \cdot \text{CMe} \begin{array}{c} \text{C}(\text{OH})_2 \cdot \text{CO} \\ \text{CH}_2 - \text{CH}_2 \end{array} \text{CHPr}^\beta$ , being the hydrate of the diketonic form of hydroxybuchu-camphor; since the latter, in aqueous solution, shows the reactions of the enolic form, the failure of the reverse change is explainable.

The acid  $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHPr}^\beta \cdot \text{CO} \cdot \text{CO}_2\text{H}$  has m. p.  $129^\circ$ ; its sodium salt forms long, transparent prisms containing water of crystallisation. The isomeric acid, also formed by the action of alkali on hydroxybuchu-camphor, forms crystals, m. p.  $52^\circ$ ; its barium salt crystallises in long, silky needles, and when strongly heated, yields a liquid with the odour of mint. For this acid the tentative formula  $\begin{array}{c} \text{CH}_2 \cdot \text{CMe}(\text{OH}) \\ \text{CH}_2 - \text{CHPr}^\beta \end{array} \text{C}(\text{OH}) \cdot \text{CO}_2\text{H}$  is suggested.

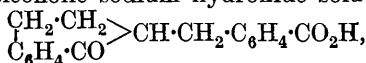
T. H. P.

**Spirans. XI. Preparation of Spirans with Five- and Seven-membered Rings.** H. LEUCHS and F. REINHART (*Ber.*, 1924, 57, [B], 1208—1214).—*Ethyl*  $\beta$ -phenylethylmalonate, b. p.  $185^\circ/15$  mm., is converted by benzyl chloride and sodium ethoxide into *ethyl benzyl*- $\beta$ -phenylethylmalonate, b. p.  $233^\circ/12$  mm.,  $237^\circ/$

16 mm., which is hydrolysed to *benzyl-β-phenylethylmalonic acid*, m. p. 153°. The acid is converted by the successive action of phosphorus pentachloride and ferric chloride into *hydrind-1-one-1-keto-1:2:3:4-tetrahydronaphthalene-2:2'-spiran*,



m. p. 111—112°, in which the presence of the ketonic group cannot be detected with phenylhydrazine or hydroxylamine. The spiran is converted by alcoholic sodium hydroxide solution into the *acid*

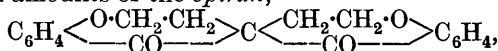


m. p. 113—115°, after previous softening. Ethyl di-β-phenylethylmalonate is hydrolysed to a mixture of di-β-phenylethylmalonic acid, m. p. 173—175° (decomp.) [Cohen and Marshall (T., 1915, 107, 896) give m. p. 194—195°], and *ethyl hydrogen di-β-phenylethylmalonate*, m. p. 103° (the ammonium and potassium salts of the latter acid are described). Di-β-phenylethylmalonic acid is transformed by phosphorus pentachloride into the corresponding *chloride*, m. p. 83°, and thence into *di-1-keto-1:2:3:4-tetrahydronaphthalene-2:2'-spiran*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CO} \end{array} \text{C}_6\text{H}_4$ , m. p. 136—

137°. Like the spiran described above, the compound is indifferent towards phenylhydrazine and hydroxylamine; it is converted by alcoholic sodium hydroxide solution into *o-β-1-keto-1:2:3:4-tetrahydronaphthylethylbenzoic acid*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \cdot \text{CO} \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , m. p. 161—162°.

*Ethyl benzyl-β-phenoxyethylmalonate*, b. p. 248°/16 mm., m. p. 53—54·5°, is converted successively into *benzyl-β-phenoxyethylmalonic acid*, m. p. 166—168° (decomp.); *benzyl-β-phenoxyethylmalonyl chloride*, m. p. 85—86°, and *benzyl-β-phenoxyethylmalonamide*, m. p. 170—171°. The chloride is decomposed by distillation under diminished pressure in the presence of ferric chloride into *1-hydrindonebutyrolactone-2-α-spiran*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CO} \end{array} \text{C} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} - \text{O} \end{array}$ ,

m. p. 110—111°, and a *substance*, (?)  $\text{C}_{18}\text{H}_{12}\text{O}_2$ , m. p. 176°. *Di-β-phenoxyethylmalonyl chloride*, m. p. 90° (corresponding *diamide*, m. p. 158—159°; *dianilide*, m. p. 187·5°), similarly suffers loss of phenol in a great measure when heated with ferric chloride, but yields small amounts of the *spiran*,



m. p. 179—181°; *phenyl di-β-chloroethylmalonate*, m. p. 113—114°, is also obtained as a product of the action.

*Di-β-phenoxyethylacetyl chloride* has m. p. 82—83°, whilst the corresponding *amide* melts at 134—136°. H. W.

**Cellulose Nitrate and Camphor.** J. B. NICHOLS (*J. Physical Chem.*, 1924, 28, 769—771).—Freezing-point determinations show

that dry pyroxylin is rapidly peptised by camphor, and, to a slight extent, by monobromocamphor. Pyroxylin is decomposed by molten camphor. Mixtures of monobromocamphor and camphor exhibit a eutectic at  $62.3^\circ$ , containing 85.5% of the first-named constituent. S. K. T.

**Dichloropinane and its Derivatives.** M. GARINO and A. D'AMBROSIO (*Gazzetta*, 1924, 54, 345—351).—For the compound  $C_{10}H_{16}Cl_2$  obtained by Naudin (A., 1882, 608), the name dichloropinane is suggested, whereas Bert's dichloro compound (A., 1923, i, 812) is regarded as dichlorocamphane. Dichloropinane, which may be conveniently prepared by the action of sulphuryl chloride on pinene, is a pale yellow, neutral liquid, unstable in the light and having a persistent and pungent odour,  $d^{15}_4$  1.1625,  $n^{20}_D$  1.5008,  $[\alpha]^{15}_D -20.175^\circ$ . When distilled in a current of steam, it undergoes decomposition in accordance with the equation  $3C_{10}H_{16}Cl_2 = C_{10}H_{16}.HCl + C_{10}H_{15}Cl_3 + C_{10}H_{15}Cl + HCl$ . Of these products, the first is pinene hydrochloride (bornyl chloride). The second, *trichloropinane* (annexed formula), is an unstable liquid,  $d^{15}_4$  1.2550,  $n^{20}_D$  1.5382,  $[\alpha]^{15}_D -3.72^\circ$ . The third compound,  $C_{10}H_{15}Cl$ , is a pale yellow liquid, b. p.  $169-170^\circ$  (decomp.),  $d^{15}_4$  1.053,  $n^{20}_D$  1.4980,  $[\alpha]^{15}_D -11.52^\circ$ .

The action of alcoholic ammonia solution on dichloropinane yields ammonium chloride and Marsh and Gardner's chlorocamphene (T., 1897, 91, 288). T. H. P.

**Formation of Borneol from Turpentine Oil.** II. Y. MURAYAMA, K. ABE, and S. YAMAGISHI (*J. Pharm. Soc. Japan*, 1924, No. 507, 341—347; cf. this vol., i, 62, and D.R.-P. 208487).—The effect of seven catalysts on the formation of borneol from an American turpentine oil, b. p.  $158-161^\circ$ ,  $d^{15}_4$  0.8644,  $[\alpha] -6.00^\circ$ , was studied. It was diluted with about twice its weight of carbon tetrachloride and warmed at  $50^\circ$ ; a mixture of anhydrous oxalic acid and one of the following catalysts was added, stirring and keeping the temperature at  $70-80^\circ$ . Using aluminium, stannic, phosphoric, zinc and ferric chlorides, Japanese acid clay and wood charcoal as catalysts, the yields of borneol obtained were 22, 21, 0, 11.5, 25, 11, and 6.6% of the theoretical, respectively. When the oil was treated with oxalic acid only, the yield was 1.6%. K. K.

**Kessyl Alcohol.** I. Y. SAHINA and G. HONGO (*J. Pharm. Soc. Japan*, 1924, No. 506, 227—238).—The physical and chemical properties of kessyl alcohol,  $C_{14}H_{24}O_2$ , m. p.  $85^\circ$ , obtained from *Valeriana officinalis*, L., var. *latifolia*, Miq., are identical with those described by Bertram and Gildemeister (A., 1891, 238) except  $[\alpha]^{23}_D -44.72^\circ$  in alcoholic solution. It gives a cherry-red coloration with a solution of vanillin in hydrochloric acid,

contains no methoxy group, is stable towards potassium permanganate, does not absorb hydrogen in the presence of platinum, is not reduced by sodium and alcohol, and gives no iodoform reaction. It gives a *urethane*,  $C_{21}H_{29}O_3N$ , colourless plates, m. p.  $168^\circ$ ; its *acetate* is a colourless, viscous liquid, b. p.  $157\text{--}158^\circ/6.5\text{ mm.}$  When oxidised with potassium dichromate and sulphuric acid, the alcohol gives an  $\alpha$ -ketone,  $C_{14}H_{23}O_2$ , colourless needles, m. p.  $105^\circ$  (*semicarbazone*, m. p.  $234\text{--}235^\circ$ ). With hydroxylamine in alkaline solution it gives two *oximes*,  $C_{14}H_{23}O_2N$ , m. p.  $153\text{--}154^\circ$  and  $42^\circ$  [or  $(+\frac{1}{2}H_2O)$  m. p.  $65\text{--}69^\circ$ ]. When treated with cold concentrated sulphuric acid, the oxime, m. p.  $153\text{--}154^\circ$ , gives a yellow powder, m. p.  $160^\circ$ , whereas with warm concentrated sulphuric acid it forms a yellow powder,  $C_{14}H_{21}ON$ , m. p.  $155^\circ$ . The  $\alpha$ -ketone is converted by boiling alcoholic hydrogen chloride into a  $\beta$ -isomeride, white needles, m. p.  $111\text{--}112^\circ$ , which gives no coloration with vanillin-hydrochloric acid; the *semicarbazone* has m. p.  $190\text{--}191^\circ$ . The  $\alpha$ -ketone is reduced by sodium and alcohol to *isokessyl alcohol*, white prisms, m. p.  $118\text{--}119^\circ$  (*phenylurethane*, m. p.  $50\text{--}52^\circ$ ). Ethyl nitrite and sodium in an ethereal solution convert the  $\alpha$ -ketone into the *compound*,  $C_{14}H_{23}O_4N$ , m. p.  $100\text{--}108^\circ$  (copper salt, m. p.  $168\text{--}169^\circ$ ). From these results, the authors conclude that kessyl alcohol is a saturated secondary alcohol having two benzene rings and an ethereal oxygen atom.

K. K.

**Constitution of Caoutchouc. VI.** H. STAUDINGER (*Ber.*, 1924, 57, [B], 1203—1208).—Harries's conception that fully reduced caoutchouc would be molecular-disperse and capable of distillation under diminished pressure without decomposition is not in harmony with the observation that hydrocaoutchouc is colloidal and is decomposed at  $350\text{--}400^\circ$  into a series of ethylenic hydrocarbons of which the most complex has (approximately) the composition  $C_{50}H_{100}$ , whereas the simplest is  $\beta$ -methyl- $\Delta^a$ -butene (identified by oxidation to methyl ethyl ketone and preparation of the *p*-nitrophenylhydrazone of the latter). The hypothesis that  $\beta$ -methyl- $\Delta^a$ -butene is the unit of hydrocaoutchouc whereas caoutchouc is derived from isoprene is in accord with the observation that hydrocaoutchouc is completely decomposed at  $350\text{--}400^\circ$  whereas caoutchouc requires only a temperature of  $300\text{--}350^\circ$ , since the substituents are usually loosely united in allyl derivatives. It is considered that caoutchouc is a derivative of ethylene of very high molecular weight in which a large number of isoprene molecules are similarly united chemically. These molecules are considered to be identical with the colloidal particles; they are not uniform and probably have very varying magnitudes which alter with changing temperature. The term "macromolecule" is proposed for this particular type. This conception of the constitution of caoutchouc is in contradiction to the properties of hydrocaoutchouc obtained by Pummerer and Burkard (*A.*, 1923, i, 49) particularly with respect to the autoxidisability of the substance to *isocaoutchouc*. Attempts to repeat the experiments of these chemists with a less

completely purified specimen of caoutchouc failed to give a completely hydrogenated product at the atmospheric pressure. At  $100^{\circ}$ , however, hydrocaoutchouc was readily prepared which was identical in all respects with the product obtained previously at  $270^{\circ}$  under high pressure in the presence of platinum or palladium. It does not suffer autoxidation. The action of zinc methyl or zinc ethyl on bromohydrocaoutchouc gives *methyl-* and *ethyl-hydrocaoutchoucs* which behave like paraffinoid hydrocarbons of high molecular weight. H. W.

**Resinic Nature of Shellac. Attempts to Effect a Partial Synthesis.** C. HARRIES and W. NAGEL (*Wiss. Veröff. Siemens-Konz.*, 1924, **3**, 12—18).—By heating aleuritic and shellolic acids (A., 1923, i, 120) together in various molecular proportions under reduced pressure for 1 hour at  $150$ — $160^{\circ}$ , lactide condensation takes place with vigorous evolution of water vapour, and clear yellow liquids are obtained which solidify on cooling to yellow, resinous masses. These products are readily soluble in most organic solvents, have low melting points, and are readily hydrolysed by alkali hydroxides, giving salts of the original acids. If the heating is continued above  $200^{\circ}$  the substances swell suddenly and are converted into harder, more infusible resins which, however, are decomposed by potassium hydroxide with the formation of potassium salts of the original acids. Aleuritic acid alone is converted at  $170^{\circ}$  into a white, opaque mass, m. p.  $35$ — $45^{\circ}$ ; shellolic acid alone gives a yellow, very brittle, resin at  $202$ — $210^{\circ}$ , which is soluble in chloroform, and on further heating decomposes with the evolution of carbon dioxide. Similar results were obtained when the amorphous acids of ordinary shellac were heated under the above conditions. It appears therefore that shellac is a mixture of products obtained by the lactide condensation of various hydroxy-carboxylic acids. A. R. P.

**Amygdalin. III. *l*-Amygdalinic Acid.** G. ZEMPLÉN and A. KUNZ (*Ber.*, 1924, **57**, [B], 1194—1200).—Amygdalin is converted by hydrolysis with barium hydroxide and acetylation of the barium salts thus produced by acetic anhydride in the presence of pyridine into a mixture of the hepta-acetyl derivatives of *d*- and *l*-amygdalinic acids which has  $[\alpha]_D^{18} + 36.1^{\circ}$  in chloroform. Solution of the mixture in warm anhydrous benzene followed by addition of ether causes the separation of *labile l*-hepta-acetylamygdalinic acid, m. p.  $115^{\circ}$  (indefinite),  $[\alpha]_D^{18} + 60.06^{\circ}$ , in long needles which cannot be recrystallised from any solvent. It is hydrolysed to *l*-amygdalinic acid,  $[\alpha]_D^{18} - 132.7^{\circ}$  in aqueous solution and yields *l*-mandelic acid,  $[\alpha]_D^{18} - 144^{\circ}$  in water. Hydrolysis of the mixture of acids having  $[\alpha]_D^{18} + 36.1^{\circ}$  in chloroform (see above) followed by re-acetylation gives a product which has  $[\alpha]_D^{18} - 8.4^{\circ}$  in chloroform, from which *stable l*-hepta-acetylamygdalinic acid, needles, m. p.  $195$ — $196^{\circ}$ ,  $[\alpha]_D^{18} - 65.5^{\circ}$  in chloroform, is isolated by repeated crystallisation from absolute alcohol. It yields *l*-mandelic acid,  $[\alpha]_D^{18} - 153.4^{\circ}$  in water, and *l*-amygdalinic acid,  $[\alpha]_D^{18} - 133.2^{\circ}$  in aqueous solution. Labile can

be transformed into stable *l*-hepta-acetylamygdalinic acid by hydrolysis with absolute methyl-alcoholic sodium methoxide solution followed by re-acetylation with acetic anhydride in the presence of pyridine. The nature of the isomerism is not explained. H. W.

**Seneginin [Seneginic Acid], the Ultimate Sapogenin from *Radix Senegae*.** E. WEDEKIND and R. KRECKE (*Ber.*, 1924, 57, [B], 1118—1120).—Crude senegin is boiled with sulphuric acid (5%) and the undissolved portion is treated with perchloric acid (3%) at 140° until further production of sugar is not observed. The product, which is designated *seneginin* or *seneginic acid*,  $C_{26}H_{44}O_6$ , forms colourless needles, m. p. about 272°,  $[\alpha]_D +38.26^\circ$  in alcoholic solution. The formation of a *diacetate*, m. p. 214° after previous softening, and of a *dimethyl ester*, m. p. 206—208°,  $[\alpha]_D +32.09^\circ$  in methyl-alcoholic solution, shows it to be a dibasic dihydroxy-acid. H. W.

**Orobanchin, a New Glucoside, extracted from Roots of *Orobanche rapum*, Thuill.** M. BRIDEL and C. CHARAUX (*Compt. rend.*, 1924, 178, 1839—1842).—Fresh roots of *O. rapum* were treated with boiling 95% alcohol and the extract was concentrated until crystals were obtained. Purification of these yielded *orobanchin*, prismatic crystals, m. p. 160°,  $\alpha_D -66.22^\circ$ . The crystals lose 10.73% of their weight when kept in a vacuum at 50°; the value of  $\alpha_D$  for the dry product is  $-74.18^\circ$ . The glucoside has reducing properties, 1.0 g. being equivalent to 0.120 g. of dextrose. Hydrolysis at 105° by 3% sulphuric acid resulted in the formation of rhamnose, dextrose, and caffeic acid, together with other products not yet identified. H. J. E.

**Hydroxymethylfurfuraldehyde.** J. A. MIDDENDORP (*Z. Ver. deut. Zuckerind.*, 1924, 814, 338—433).—A German translation of the paper in *Rec. trav. chim.*, 1919, 38, 1—71 (see A., 1919, i, 129). F. A. M.

**Elsholtzia Ketone (Elsholtzione).** Y. ASAHINA [with Y. MURAYAMA, B. SHIBATA, T. KARIYONE, S. KUWADA, and M. ASANO] (*Acta Phytochim.*, 1924, 2, 1—23; cf. A., 1915, i, 429; 1920, i, 495; 1922, i, 1047).—A review of previous work on the constitution of elsholtzione and of elsholtzic acid, the following additional evidence being given in support of the previously assigned formulæ. Crude elsholtzione is best purified by boiling the fraction of b. p. 210—220°, 95—110°/15 mm., with hydroxylamine hydrochloride and sodium acetate in absolute alcohol for 2—3 hours: the oxime thus obtained is then hydrolysed by boiling with 5% hydrochloric acid. The pure ketone (b. p. 92°/9 mm.) when treated in dry ethereal solution with amyl nitrite and sodium, affords *ethyl elsholtzate*, colourless leaflets, m. p. 49°, b. p. 205°, and *isobutylalldoxime*. Elsholtzic acid, the preparation of which has been described, gives a *sodium salt* (+1H<sub>2</sub>O) and a *potassium salt*, both colourless crystals, *calcium*, *barium*, and *silver salts*, anhydrous and colourless, *lead salt* (+1H<sub>2</sub>O), white leaflets, *cupric salt* (+6H<sub>2</sub>O),



green leaflets, *ferric* salt,  $[(C_6H_5O_3)_2Fe]_2O \cdot 9H_2O$ , yellow needles, *methyl* ester, colourless leaflets, m. p. 36—38°, *chloride*, needles, m. p. 21—22°, *amide*, m. p. 85—86°, and an *anilide*, m. p. 91°.

Furan- $\alpha$ -carboxylic acid, when treated with Caro's acid, gives carbon dioxide, and fumaric, maleic, and succinic acids. Elsholtzic acid, when similarly treated, gives carbon dioxide and an oily product which, after being distilled in steam and then reduced with hydrogen and platinum black, gives methylsuccinic acid. Ethyl elsholtzate, when treated with ethyl acetate and sodium, gives *ethyl elsholtzoylacetate*,  $C_4H_2O(Me) \cdot CO \cdot CH_2 \cdot CO_2Et$ , a viscous, yellow oil of unpleasant odour, b. p. 145—150°/15 mm.,  $d_4^{17}$  1.1437,  $n_D^{19}$  1.50044. This ester, when heated with hydroxylamine hydrochloride and 20% sodium hydroxide solution, gives no oxime, but a *substance*,  $C_8H_7O_3N$ , colourless needles, m. p. 95°, which is probably an isooxazolone derivative. When elsholtzoyl chloride is treated at 190—200° in direct sunlight with 2 mols. of bromine, the product, after decomposition with water, yields 3-*aldehydofuran-2-carboxylic acid*, colourless needles, m. p. 158°, *phenylhydrazone*, yellow needles, sintering at 166°, m. p. 171° (decomp.). The aldehydo-acid, when treated with hydroxylamine hydrochloride and sodium acetate, gives an *oxime*, m. p. 225°, but when digested with alcoholic hydroxylamine hydrochloride gives a *substance*, softening at 105°, m. p. 211°, which has no constant composition, and is probably an oxime anhydride. The oxime, when heated with acetic anhydride, gives 3-*cyanofuran-2-carboxylic acid*, white needles, m. p. 183°; the latter when oxidised with ammoniacal silver oxide solution gives furan-2 : 3-dicarboxylic acid (*methyl ester*, m. p. 37°; cf. A., 1922, i, 1047). 2-Methylfuran-3-carboxylic acid (preparation from ethyl acetoacetate, A., 1911, i, 319) gives a *chloride*, fuming liquid, b. p. 68—70.5°/14 mm., colourless when pure; if this chloride is treated at 120—140° in direct sunlight with bromine, the product, after decomposition with water and treatment in succession with silver oxide and with zinc and ammonium chloride, gives furan-2 : 3-dicarboxylic acid, prisms by sublimation, m. p. 221°. The acid and its methyl ester are identical with the similar acid and ester obtained from elsholtzic acid.

[With M. TANAKA.]—Elsholtzic acid, when heated at 210—230° in a closed tube, gives 3-*methylfuran*, a colourless liquid, b. p. 65.5°,  $d_4^{18}$  0.923,  $n_D^{18}$  1.4255.

The colours developed by many furan derivatives with vanillin solution are tabulated: they are mostly red or reddish-violet. 3-Methylfuran gives a bluish-green pine-shaving reaction.

F. G. M.

**Thioindigo and its Derivatives.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (O. SPENGLER and A. THURM) (D.R.-P. 386889; from *Chem. Zentr.*, 1924, i, 1449).—The following compounds, obtained from the halogenation of  $\omega$ -disulphides of aryl-methylketones and condensation of the resulting products, are mentioned: *di(benzoylmethyl) disulphide*, m. p. 75—76°; *di-(4-methylbenzoylmethyl) disulphide*, m. p. 85.5—86.5°; 6 : 6'-*dimethyl-*

*thioindigo*; *di*-(3 : 4-dichlorobenzoylmethyl) *disulphide*, colourless leaflets, m. p. 89—90°. G. W. R.

**Synthesis of Ephedrine.** E. FOURNEAU and S. KANAO (*Bull. Soc. chim.*, 1924, [iv], 35, 614—625).—A critical survey of the published researches on the constitution and synthesis of ephedrine, for details of which the original should be consulted. A comprehensive bibliography is appended. The base obtained by reducing, with sodium amalgam, the product of the action of methylamine on brominated benzyl methyl ketone (cf. Emde, A., 1906, i, 945; 1909, i, 708; 1910, i, 479; 1911, i, 714) is identical with that obtained starting from propenylbenzene (Fourné and Puyal, A., 1923, i, 238). The action of methylamine on brominated phenyl ethyl ketone is much slower than in the preceding case, and the base obtained on reducing the product is identical with *ψ*-ephedrine, whilst racemic ephedrine itself appears to have been first obtained by Eberhard (A., 1915, i, 834; 1917, i, 392; 1920, i, 875) by carrying out the reduction with hydrogen in presence of palladium.

F. G. W.

**Actinine.** D. ACKERMANN, F. HOLTZ, and H. REINWEIN (*Z. Biol.*, 1924, 81, 61—64; cf. A., 1923, i, 1155; this vol., i, 243).—There is doubt whether the formula of the base "actinine," isolated from a species of sea-anemone by the authors, is  $C_{13}H_{24}O_5N_2$  or  $C_7H_{13}O_2N$ . The latter is the formula of stachydrine, hitherto found only in plants. The discovery of trigonelline in an animal and the frequent occurrence of glycine-betaine makes it quite probable that stachydrine, which is also a betaine, should occur in the animal world. From a comparison of the composition, m. p., and other properties of actinine chloraurate, chloroplatinate, and of the compounds obtained with potassium ferro- and ferri-cyanides with those of similar compounds of stachydrine, it is considered that actinine is identical with stachydrine, although the evidence is not conclusive.

C. T. G.

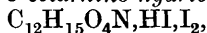
**Supposed Calcium-Nicotine Compounds.** R. W. THATCHER. —(See ii, 635.)

**Amination of Nicotine with Sodamide and Potassamide.** A. E. TSCHITSCHIBABIN and A. W. KIRSSANOW (*Ber.*, 1924, 57, [B], 1163—1168).—In a previous communication (Tschitschibabin and Buchholz, A., 1923, i, 594) the formation of one of the two possible 2-aminonicotines (m. p. 124—125°) has been described. It is now found that both isomerides are produced in approximately equal amounts when nicotine dissolved in xylene is heated with sodamide at 135—140°. They are most readily separated from one another by taking advantage of the ready solubility of 6-amino-3-methylpyrrolpyridine in water, in which 2-amino-3-methylpyrrolpyridine (m. p. 124—125°) is very sparingly soluble. 6-Amino-3-methylpyrrolpyridine has m. p. 60°, b. p. 300° (slight decomp.), or 167°/12 mm. The *hydrochloride*, *chloroplatinate* (+H<sub>2</sub>O), *nitrate*, *sulphate*, and *picrate*, m. p. 225° (decomp.), are described. The *hydrochloride*, *nitrate*, and *sulphate* of 2-amino-

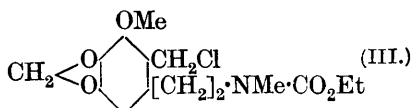
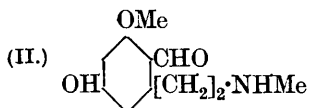
3-methylpyrrolpyridine have been prepared. Treatment of the aminonicotines dissolved in dilute sulphuric acid with bromine yields, respectively, 5-bromo-2-amino-3-methylpyrrolpyridine, m. p. 138—138·5°, and 5-bromo-6-amino-3-methylpyrrolpyridine, m. p. 111—112°. 6-Amino-3-methylpyrrolpyridine hydrochloride dissolved in sulphuric acid (5%) is converted by sodium nitrite into 6-hydroxy-3-methylpyrrolpyridine, m. p. 103·5—104°. The amines dissolved in saturated hydrochloric acid solution are slowly converted by sodium nitrite at 20—30° into the corresponding chloronicotines; 2-chloro-3-methylpyrrolpyridine has b. p. 268—269°/740 mm.,  $d_4^{20}$  1·1378,  $d_4^1$  1·1520,  $n_D^{25}$  1·5457, whereas 6-chloro-3-methylpyrrolpyridine has b. p. 270—271°/742 mm.,  $d_4^{20}$  1·100,  $d_4^1$  1·1162,  $n_D^{25}$  1·5485. Oxidation of the chloro compounds with potassium permanganate gives 2-chloropyridine-3-carboxylic acid, m. p. 193°, and 6-chloropyridine-3-carboxylic acid, m. p. 199°, respectively.

The aminonicotines and their salts are optically inactive, so that their production is accompanied by racemisation. The physiological action of the amino- and 6-hydroxy-nicotines is similar to, but markedly less toxic than, that of nicotine. H. W.

**Change of Cotarnine and its Derivatives by Ladenburg's Reduction.** H. KONDO and T. NAKAZATO (*J. Pharm. Soc. Japan*, 1924, No. 507, 326—341).—By reducing hydrocotarnine with sodium and amyl alcohol, Pyman and Remfry (T., 1912, 101, 1595) obtained hydrohydrastinine and a small amount of a mixture of four phenolic bases. Applying the method to cotarnine, the authors have isolated hydrohydrastinine, a white, crystalline powder, m. p. 268°, and a phenolic base (I), m. p. 199°, identical with Pyman's 6-hydroxy-8-methoxy-2-methyltetrahydroisoquinoline; the *hydrobromide* of its benzoyl derivative melts at 226—228°. The yields of the former free base and of (I) were 20% and 10% of the material used, respectively. Pyman's three other bases have not been isolated. By heating (I) with concentrated hydrochloric acid in a sealed tube, the *dihydroxy* compound,  $C_9H_9NMe(OH)_2$ , m. p. 220°, resulted, which gave a brown coloration with ferric chloride. When oxidised with iodine in alcoholic solution, hydrocotarnine gave *cotarnine hydriodide di-iodide*,

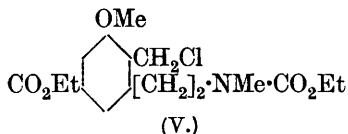
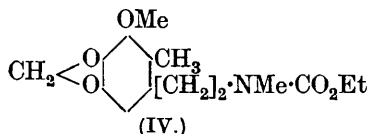


m. p. 144°. By the same method, (I) gave the *hydriodide* of an aldehydo-base,  $C_{11}H_{15}O_3N, HI$ , needles, m. p. 202°. The free base,  $C_{11}H_{15}O_3N$ , colourless prisms, m. p. 146°, has the formula (II).



It reduces ammoniacal silver nitrate solution, but not Fehling's solution; the *semicarbazone* melts at 208°. The base (I) does not react with acetic anhydride or benzoyl chloride, but is converted by benzoic anhydride into a *monobenzoyl* derivative (*hydrobromide*,  $C_{18}H_{19}O_3N, HBr$ , yellow prisms, m. p. 226—228°). The nucleus

of (I) cannot be split by heating with benzoic anhydride in a sealed tube. When a mixture of anhydrous hydrocotarnine and ethyl chloroformate was heated for 2 hours, a *substance* (III), colourless prisms, m. p. 122°, was obtained. By reducing (III) with 3%



sodium amalgam in alcoholic solution at room temperature, *substance* (IV),  $\text{C}_{15}\text{H}_{21}\text{O}_5\text{N}$ , was obtained as colourless prisms, m. p. 62°. This was not affected by further treatment, in boiling alcohol, with sodium amalgam. If (III) is reduced with a large excess of sodium amalgam in boiling alcohol, hydrocotarnine is produced as the main product and is accompanied by a small amount of (IV). On heating (I) with ethyl chloroformate, a brown, amorphous *substance* (V),  $\text{C}_{17}\text{H}_{24}\text{O}_6\text{NCl}$ , m. p. 132–139°, was obtained.

K. K.

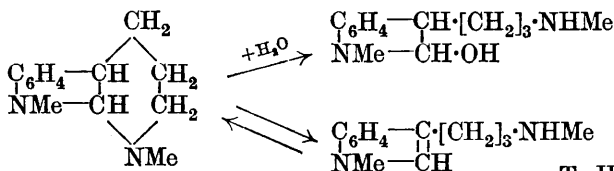
**Fluorescence of the Alkaloids of the *iso*Quinoline and Tetrahydroisoquinoline Group: Papaverine, Narcotine, Hydrastine, and their Decomposition Products.** E. BAYLE and R. FABRE (*Compt. rend.*, 1924, 178, 2181–2183).—The colour and intensity of the fluorescence of the alkaloids excited by the mercury line 3650 (taking the intensity of sodium salicylate as 20) is as follows: Papaverine, whitish-blue, 6; hydrastine, greenish-white, 55; narcotine, very faintly violet, not measurable; narceine, bluish-violet, 7; veratric acid, bluish-white, 5; opianic acid, bluish-white, 10; potassium opianate, blue, 5; hydrastinine and cotarnine, nil; hydrastine hydrochloride, blue, 36; hydrastinine hydrochloride, 4; cotarnine hydrochloride, yellow, 35.

A. COUSEN.

**Tautomerism of Eserine.** M. and M. POLONOVSKI (*Compt. rend.*, 1924, 179, 57–60).—Further results confirm the view that eseretholemethine is a pseudo-base with an aldolic hydroxyl (cf. *ibid.*, 178, 2078), the action of sodium on the base in ethereal solution yielding a voluminous, amorphous precipitate of the sodium salt, which is decomposed by water into sodium hydroxide and the original methine. The ethoxide is converted by hydrochloric acid quantitatively into eserethole methochloride, and, when treated with methyl iodide (2 mols.) in absolute alcohol yields the dimethiodide, m. p. 207° (A., 1923, i, 939).

The action of hydrogen cyanide on eseretholemethine gives the basic *cyanoeseretholemethine* (3-β-dimethylaminoethyl-2-cyano-1-methyl-2:3-dihydroindole), a colourless oil,  $[\alpha]_D -10^\circ$ , forming a *methiodide*,  $\text{C}_{16}\text{H}_{23}\text{ON}_2 \cdot \text{CN} \cdot \text{MeI}$ .

It appears likely that eserine can react, besides, as the ordinary tertiary basic, tricyclic form, also as a secondary, open-chain base, either hydrated (eserinol) or anhydrous (eserinamine), the latter being tautomeric with eserine:



T. H. P.

**Physostigmine (Eserine). II. Synthesis of Physostigmol Ethyl Ether.** E. STEDMAN (*J. Chem. Soc.*, 1924, 125, 1373—1376).—When eserethole methiodide is heated under greatly reduced pressure, it fuses and physostigmol ethyl ether sublimes slowly therefrom. It was not found possible to investigate the latter substance by a process of degradation, but an indication was given that physostigmol is 5-hydroxy-1:3-dimethylindole. By Kermack, Perkin, and Robinson's method (*ibid.*, 1921, 119, 1622), methyl-*p*-phenetidine was converted first into nitrosomethyl-*p*-phenetidine, which was reduced to *p*-ethoxyphenylmethylhydrazine. This was condensed with  $\alpha$ -ketoglutaric acid and the product heated to drive off carbon dioxide, whereby 5-ethoxy-1:3-dimethylindole was obtained, identical with physostigmol ethyl ether. The synthesis serves to locate the position of the hydroxyl group in eseroline.

A. COUSEN.

**Alkaloids of Yohimbehe Bark.** P. W. DANCKWORTT and P. LUY (*Arch. Pharm.*, 1924, 262, 81—104).—The residues from the technical extraction of yohimbine contain, besides unseparated yohimbine, a phenol-like constituent and another *alkaloid*,  $\text{C}_{20}\text{H}_{24}\text{O}_3\text{N}_2$  (?), m. p. 133—135° (with previous darkening),  $[\alpha]_D^{25} +122.32^\circ$  in alcohol. This substance is isolated as an amorphous mass, neither it nor any derivative being ever obtained in a crystalline state. The following salts are all pale yellow substances, darkening before they melt or decompose: *hydrochloride*, m. p. 215—216° (this salt is soluble in acetone and on this property the separation from yohimbine was based, the alkaloid mixture being originally extracted as oxalate); *nitrate*, m. p. 185°; *acetate*, m. p. 155—156°; *oxalate*, m. p. 215° (decomp.); *sulphate*, decomp. 120°; *picrate*, decomp. 140—145°; *picrolonate*, decomp. 145—150°. A *chloroaurate* and a *chloroplatinate* are described, but neither contains the expected percentage of metal. A (mono) *acetyl* derivative having m. p. 102—103°, and, like yohimbine (cf. Barger and Field, *T.*, 1915, 107, 1025), a *sulphonic acid* (not crystalline), m. p. 293—298° (decomp.), are formed. When treated with methyl iodide in ether solution, the substance gives what appears to be a mixture of *mono*- and *di*-methiodides, whilst this with more methyl iodide at 125° yields apparently a dimethiodide of a di-iodo derivative. About 75% of the calculated amount of methyl iodide, assuming one methoxyl group to be present, was obtained by Zeisel's method. The substance seems to contain no carbonyl or methylenedihydroxy groups, and the presence of an *N*-methyl group, although indicated, was not proved quantitatively. A *dihydro* derivative, m. p. 115°, is obtained by reduction with sodium amalgam. Yohimbine by

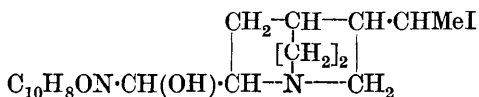
similar treatment is also reduced, but to what stage is not certain (the *product* has m. p. 215—215.5°), whilst if the reduction be carried out with Devarda's alloy in alkaline alcoholic solution an intensely coloured *substance*, m. p. about 210—220°, is obtained. Yohimbine is decomposed by the action of hydrochloric acid at 100°, a *compound*, m. p. about 270°, apparently not yohimboic acid (Spiegel, A., 1903, i, 274), being formed. The new alkaloid is decomposed by hot alcoholic sodium hydroxide and affords an *acid*, m. p. 151—153°, presumably analogous to yohimboic acid (*loc. cit.*). When treated with "bromide-bromate" solution, yohimbine takes up 3.4 atomic proportions of bromine, whilst with iodine 3 atomic proportions are taken up and the product is periodide-like in nature. The new base may possibly be identical with the yohimbenine described by Spiegel (A., 1899, i, 966; 1903, i, 195).  
W. A. S.

**Hydriodoquinine and its Transformation Products.** K. W. ROSENMUND and C. KITTLER (*Arch. Pharm.*, 1924, **262**, 18—24).—Hydriodoquinine, isolated as the dihydriodide  $C_{20}H_{27}O_2N_2I_3$ , pale yellow crystals discoloured at 215°, decomp. 235° (cf. Lippmann and Fleissner, A., 1891, 1517; Skraup, A., 1892, 83; 1893, i, 737) is a mixture of two substances. The base,  $C_{20}H_{25}O_2N_2I$ , was separated into two distinct crops of crystals, mixed crystals also being formed. *Base I* forms clusters of needles,  $[\alpha]_D -74.3^\circ$ ; *dihydrochloride*, pale yellow prisms; *base II*, felted, opaque needles more soluble in benzene and less soluble in ether than I,  $[\alpha]_D -128.3^\circ$ ; *dihydrochloride*, bright yellow needles. On heating, both I and II become yellow at 105—110°, blacken at 120—130°, and decompose at 140—150°.

*Base I*, treated for several days with alcoholic sodium hydroxide and a little copper acetate, yields pseudoquinine, m. p. 186°. Prolonged heating with cuprous cyanide in benzene solution converts I into *hydrocyanoquinine*,  $C_{21}H_{15}O_2N_3$ , m. p. 175°, whilst reduction by means of hydrogen with a catalyst in neutral alcoholic solution gives dihydroquinine,  $C_{20}H_{26}O_2N_2$ , m. p. 168°, identical with the product of hydrogenation of pseudoquinine.

*Base II*, when treated with alcoholic sodium hydroxide, cuprous cyanide, or hydrogen in the same way, yields in each case niquine, m. p. 146° (Skraup, A., 1893, i, 56), for which the formula  $C_{20}H_{24}O_2N_2$  is preferred to that adopted by Skraup,  $C_{19}H_{24}O_2N_2$ , since these three mild reactions are not likely to have caused loss of an atom of carbon. In the last two reactions there were also formed *substances* of m. p. 85—95° (decomp.) and 92—93°, respectively.

*Base I* has the true hydriodoquinine structure, the iodine atom probably occupying the



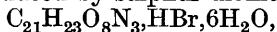
$\alpha$ -position in the side chain as in the annexed formula; but in *base II* the bridge in the quinuclidine nucleus has probably already been ruptured as suggested by

Léger in the case of niquine (A., 1919, i, 597).

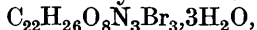
G. M. B.

**Strychnos Alkaloids. XLII. Action of Halogen on Cacotheline and Related Substances.** H. LEUCHS and C. TAUBE (*Ber.*, 1924, 57, [B], 1092—1098).—The final product of the action of bromine on cacotheline is the hydrobromide of an acid,  $C_{19}H_{22}O_6N_2$  (cf. Hanssen, *Ber.*, 1897, 20, 452). The intermediate products of the change have now been investigated. It appears probable that Hanssen's compound is a  $\gamma$ -aldehydo- or an  $\alpha$ -keto-acid, although the reactions characteristic of these groups have not been observed with it.

Cacotheline is converted by treatment with bromine in aqueous solution at  $20^\circ$  into the substance,  $C_{21}H_{23}O_8N_3Br_2$ , which liberates iodine from potassium iodide and evolves bromopierin when boiled with water. It is reduced by sulphur dioxide to the salt,



which, when dried or crystallised from *N*-hydrobromic acid, readily loses carbon dioxide and yields the compound,  $C_{20}H_{23}O_6N_3 \cdot HBr$ . The free acid,  $C_{20}H_{23}O_6N_3$ , its hydrochloride and nitrate are described. Methylcacotheline and bromine yield the substance,



yellow prisms, which is reduced by sulphur dioxide under certain conditions mainly to the product,  $C_{22}H_{26}O_8N_3Br$ , which readily loses carbon dioxide when dried or treated with warm water and yields the compound,  $C_{21}H_{26}O_6N_3Br$ .

The product of the action of bromine on the nitroquinone hydrate of brucinesulphonic acid is shown to be reduced by sulphur dioxide to a substance,  $C_{20}H_{23}O_9N_3S$ , whilst the corresponding amine hydrochloride has the composition,  $C_{20}H_{23}O_6N_3S \cdot HCl \cdot 3H_2O$ ; the free amine,  $C_{20}H_{23}O_6N_3S$ , is described. Bromine transforms the compound,  $C_{20}H_{23}O_9N_3S$  into the substance,  $C_{20}H_{23}O_{10}N_3SBr_2$  or  $C_{20}H_{25}O_{10}N_3SBr_2$ .

Cacotheline is converted by chlorine at  $0^\circ$  into the compound,  $C_{21}H_{23}O_8N_3Cl_2$ , which is transformed by 3*N*-nitric acid into the substance,  $C_{21}H_{23}O_8N_3Cl_2 \cdot HNO_3$ . Similarly, methylcacotheline yields the substance,  $C_{22}H_{25}O_8N_3Cl_2 \cdot 5H_2O$ , which is also obtained in the anhydrous condition. The products do not appear to be similar to those yielded by bromine under analogous conditions. H. W.

**Attempts to Prepare 2-Methoxy-1-methylpiperidine. Hydrogenation of certain Pyridine Derivatives.** T. B. GRAVE (*J. Amer. Chem. Soc.*, 1924, 46, 1460—1470).—Reduction of 2-methoxypyridine, with sodium and alcohol, electrolytically in dilute sulphuric acid, or with hydrogen in acetic or hydrochloric acid, or methyl alcohol, in presence of platinum, yields piperidine. 2-Methoxymethylpyridinium sulphate yields 1-methylpiperidine when treated with hydrogen in methyl alcohol in presence of platinum black, whilst 2-chloropyridine yields similarly a mixture of pyridine and piperidine. 2-Aminopyridine, in dilute hydrochloric acid solution, in presence of colloidal platinum or platinum black, absorbs hydrogen with quantitative formation of 2-iminopiperidine hydrochloride. The free base can be obtained from the hydrochloride by means of silver oxide, but is hydrolysed, on

boiling in aqueous solution, to 2-piperidone. In neutral aqueous solution, 2-aminopyridine hydrochloride is hydrogenated in presence of platinum oxide with formation of piperidine and ammonia. 2-Iminopiperidine hydrochloride could not be reduced in neutral aqueous solution in presence of platinum black, but yielded piperidine and ammonia in presence of platinum oxide. 1-Methyl-2-pyridone yielded 1-methyl-2-piperidone when treated with hydrogen in presence of platinum black in hydrochloric acid solution. The following corrected m. p. are reported: piperidine hydrochloride,  $244.5^{\circ}$ , piperidine picrate,  $150.5^{\circ}$ , and 1-benzoyl-2-piperidone,  $120^{\circ}$ .  
F. G. W.

### Action of Organo-magnesium Compounds on Nitriles.

P. BRUYLANTS (*Bull. Acad. Roy. Belg.*, 1924, [v], **10**, 126—140).—The action of magnesium methyl bromide and other organo-magnesium compounds on various *tert.*- $\alpha$ -aminonitriles (cf. A., 1923, i, 762) yields no ketones, but proceeds almost exclusively in accordance with the scheme:  $\text{CN}\cdot\text{CHR}\cdot\text{N} < + \text{MgR}'\text{X} \rightarrow \text{MgX}\cdot\text{CN} + \text{CHRR}'\cdot\text{N} <$ ; in certain cases, the accessory reaction,  $2\text{CN}\cdot\text{CHR}\cdot\text{N} < + 2\text{MgR}'\text{X} \rightarrow 2\text{MgX}\cdot\text{CN} + \text{R}'\cdot\text{R}' + >\text{N}\cdot\text{CHR}\cdot\text{CHR}\cdot\text{N} <$ , also takes place.

The action of magnesium methyl bromide on  $\alpha$ -piperidinopropiononitrile (cf. Knoevenagel, A., 1904, i, 990) yields isopropylpiperidine (cf. Ladenburg, A., 1882, 535, 1194) and  $\beta\gamma$ -dipiperidinobutane,  $(\text{CHMe}\cdot\text{C}_5\text{H}_{10}\text{N})_2$ , which is a colourless liquid, b. p.  $294\text{—}297^{\circ}/763\text{ mm.}$ , has the normal molecular weight in freezing benzene, and forms a *chloroaurate*, m. p.  $210\text{—}215^{\circ}$  (decomp.), and a *chloroplatinate*, m. p.  $255^{\circ}$  (decomp.).

With piperidinoacetonitrile, magnesium methyl bromide yields (1) ethylpiperidine (cf. Ladenburg, A., 1882, 534), the picrate of which has m. p.  $165^{\circ}$  (Dennstedt, A., 1890, 1429, gave m. p.  $163^{\circ}$ ), and (2) a small proportion of a compound, b. p.  $200\text{—}220^{\circ}$ , not yet identified.

$\alpha$ -Piperidinobutyronitrile,  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CHEt}\cdot\text{CN}$ , prepared by the interaction of propionaldehyde, piperidine hydrochloride, and potassium cyanide, is a colourless liquid with a faint odour, b. p.  $218\text{—}220^{\circ}$  (slight decomp.),  $108\text{—}110^{\circ}/17\text{ mm.}$ ,  $d_4^{20}$  0.9245,  $n_D^{20}$  1.4628. With magnesium methyl bromide it yields: (1) *methyl-ethylpiperidinomethane*,  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CHMeEt}$ , which is a colourless liquid with a pronounced basic odour, b. p.  $175\text{—}176^{\circ}/768.4\text{ mm.}$ ,  $d_4^{20}$  0.8378,  $n_D^{20}$  1.4506, and forms a microcrystalline *picrate*, m. p.  $96\text{—}98^{\circ}$ , and a *methiodide* crystallising in long needles, m. p.  $210\text{—}212^{\circ}$  (decomp.); (2) a small amount of a product of higher boiling point. With magnesium phenyl bromide, it forms *phenylethylpiperidinomethane*,  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CHPhEt}$ , which is a colourless liquid, b. p.  $275\text{—}276^{\circ}/769.5\text{ mm.}$ ,  $d_4^{20}$  0.9549,  $n_D^{20}$  1.5251, exhibits the normal molecular weight in freezing benzene, and forms an uncrystallisable *methiodide*. With magnesium benzyl bromide it gives *benzylethylpiperidinomethane*,  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CHEt}\cdot\text{CH}_2\text{Ph}$ , which is a colourless liquid, b. p.  $293\text{—}295^{\circ}/770\text{ mm.}$ ,  $d_4^{20}$  0.9431,  $n_D^{20}$  1.5198, and shows normal cryoscopic behaviour in benzene.



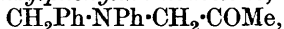
$\alpha$ -Diethylaminovaleronitrile, prepared from diethylamine hydrochloride, potassium cyanide, and butyronitrile, is a colourless liquid, b. p. 94—96°/17 mm.,  $d_4^{20}$  0.8545,  $n_D^{20}$  1.4315, with an odour recalling those of the amine and aldehyde. With magnesium ethyl bromide it yields *ethylpropyldiethylaminomethane*,  $\text{NEt}_2\cdot\text{CHEtPr}$ , which is a colourless liquid, b. p. 174°/772 mm.,  $d_4^{20}$  0.7736,  $n_D^{20}$  1.4243, and has the normal molecular weight in freezing benzene.

T. H. P.

**Piperidine Derivatives. A Cyclic and an Open-chain Compound Related in Structure to Cocaine.** S. M. McELVAIN (*J. Amer. Chem. Soc.*, 1924, **46**, 1721—1727).—Ethyl 4-benzoxyl-1-methylpiperidine-3-carboxylate hydrochloride has been prepared. It is as toxic as cocaine, but is a less effective anæsthetic. The corresponding open-chain compound,  $\beta$ -carbethoxyethyl- $\gamma$ -benzoxypropylmethylamine,  $\text{CH}_2\text{OBz}[\text{CH}_2]_2\cdot\text{NMe}[\text{CH}_2]_2\cdot\text{CO}_2\text{Et}$ , prepared for comparison, is only about one-third as toxic as the piperidine derivative, but scarcely produces anæsthesia. Methylamine hydrochloride and ethyl  $\beta$ -bromopropionate in alcoholic solution condense in the presence of silver oxide, giving  $\beta\beta'$ -dicarbethoxydiethylmethylamine,  $\text{NMe}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ , b. p. 136—138°/4 mm.,  $d_{20}^{20}$  1.0190,  $n_D^{20}$  1.4411 (yield 65%), which is converted by sodium and xylene into *ethyl 1-methyl-4-piperidone-3-carboxylate*, b. p. 114—116°/4 mm.,  $d_{20}^{20}$  1.0660,  $n_D^{20}$  1.4802 (*hydrochloride*, m. p. 128—129°) (yield 57%). This keto ester tends to isomerise on standing, yielding a product which is probably an internal quaternary salt, whilst reduction with platinum oxide catalyst in alcoholic solution (cf. this vol., i, 417) converts it into *ethyl 4-hydroxy-1-methylpiperidine-3-carboxylate*, a viscous, colourless oil, b. p. 122—124°/4 mm.,  $d_{20}^{20}$  1.0879,  $n_D^{20}$  1.4742. The hydrochloride of the latter is converted by benzoyl chloride into *ethyl 4-benzoxyl-1-methylpiperidine-3-carboxylate hydrochloride*, m. p. 181—183°.  $\beta$ -Bromopropionic acid and methylamine condense in aqueous solution in the presence of sodium hydrogen carbonate, and the product on esterification gives a 37% yield of ethyl  $\beta$ -methyaminopropionate, b. p. 59—61°/4 mm.,  $d_{20}^{20}$  1.0082,  $n_D^{20}$  1.4443 (cf. Gansser, A., 1909, i, 702), and 11% of  $\beta\beta'$ -dicarbethoxydiethylmethylamine. Ethyl  $\beta$ -methyaminopropionate and trimethylenedichlorohydrin at 140—150° yield  $\beta$ -carbethoxyethyl- $\gamma$ -hydroxypropylmethylamine, b. p. 123—125°/2 mm.,  $d_{20}^{20}$  1.0190,  $n_D^{20}$  1.4450, whilst with  $\gamma$ -chloropropyl benzoate  $\beta$ -carbethoxyethyl- $\gamma$ -benzoxypropylmethylamine *hydrochloride*, m. p. 103—105°, is obtained.

R. B.

\* **Tertiary Aminoketones and their Use in Ring Syntheses.** K. H. BAUER and K. BÜHLER (*Arch. Pharm.*, 1924, **262**, 128—136).—Compounds of the type  $\text{CH}_2\text{Ph}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{R}$  should suffer intramolecular condensation to give either *isoquinoline* or *indole* derivatives (cf. Mannich and Kuphal, A., 1912, i, 850; Rügheimer and Schön, A., 1909, i, 605). Actually the latter reaction takes place exclusively; thus, *benzylphenylaminoacetone*,



b. p. 320—334°, produced by interaction of benzylaniline and

chloroacetone in a sealed tube at 100°, the *hydrochloride* of which has m. p. 193°, undergoes this condensation when treated in hot xylene with phosphorus pentoxide, yielding 1-benzyl-3-methylindole, m. p. 75°, b. p. 340—350° (*picrate*, m. p. 167°). Similarly,  $\omega$ -bromoacetophenone and benzylaniline give directly in cold alcohol 1-benzyl-3-phenylindole, needles, m. p. 108°. This yields a *hydrochloride*, m. p. 160°, and when distilled over zinc dust breaks down into toluene and 2-phenylindole. (As 3-phenylindole is converted into the 2-isomeride when heated with zinc chloride, the formation of 2-phenylindole here is considered not to be surprising.) Even when a *m*-hydroxy group is present in the benzyl radical—an introduction that should facilitate the *isoquinoline* condensation—the reaction takes the same course; thus, *m*-hydroxybenzylaniline, prisms, m. p. 103—104°, obtained by reducing *m*-hydroxybenzylideneaniline, affords, when treated with  $\omega$ -bromoacetophenone, 1-*m*-hydroxybenzyl-3-phenylindole, rhombohedra, m. p. 148—149°, the *picrate* of which forms prisms, m. p. 112°. When the compound is distilled over zinc dust, it yields *m*-cresol and 2-phenylindole. Methyl 5-chloromethylsalicylate prepared by treating methyl salicylate with chloromethyl ether and hydrochloric acid, forms needles, m. p. 68°, and when acted on by sodium methoxide is converted into methyl 5-methoxymethylsalicylate, needles, m. p. 118°, whilst with diazomethane it affords methyl 2-methoxy-5-chloromethylbenzoate, an oil, b. p. 165—170°/22 mm., and with ammonia, or via the *phthalimido* compound (prisms, m. p. 160—162°) it yields methyl 5-aminomethylsalicylate, an oil, the *hydrochloride* of which has m. p. 122°; with aniline, methyl 5-phenylaminomethylsalicylate,  $\text{NHPh}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{Me}$ , scales or needles, m. p. 107°, is obtained, and when this is treated in a sealed tube at 120° with chloroacetone, a semi-solid substance is produced which is converted into 1-(4-hydroxy-3-carbomethoxybenzyl)-3-methylindole, prisms, m. p. 99—100°, when treated in hot xylene solution with phosphorus pentoxide.

W. A. S.

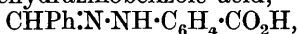
**Isatin and Related Compounds. V. Nitroisatins.** W. BORSCHÉ, H. WEUSSMANN, and A. FRITZSCHE (*Ber.*, 1924, **57**, [B], 1149—1152).—A preliminary note induced by the recent communications of Rupe and Stöcklin (this vol., i, 764) and of Karrer and Haebler (this vol., i, 722).

5-Nitroisatin is converted by hydroxylamine hydrochloride and sodium hydroxide into 5-nitroisatinic acid oxime, m. p. 209—210°, and 5-nitroisatinoxime, decomp. 225°. 5-Nitroisatinhydrazone forms yellow needles, decomp. above 300°. 5-Nitroisatin is converted by malonic acid in hot glacial acetic acid solution into 6-nitro-2-hydroxyquinoline-4-carboxylic acid, m. p. above 300°. 1-Methylisatin is converted by sulphuric acid and potassium nitrate into 5-nitro-1-methylisatin, m. p. 203° [*hydrazone*, m. p. 210° (decomp.)]. Isatinoxime is converted at 230° into *o*-aminobenzonitrile, but an analogous reaction with 5-nitroisatinoxime could not be effected. 6-Nitroisatinoxime, m. p. 238—239°, is prepared by the action of nitrous acid on 6-nitro-oxindole.

*p*-Nitroisonitrosoacetanilide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH} : \text{N} \cdot \text{OH}$ , m. p. 204—206°, is prepared from *p*-nitroaniline, hydroxylamine, and chloral hydrate in boiling aqueous solution; the corresponding meta and ortho compounds, m. p. 181° and 142°, respectively, are also described. The conversion of these compounds into isatins has not yet been effected satisfactorily. The diisonitrosoacetyl derivative of *p*-phenylenediamine, which is unchanged below 285°, is converted by concentrated sulphuric acid at 70—80° into 5-isonitrosoacetylaminoisatin, a reddish-brown powder which does not change below 285°; in this instance, condensation occurs at only one side of the molecule.

H. W.

**N-Aminoisatin.** R. STOLLÉ and W. BECKER (*Ber.*, 1924, 57, [B], 1123—1124; cf. Neber and Keppler, this vol., i, 761).—Benzylidenephénylhydrazine and oxalyl chloride in ethereal solution yield the compound,  $\text{CHPh} : \text{N} \cdot \text{NPh} \cdot \text{CO} \cdot \text{COCl}$ , m. p. 110° (corresponding anilide, m. p. 200°), which passes at 150° or when treated with aluminium chloride in the presence of carbon disulphide into 1-benzylideneaminoisatin,  $\text{CO} < \begin{smallmatrix} \text{CO} \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{N} \cdot \text{N} : \text{CHPh}$ , m. p. 147°. The latter compound is oxidised by hydrogen peroxide in alkaline solution to *o*-benzylidenehydrazinobenzoic acid,



m. p. 224°. 1-Benzylideneaminoisatin is transformed by boiling hydrochloric acid into benzaldehyde and indazole-3-carboxylic acid, m. p. 258° (decomp.) (acetyl derivative, m. p. 188°), and by sodium hydroxide solution into 3-phenylcinnoline-4-carboxylic acid,  $\begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{C}(\text{CO}_2\text{H}) \\ \text{N} = \text{N} \end{smallmatrix} > \text{CPh}$ , m. p. 244° (decomp.).

H. W.

**The Characteristic of Pyridone Tautomerism.** A. E. TSCHITSCHIBABIN and N. P. JELETZKY (*Ber.*, 1924, 57, [B], 1158—1161).—It has not previously been found possible to decide whether the conversion of 2-alkoxypyridines into 1-alkylpyridones occurs directly or through the intermediate production of quaternary alkyl halides. Since, however, 2-phenoxyppyridine is convertible by heat into 1-phenylpyridone, it is established that direct conversion is possible.

1-Phenyl-2-quinolone, m. p. 138°, is prepared by heating the potassium derivative of carbostyryl with bromobenzene and copper powder at 250°. 2-Phenoxyppyridine is converted at a red heat partly into 1-phenyl-2-pyridone; under similar conditions, 2-phenoxyquinoline gives 1-phenyl-2-quinolone. The potassium derivative of carbostyryl and allyl bromide give 1-allyl-2-quinolone, b. p. 326—329°, the chloroplatinate of which is described. An attempt to prepare 2-allyloxyquinoline by the action of 2-chloroquinoline on a solution of sodium in allyl alcohol yielded 1-allyl-2-quinolone.

H. W.

**Tautomerism of 2-Aminopyridine. II. Formation of Dicyclic Derivatives of 2-Aminopyridine.** A. E. TSCHITSCHIBABIN (*Ber.*, 1924, 57, [B], 1168—1172).—The ability of

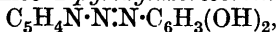
2-aminopyridine to react in the tautomeric pyridone-2-imine form is shown by its power to condense with ethyl malonate and allied compounds to form pyrimidine derivatives. Thus, 2-aminopyridine and ethyl malonate at 165—195° yield 4 : 6-diketo-1 : 2-divinylene-1 : 4 : 5 : 6-tetrahydropyrimidine (annexed formula), decomp. 295—298° when rapidly heated, which is converted by concentrated nitric acid into 5-nitro-4 : 6-diketo-1 : 2-divinylene-tetrahydropyrimidine, decomp. 255°. With ethyl methylmalonate 2-aminopyridine yields 4 : 6-diketo-5-methyl-1 : 2-divinylene-tetrahydropyrimidine, decomp. 302—303°, and with ethyl ethylmalonate it gives 4 : 6-diketo-5-ethyl-1 : 2-divinylene-tetrahydropyrimidine, decomp. 260°; it does not appear to react analogously with ethyl diethylmalonate. The action of even a large excess of ethyl oxalate on 2-aminopyridine gives only *di*-2-pyridyloxamide,  $(\text{CO}\cdot\text{NH}\cdot\text{C}_5\text{H}_4\text{N})_2$ , m. p. 161—162°, which is also formed when the substances react in absolute alcoholic solution in the presence of sodium alkoxide; under the latter conditions, ethyl malonate does not yield the pyrimidine derivative described above.

H. W.

**Preparation of Hydroxycarboxylic Acids from Hydroxypyridines.** A. E. TSCHITSCHIBABIN and A. W. KIRSSANOW (*Ber.*, 1924, 57, [B], 1161—1163).—The sodium salt of 2-pyridone or freshly-distilled 2-pyridone in the presence of ignited, powdered potassium hydroxide is converted by carbon dioxide under 20 atmospheres pressure at 180—200° into 2-hydroxypyridine-5-carboxylic acid, m. p. 304° (decomp.). The synthesis is analogous to Kolbe's synthesis of salicylic acid, from which it differs in that the carboxyl group enters in the para and not the ortho position to the hydroxyl group. When, as in carbostyrl, the para position is occupied the synthesis does not appear to take place even under conditions more drastic than those outlined above.

H. W.

**Diazotisation and Nitration of 4-Aminopyridine.** E. KOENIGS, G. KINNE, and W. WEISS (*Ber.*, 1924, 57, [B], 1172—1178).—4-Chloropyridine-2 : 6-dicarboxylic acid is converted by concentrated aqueous ammonia into ammonium hydrogen 4-aminopyridine-2 : 6-dicarboxylate, m. p. 299° (corr.), from which 4-aminopyridine-2 : 6-dicarboxylic acid, m. p. 297° (corr.), is readily isolated. The copper hydrogen salt, the carbethoxy derivative, m. p. 304° (corr.) after previous softening, the benzoyl derivative, m. p. 309° (corr.), and the ethyl ester, m. p. 149—151° [*hydrochloride*, m. p. 283—284°, and *chloroaurate*, m. p. 178° (corr.) of the latter], are described. The acid is converted by distillation with lime into 4-aminopyridine [*chloroaurate*, m. p. 283—284° (corr.); *chloroplatinate*, m. p. 251—252° (corr.); *picrate*, m. p. 215—216° (corr.); *hydrogen sulphate*; *benzoyl derivative*, m. p. 202° (corr.)]. 4-Aminopyridine can be diazotised by cautious addition of nitrosylsulphuric acid to its solution in fuming nitric acid; the product is converted in the usual manner into 4-pyridylazoresorcinol,

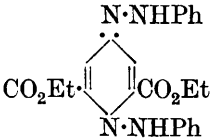


4-pyridylazodimethylaniline dinitrate, m. p. 76—77° (corr.), and

*4-pyridylazo-m-phenylenediamine*, m. p. 263—264° (corr.). *4-Nitroaminopyridine*,  $C_5H_4N \cdot NH \cdot NO_2$ , m. p. 243—244° (corr.), is most conveniently prepared by the cautious addition of nitric acid (*d* 1.52) to a solution of 4-aminopyridine in concentrated sulphuric acid; the *hydrochloride*, m. p. 240° after softening at 210°, *nitrate*, m. p. 202—204° (corr.), *chloroplatinate*, m. p. 209° (corr.), *sodium salt*, m. p. 260—261°, *potassium salt*, m. p. 301—302°, and *benzoyl derivative*, m. p. 226° (corr.), are described. 4-Nitroaminopyridine is reduced by stannous chloride and concentrated hydrochloric acid to 3:4-diaminopyridine which could not be isolated in the homogeneous condition (during the action a partial isomerisation of 4-nitroamino- into 3-nitro-4-amino-pyridine appears to take place); the *chloroplatinate*, m. p. 231—232° (corr.), and the *dibenzoyl derivative*, m. p. 213° (corr.), are described. The diamine condenses with glyoxal to form 3:4-pyridopyrazine,  $C_5H_3N \begin{smallmatrix} \diagup N=CH \\ \diagdown N=CH \end{smallmatrix}$ , m. p. 153° [*chloroplatinate*, m. p. 248—249° (corr.)]. H. W.

**Products of the Nitration of 4-Aminopyridine.** E. KOENIGS, M. MIELDS, and H. GUBLT (*Ber.*, 1924, 57, [B], 1179—1187; cf. Koenigs, Kinne, and Weiss, preceding abstract).—An extended examination of the primary product of the nitration of 4-aminopyridine has shown it to be 4-nitroaminopyridine instead of the expected 3-nitro-4-aminopyridine. The substance is converted by diazotisation in concentrated hydrochloric acid solution or by evaporation with concentrated hydrochloric acid into 4-chloropyridine; under the latter conditions a *dichloropyridine*, needles which sublime at 160°, is also produced [*additive compound* with mercuric chloride, m. p. 246—248° (decomp.)]. The nitroamine is reduced by zinc dust and sodium hydroxide solution to 4-hydrazinopyridine, which could not be isolated in the homogeneous condition, but is characterised by several derivatives (Koenigs and Zscharn, unpublished work). 4-Nitroaminopyridine is transformed by concentrated sulphuric acid at 160° into 3-nitro-4-aminopyridine, m. p. 200° (*hydrochloride*, m. p. 258—259°; *chloroplatinate*, m. p. 256°; *picrate*, m. p. 197—198°). Treatment of 4-aminopyridine dissolved in concentrated sulphuric acid with nitric acid (*d* 1.52) results in the production of 3-nitro-4-nitroaminopyridine, m. p. 202° (decomp.); the very unstable *hydrochloride*, the *picrate*, m. p. 188—189°, and the *potassium salt* are described. The compound can also be prepared by the nitration of 4-nitroaminopyridine, but not from 3-nitro-4-aminopyridine. If 4-aminopyridine is nitrated as described above and the solution is heated for a short time at 170—175°, 3:5-di-nitro-4-aminopyridine, m. p. 170—171°, is produced; the *picrate*, m. p. 147° (indef.), the *chloroaurate*, m. p. 228—229°, and the *disodium salt* are described. 3-Nitro-4-aminopyridine is converted by boiling barium hydroxide solution into 3-nitro-4-hydroxypyridine, m. p. 284° (decomp.), identical with the product described by Koenigs and Freter (following abstract). Reduction of 3-nitro-4-aminopyridine with stannous chloride and concentrated hydrochloric acid yields 6-chloro-3:4-diaminopyridine, m. p. 162° [*hydro-*

chloride ( $+\frac{1}{2}\text{H}_2\text{O}$ ), m. p.  $218^\circ$ ; *chloroplatinate*; *dibenzoyl* derivative, m. p.  $218^\circ$ ]; the substance can be diazotised in dilute hydrochloric acid solution, thus establishing beyond doubt the presence of an amino group in position 3. Similarly, 3 : 5-dinitro-4-aminopyridine is converted by stannous chloride and concentrated hydrochloric acid into 2 : 6-dichloro-3 : 4 : 5-triaminopyridine, m. p.  $206^\circ$ ; the hydrochloride,  $\text{C}_5\text{H}_6\text{N}_4\text{Cl}_2\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , m. p.  $220^\circ$ , is described. 3-Nitro-4-aminopyridine is converted by bromine in glacial acetic acid solution into a mixture of 3-nitro-4-aminopyridine hydrobromide ( $+\text{3H}_2\text{O}$ ), m. p.  $266^\circ$ , and 5-bromo-3-nitro-4-aminopyridine, m. p.  $181^\circ$  (*chloroplatinate*, m. p.  $276^\circ$ ).


 Ethyl acetonedioxalate is converted by phenylhydrazine in boiling alcoholic solution into ethyl 1-anilino-4-phenylhydrazonodihydro-pyridine-2 : 6-dicarboxylate (annexed formula), m. p.  $194^\circ$ , which could not be reduced to aminopyridinedicarboxylic acid. H. W.

**Nitration of 4-Hydroxypyridine.** E. KOENIGS and K. FRETER (*Ber.*, 1924, 57, [B], 1187—1192).—3-Nitro-4-hydroxypyridine, m. p.  $269\text{--}270^\circ$  (decomp.), is prepared by adding 4-hydroxypyridine nitrate, m. p.  $190^\circ$ , to a cold mixture of nitric acid (*d* 1.52) and fuming sulphuric acid (70%  $\text{SO}_3$ ) and subsequently heating the mixture to gentle ebullition; the product appears to be identical with the substance, m. p.  $284^\circ$  (decomp.), described by Koenigs, Miels, and Gurlt (preceding abstract). 5-Bromo-3-nitro-4-hydroxypyridine, prepared from 3-nitro-4-hydroxypyridine and bromine water, has m. p.  $370^\circ$  after darkening at  $350^\circ$ . Protracted heating of 4-hydroxypyridine with a mixture of fuming nitric and sulphuric acids leads to the formation of 3 : 5-dinitro-4-hydroxypyridine, m. p.  $325^\circ$ ; the monohydrate and the monosodium salt, m. p.  $314\text{--}315^\circ$ , are described. Phosphorus pentachloride converts 3-nitro-4-hydroxypyridine into 4-chloro-3-nitropyridine, which, probably by reason of the extreme lability of the halogen atom, could not be obtained in the homogeneous state; the *chloroplatinate*, m. p.  $222^\circ$  (decomp.), and the *picrate*, m. p.  $120^\circ$ , are described. The substance is converted by hot water into 3-nitro-4-hydroxypyridine and by aqueous ammonia into 3-nitro-4-aminopyridine. Under certain conditions, it is transformed by an alcoholic solution of sodium ethoxide into 3-nitro-4-ethoxypyridine, m. p.  $49\text{--}50^\circ$  [*hydrochloride*, m. p.  $160^\circ$ ; *chloroplatinate*, m. p.  $246\text{--}248^\circ$  (decomp.)]. Reduction of 3-nitro-4-ethoxypyridine by stannous chloride and concentrated hydrochloric acid gives 6-chloro-3-amino-4-ethoxypyridine, m. p.  $73^\circ$  (*chloroplatinate*, decomp. above  $280^\circ$ ; *picrate*, m. p.  $197^\circ$ ). 3-Nitro-4-hydrazinopyridine has m. p.  $200^\circ$ . H. W.

#### Antiseptic Action of Anil-pyridines and Anil-quinolines.

C. H. BROWNING, J. B. COHEN, S. ELLINGSWORTH, and R. GULBRANSEN (*J. Path. Bact.*, 1924, 27, 121—122; cf. *Brit. Med. J.*, 1923, II, 326).—In general, the anil series shows a marked resemblance to the analogous styryl series in possessing marked anti-

septic properties. In both series, alterations in the side-chain occupying the 6-position are not very marked in their effect.

CHEMICAL ABSTRACTS.

**Derivatives of Quinoline.** S. LOEWE (D.R.-P. 380918; from *Chem. Zentr.*, 1924, i, 1446).—The following compounds are mentioned: 2- $\beta$ -Aminoethylquinoline; its *dipicrate*, m. p. 202°; 2- $\beta$ -methylaminoethylquinoline; its *picrate*, m. p. 185—188°; 2- $\beta$ -piperidylethylquinoline; its *dipicrate*, leaflets, m. p. 145° (decomp.); 4- $\beta$ -dimethylaminoethylquinoline; its *dipicrate*, yellow, crystalline powder, m. p. 203°. G. W. R.

**Manufacture of Alkylxyacridines.** L. CASSELLA & Co., G.M.B.H. (Brit. Pat. 217715).—Hydroxyacridines may be converted into *O*-alkyl ethers, without the nitrogen being alkylated, by the action of alkylating agents in the presence of acid-binding substances; e.g., a mixture of mono- and di-methoxyacridines is obtained by stirring 3:6-dihydroxyacridine, dissolved in aqueous sodium hydroxide, with methyl sulphate. The preparation of the following is described: 3:6-Dimethoxyacridine, pale yellow crystals, m. p. 138—139°, giving a green fluorescence in acid solution; 3:6-di-hydroxyacridine monomethyl ether, small, bright yellow crystals, m. p. above 300°, giving a green fluorescence in acid solution; 3:6-diethoxyacridine, yellow needles, m. p. about 142—143°; 3:6-dihydroxyacridine monoethyl ether, yellow crystals, m. p. above 300°, giving a green fluorescence in concentrated sulphuric acid; 3:6-dimethoxy-2:7-dimethylacridine (from the hydroxy-base and methyl *p*-toluenesulphonate), straw-coloured needles, m. p. 235—238°, giving a green fluorescence in sulphuric acid; 3:6-dihydroxy-2:7-dimethylacridine monomethyl ether, a bright yellow solid, m. p. above 300°; 3:6-dihydroxyacridine di- $\beta$ -hydroxyethyl ether (from 3:6-dihydroxyacridine and ethylene chlorohydrin), reddish-yellow crystals, m. p. 200°, giving a slight green fluorescence in concentrated sulphuric acid. The new compounds are non-toxic and are valuable bactericides. W. T. K. B.

**Pyrimidines. VI. New Colour Tests for Uracil and Cytosine.** O. BAUDISCH (*J. Biol. Chem.*, 1924, 60, 155—166).—If uracil or cytosine be treated with ferrous hydrogen carbonate and air, a brilliant lemon-yellow pigment is formed by subsequent autoxidation. Dihydroisobarbituric acid is first produced. After filtration from the ferric hydroxide and further exposure to air, this is converted into the deep red ferrous salt of isobarbituric acid and, by further autoxidation, the solution changes colour from the surface downwards to bright yellow. The yellow colour develops much more quickly from cytosine than from uracil, the ammonia produced from the former acting as a catalyst and hastening autoxidation. The yellow compound has not been obtained in sufficient quantity for analysis, but its chemical reactions are described. In alkaline solutions, it has an oxidation-reduction power which is well shown with methylene-blue; it reduces ammoniacal silver nitrate and phosphomolybdic acid, giving a deep blue colour with

the latter. Diazobenzenesulphonic acid gives an intense, but temporary, brilliant red colour. These tests are very delicate. The chemical properties of uracil and cytosine are compared with those of indole and anthracene compounds and other substances widely distributed in plants and animals, and their significance in biochemical processes is discussed. It is considered that the pyrimidines or their decomposition products possess the functions of respiration pigments. C. T. G.

**Alkylation of Indazoles.** K. VON AUWERS and H. G. ALLARDT (*Ber.*, 1924, 57, [B], 1098—1106).—In continuation of previous investigations (Auwers and Schaich, A., 1921, i, 806), the effect of experimental conditions on the formation of 1- or 2-alkylindazoles has been systematically examined. The action of ethyl iodide on the alkali derivatives of indazole leads preferentially to the production of 2-ethylindazole, whereas 1-ethylindazole predominates when the mercury or silver salt is employed. Since, however, indazole sodium is converted by methyl iodide or benzyl chloride at 100° almost exclusively into 2-methyl- or 1-benzyl-indazole, respectively, the results have no bearing on the constitution of salts of indazole. The preferential formation of 1-alkylindazoles at higher temperatures (*cf. loc. cit.*) does not appear to be a general phenomenon; the effect of concentration is not manifested in one particular direction. Comparative alkylations with methyl, ethyl, propyl, isopropyl, butyl, isobutyl, allyl, and benzyl bromides indicate that the production of 1-alkyl derivatives is predominating in the cases of the allyl, benzyl, and isopropyl compounds, in which the halogen atom is particularly reactive, but, in these cases, the course of the change is not entirely independent of the particular halogen atom present in the halide.

The following new alkylindazoles are described incidentally. 2-isoPropylindazole, b. p. 140—142°/15 mm., and the corresponding picrate, m. p. 138—140°; 1-methyl-2-isopropylindazolium iodide, m. p. 132—135° (corresponding picrate, m. p. 191—192·5°), which passes when heated into 1-methylindazole and isopropyl iodide; 2-methyl-1-isopropylindazolium iodide, m. p. 183°, which yields 1-isopropylindazole when heated; 1-n-butylindazole, b. p. 135—136°/13 mm. (picrate, m. p. 92°), and 2-n-butylindazole, b. p. 153°/13 mm. (picrate, m. p. 140·5°); 1-isobutylindazole, b. p. 133°/16 mm. (picrate, m. p. 72·5—73·5°), and 2-isobutylindazole, b. p. 150—152°/13 mm. (picrate, m. p. 122—123°); 2-p-nitrobenzylindazole, m. p. 91—91·5° (the picrate exists in two forms, dark yellow crystals and long, flesh-coloured needles, m. p. 142—143°); the constitution of the substance is established by its conversion successively into 2-p-aminobenzylindazole, m. p. 117—118°, and the known 2-benzylindazole; 2-o-nitrobenzylindazole, m. p. 72·5—73·5° (the picrate, m. p. 147°, appears to exist in three modifications). H. W.

**Action of Cyanogen Halides on Phenylhydrazine. IX. o-Phenylenethioammeline.** G. PELLIZZARI (*Gazzetta*, 1924, 54, 451—456; *cf. A.*, 1921, i, 620; 1922, i, 585; this vol., i, 771).—When treated with ammonium hydrosulphide,  $\alpha\beta$ -dicyano-o-



phenyleneguanidine unites with a molecule of hydrogen sulphide to form *o*-phenylenethioammeline,  $\text{C}_6\text{H}_4\text{N}(\text{CN})\text{C}\cdot\text{NH}\cdot\text{CN} + \text{H}_2\text{S}$

The fact that this compound remains unchanged on protracted boiling with concentrated hydrochloric acid indicates that the carbimido group occupies the  $\beta$ - and not the  $\alpha$ -position, since in the latter case such group would be converted into carbonyl by this treatment. When its alkaline solution is boiled, *o*-phenylenethioammeline loses hydrogen sulphide and is converted into the *o*-phenyleneammeline obtained by the action of hydrochloric acid on phenylenemelamine (*loc. cit.*), together with phenylenediguamide and phenyleneguanylcarbamide, which are products of the decomposition of *o*-phenyleneammeline.

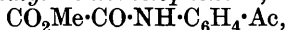
Thus, in the union of a molecule of a primary amine with  $\alpha\beta$ -dicyano-*o*-phenyleneguanidine, the melamine nucleus is closed by means of the nitrogen atom of the amine in such a manner that the alkyl group remains connected directly with the nucleus to form an isomelamine derivative. When, however, a molecule of hydrogen chloride or sulphide combines with  $\alpha\beta$ -dicyano-*o*-phenyleneguanidine, the closure of the nucleus is necessarily effected by the nitrogen of one of the two cyanogen groups, the other nitrogen atom forming the carbimido group; the chlorine atom is fixed in the position corresponding with the  $\beta$ -cyanogen, but the sulphhydryl group enters in the  $\alpha$ -position. Although the chloro derivative reacts readily with amines, the thio compound does not react in this way.

*o*-Phenylenethioammeline forms hard, white, crystalline aggregates (decomp. above 300°), and has a slightly acid character.

T. H. P.

**Quinazolines. XXXVI. A Quinazoline Analogue of Cinchophen (Atophan). Synthesis of New Quinazolinecarboxylic Acids from Isatin and from *o*-Aminoacetophenone.** M. T. BOGERT and F. P. NABENHAUER (*J. Amer. Chem. Soc.*, 1924, **46**, 1702—1707).—When treated with benzoyl chloride and potassium hydroxide, isatin affords benzoylisatoic acid (yield, 38%),  $\text{NHBz}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , m. p. 167—168°. This, when heated at 150° with alcoholic ammonia (cf. Bischler, A., 1891, 745), is converted into 2-phenylquinazoline-4-carboxylic acid, pale yellow needles, m. p. 150—151°, a quinazoline analogue of cinchophen (2-phenylquinoline-4-carboxylic acid), which it resembles in certain properties. Both compounds lose carbon dioxide when heated, thus yielding the corresponding 2-phenylquinazoline or -quinoline. Acetylisatoic acid, m. p. 152—154° (cf. Suida, A., 1878, 586), is obtained (yield, 86%) by oxidising *o*-acetoaminoacetophenone with potassium permanganate below 0° (cf. Glücksmann, A., 1890, 1416) and is converted by alcoholic ammonia at 100—110° into 2-methylquinazoline-4-carboxylic acid, pale yellow, thick prisms (dihydrate), m. p. 175.5—176.5°, giving 2-methylquinazoline when heated. Other acyl derivatives of isatoic acid may be obtained similarly.

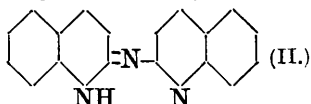
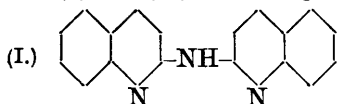
Thus *o*-phthaloylaminoacetophenone, prisms, m. p. 151.5°, from *o*-aminoacetophenone and phthalic anhydride in benzene solution, yields *phthaloylisatinic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , scales, m. p. 151.5°, which with methyl-alcoholic ammonia at 140° yields 2-*o*-carboxyphenylquinazoline-4-carboxylic acid, platelets, m. p. 188—189°. Preliminary physiological tests have been made on the diammonium salt of this acid. Acyl derivatives of *o*-aminoacetophenone themselves condense with alcoholic ammonia, yielding quinazolines. Thus *o*-phthaloylaminoacetophenone yields 2-*o*-carboxyphenyl-4-methylquinazoline, needles, m. p. 185—186° (decomp.). *o*-Methoxalylaminoacetophenone,



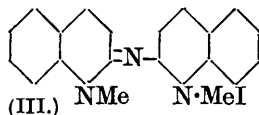
needles, m. p. 128°, from methyl oxalate and *o*-aminoacetophenone, and *o*-oxamaminoacetophenone,  $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{Ac}$ , m. p. 238°; both yield 4-methylquinazoline-2-carboxylic amide, pale yellow prisms, m. p. 235.5°, which is converted into 4-methylquinazoline by boiling hydrochloric acid. *o*-Aminoacetophenone is converted by methyl iodide and methyl alcohol at 100° into *o*-dimethylaminoacetophenone, a pale yellow oil, b. p. 91—94°/1.5 mm. (picrate, m. p. 183—184°).

R. B.

**Synthesis of an Azocyanine.** (Miss) F. M. HAMER (*J. Chem. Soc.*, 1924, 125, 1348—1357).—Azocyanines are analogues of the cyanine dyes having a nitrogen atom as a link between the quinoline nuclei. By heating 2-aminoquinoline with 2-chloroquinoline the hydrochloride of 2:2'-diquinolylamine is obtained (4-aminoquinoline does not so react). This substance exists in two modifications (I) and (II), according to the theory of Scheibe (cf. A., 1921,



i, 451). The action of methyl iodide on this substance produces a mixture of 2:2'-diquinolylamine hydriodide ( $\text{C}_{18}\text{H}_{14}\text{N}_3\text{I}$ ) and the azocyanine, 1-methyldihydroquinolenyl-2-quinolyl-2'-imine methiodide (III). A second method of preparation is that of converting the acetyl derivative of 2:2'-diquinolylamine first into its dimethosulphate, which with sodium hydroxide gives 1-methyldihydroquinolenyl-2-quinolyl-2'-imine, then treating the base with hydriodic acid. A comparison with the analogous 1:1'-dimethylpseudoisocyanine iodide shows that the replacement of  $\text{:CH}\cdot$  by  $\text{:N}\cdot$  causes a shift of the absorption bands towards the more refrangible region of the spectrum.



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A. COUSEN.

**Derivatives of 2-Aminopyridine, 2-Aminoquinoline, and 4-Aminoquinoline.** E. DIEPOLDER [with K. DACHLAUER, E. DEUERLEIN, and E. WOLFEL] (*J. pr. Chem.*, 1923, 106, 41—65).—The chief product of the interaction of 2-chloropyridine and *o*-aminophenol is 2-*o*-hydroxyphenylimino-1:2-dihydropyridine

(Steinhauser and Diepolder, A., 1916, i, 739). Its *hydrochloride* (white plates, m. p. 153—154°), *picrate* (yellow needles, m. p. 170—173°), *chloroplatinate* [dark yellow plates, m. p. 180° (decomp.)], *mercurichloride*,  $C_{11}H_{10}ON_2 \cdot HCl \cdot 2HgCl_2$  (colourless needles, m. p. 149—151°), and *mercuric chloride additive* compound,

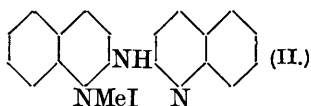
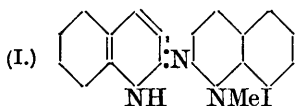
$C_{11}H_{10}ON_2 \cdot 2HgCl_2$  (fine needles, m. p. 160—162°), are now described. With nitrous acid, it yields the 1-nitroso derivative, yellowish-brown needles, m. p. 275—276° (decomp.).

The *methiodide*, pale brown prisms, m. p. 188—191° (decomp.), when dissolved in sodium hydroxide solution, loses hydrogen iodide and gives 2-o-hydroxyphenylimino-1-methyl-1:2-dihydropyridine (needles, m. p. 116—117°), isomeric with the product (m. p. 159°), previously obtained from 2-chloropyridine and o-anisidine.

o-Hydroxyphenyl-2:2'-dipyridylamine,  $OH \cdot C_6H_4 \cdot N(C_5H_4N)_2$ , is produced by heating 2-chloropyridine (2 mols.) and o-aminophenol (1 mol.) in sealed tubes in presence of zinc chloride or barium oxide. It forms white needles, m. p. 187°, and is formed as a by-product in the preparation of the above imine. The *hydrochloride*, a white, flocculent precipitate, has m. p. 242—244° (sintering at 132°). The *chloroplatinate*, orange-yellow needles, m. p. 212—215°; *chloroaurate*, orange plates, m. p. 195°; *picrate*, yellow needles, m. p. 190°; *mercurichloride*, needles, m. p. 206—208°; *mercuric chloride additive* compound, white prisms, m. p. 169—172°, are described.

2:2'-Dipyridylamine, from 2-amino- and 2-chloro-pyridine, forms a *mercurichloride*,  $C_{10}H_8N_3 \cdot HCl \cdot HgCl_2$  (colourless needles, m. p. 225° with previous sintering), and a *methiodide* (yellow prisms, m. p. 288—291°), stable to cold alkali and losing methyl iodide, not hydrogen iodide, when warmed with alkali.

2:2'-Diquinolylamine, from 2-amino- and 2-chloro-quinoline, white needles, m. p. 161°, does not react with benzaldehyde. The following derivatives are described: *Hydrochloride*, yellow prisms, m. p. above 305°; *chloroaurate*, orange needles, m. p. 306°; *mercurichloride*, pale yellow prisms, m. p. 272°; *monopicrate*, yellow plates, m. p. 286°; *dipicrate*, yellow needles, m. p. 297° (decomp.); *nitrosoamine*, pale yellow needles, m. p. 238° (decomp.). It forms a *monomethiodide*, yellow plates, m. p. 246—278° (decomp.), stable to cold alkali. Presumably this has formula (I), as hydriodic acid (not, as is the case, methyl iodide) should be removed by the action of alkali if (II) were the formula.



4:4'-Dimethyl-2:2'-diquinolylamine, yellow prisms, m. p. 167·5°, was formed by the interaction of 2-chloro-4-methylquinoline and 2-amino-4-methylquinoline. The *hydrochloride*, yellow prisms, m. p. 292—297°; the *mercurichloride*, needles, m. p. 249°; *chloroplatinate*, yellow needles, m. p. 280° (decomp.); the *mono-*  
m m 2

*picrate*, yellow needles, decomp. at 286—299°; the *dipicrate*, dark yellow needles, decomp. at 265—289°; *nitrosoamine*, pale yellow needles, decomp. 238°, and the *methiodide*, yellow prisms, sintering at 245°, m. p. (decomp.) 290°, are described. The methiodide loses methyl iodide when warmed with alkali.

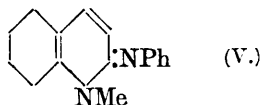
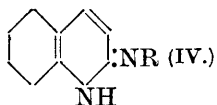
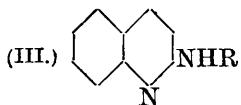
2-Pyridyl-2'-quinolylamine, obtained similarly, forms pale yellow plates sintering at 104°, m. p. 108°. The *hydrochloride*, yellow needles, m. p. 215—216° (decomp.); *monopicate*, needles, m. p. 242—244°; *mercuric chloride additive* compound, pale yellow needles, m. p. 210°; *mercurichloride*, pale yellow prisms, m. p. 245°; *methiodide*, yellow plates, m. p. 208° (giving methyl iodide with warm alkali), are described.

2-Pyridyl-4'-methyl-2'-quinolylamine, from 2-aminopyridine and 2-chloro-4-methylquinoline, forms pale yellow prisms, sintering at 158°, m. p. 174°. The *hydrochloride*, needles, m. p. 241°, and the *methiodide*, yellow prisms, m. p. 208°, decomposed by warm alkali, are described.

4-Methyl-2:2'-diquinolylamine forms yellow prisms, m. p. 129° (darkening at 126°). The *hydrochloride*, pale yellow needles, m. p. 267—275° (decomp.); *monopicate*, yellow prisms, m. p. 287° (decomp.), and the *methiodide*, long, yellow prisms, m. p. 247—253° (decomp.), decomposed by warming with alkali, are described.

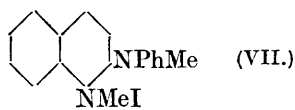
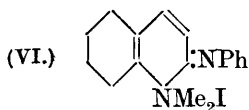
These bases are peculiar in that they only give monomethiodides, these being readily decomposed on warming with alkalis.

*Note on the Substituted Aminoquinolines.*—The experimental part of this work is not yet described, but a summary is given. Two possible formulæ (III) or (IV) exist for the substituted 2-(or 4)-aminoquinolines:



Hitherto in no cases have the isomerides been found to exist side by side, but two methyl derivatives have now been isolated. The substituted aminoquinolines are formed by the interaction of the chloroquinoline and the corresponding amine, and the methyl derivatives (e.g., V) are formed by the action of alkali on the methiodide.

The methiodide (VI) differs from that (VII) formed by the interaction of 1-methyl-2-iodoquinolinium iodide and methylaniline.



The 4-phenylamino derivative also gives a methiodide differing from that prepared by the interaction of methylaniline and 1-methyl-4-iodoquinolinium iodide.

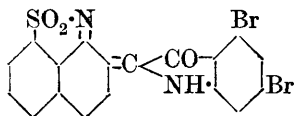
With nitrous acid, these amines give 1-nitroso derivatives. The position of the nitroso radical is shown by the fact that they are

not basic and are not converted by alcoholic hydrogen chloride into *p*-nitroso derivatives.

Neither 2-aminoquinoline nor its methiodide reacts with aldehydes, although 2-aminopyridine readily does so. A. E. C.

**Some Derivatives of 1:8-Naphthasultam.** W. KÖNIG and E. WAGNER (*Ber.*, 1924, **57**, [B], 1056—1061; cf. Zincke, A., 1916, i, 426; 1917, i, 38; 1918, i, 550).—The analogy between 1:8-naphthasultam and  $\alpha$ -naphthol can be further traced in their indole-indigotin derivatives, and the relative positions of the absorption bands of 2-naphthalene-2'-indole-indigotin and 2-naphthasultam-2'-indole-indigotin (1:8-sultam-2-naphthalene-2'-indole-indigo) are similar, the different values obtained in the latter case from those given by Friedländer and Sander (this vol., i, 662, 663) being attributed to the use of different solvents. Analogies are also observed between *N*-phenyl- and *N*-*p*-tolyl-1:8-naphthasultam and the  $\alpha$ -naphthol derivatives ( $\alpha$ -naphthyl phenyl ethers), which couple rapidly with diazotised 2:4-dinitroaniline in acetic acid solution (cf. K. H. Meyer, A., 1914, i, 882) yielding dyes the absorption curves of which suggest that the coupling has taken place in the *p*-position. The partial removal of the aryl residue observed in the case of  $\alpha$ -naphthyl phenyl ether was not detected.

2-Naphthasultam-2'-[5':7'-dibromoindole]-indigotin (annexed formula), dark blue needles, subliming about 200°, obtained by converting 5:7-dibromoindole into its chloride with phosphorus pentachloride in benzene solution, and heating this with naphthasultam, resembles dibromo-2-naphthalene-2'-naphtholindigotin. On heating with 10% sodium hydroxide solution, 2-naphthasultam-2'-indole-indigotin yields, besides anthranilic acid, 1:8-naphthasultam-2-aldehyde,  $\text{CHO} \cdot \text{C}_{10}\text{H}_5 \begin{smallmatrix} \text{SO}_2 \\ \text{NH} \end{smallmatrix}$ , small,



colourless crystals, decomp. above 200°, giving a yellow sodium salt. *N*-Phenyl-naphthasultam, colourless needles, m. p. 158°, from phosphoryl chloride and potassium *N*-phenyl-1-naphthylamine-8-sulphonate, couples with 2:4-dinitrobenzenediazonium sulphate, yielding 4-[2':4'-dinitrobenzeneazo]-*N*-phenyl-1:8-naphthasultam, reddish-brown needles, m. p. 240°, giving a yellowish-red solution in alcohol gradually changed through red, violet, and blue to green by alkali. On nitration in the usual way, *N*-phenyl-naphthasultam yields 4-nitro-1-phenylaminonaphthalene-8-sulphonic acid, whilst nitration in acetic acid gives 4-nitro-*N*-phenyl-1:8-naphthasultam, long, yellow needles, m. p. 200°, yielding 4-amino-*N*-phenyl-1:8-naphthasultam, deep yellow lancets, m. p. 185°, which after diazotisation couples with  $\beta$ -naphthol and R-salt, giving bright red dyes. *N*-*p*-Tolyl-naphthasultam, m. p. 152°, similarly obtained from sodium *N*-*p*-tolyl-1-naphthylamine-8-sulphonate, gives 4-[2':4'-dinitrobenzeneazo]-*N*-*p*-tolyl-1:8-naphthasultam, m. p. 195°. *N*-Methyl-1:8-naphthasultam couples with diazotised 2:4:6-trinitroaniline in acetic acid solution, yielding 4-[2':4':6'-tri-

*nitrobenzeneazo*]-*N*-methyl-1:8-naphthasultam, red needles, m. p. 293°, whilst *N*-methyl-*p*-toluenesulphonyl- $\alpha$ -naphthylamine does not couple. R. B.

**The Interaction of Benzenesulphonazide and Ethyl Malonate.** T. CURTIUS and G. EHRHART (*J. pr. Chem.*, 1923, [ii], 106, 66—75).—When a mixture of benzenesulphonazide and ethyl malonate is boiled at 110°/20—25 mm. for some hours, then shaken with alkali and neutralised in the cold with acid, the first product is 5-hydroxy-1-benzenesulphonyl-1:2:3-triazole-4-carboxylic acid, a yellow oil, which slowly isomerises to the corresponding triazolone, a solid, forming weakly anisotropic rhombohedra, decomp. 106°.

The ethyl ester is best prepared by treating the sulphonazide with ethyl sodiomalonate in alcohol, adding water, cooling, and acidifying. A viscous oil is produced which behaves as an *enol* towards ferric chloride; on keeping, it isomerises to the solid triazolone, anisotropic rhombs, which melt at 79° and slowly evolve nitrogen at 110°.

The products of acid hydrolysis of the triazolone ester are benzenesulphonamide, glycollic acid, nitrogen, and carbon dioxide, indicating that the keto-group is in position (5). Its stability to concentrated hydrochloric acid and the fact that nitrogen is only eliminated very slowly on heating, and not at all by the addition of iodine, indicate that it is not a diazo derivative of the formula  $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}(\text{N}_2)\text{CO}_2\text{Et}$ . However, the ester reacts with ammonia and hydrazine as if it possessed a diazo structure. With aqueous ammonia under pressure, the ammonium salt of 5-hydroxy-1-benzenesulphonyl-1:2:3-triazole-4-carboxylamide is produced which on acidification yields the free hydroxy compound as a viscous oil; this isomerises into 5-hydroxy-1:2:3-triazole-4-benzenesulphonylcarboxylamide,  $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_2\text{HON}_3$ , anisotropic prisms which decompose on heating.

By the action of hydrazine on the ester, nitrogen and ammonia were evolved, and the hydrazine salt of 1-amino-5-hydroxy-1:2:3-triazole-4-benzenesulphonylcarboxylamide (annexed formula) was produced as small plates, which on neutralisation gave the free hydroxy-amide as small, colourless prisms.

This substance affords a *benzylidene* derivative, forming colourless anisotropic prisms. A. E. C.

**isoOxazoline Oxides. II. Benzoyldiphenylisoxazoline Oxide.** E. P. KOHLER (*J. Amer. Chem. Soc.*, 1924, 46, 1733—1747; cf. this vol., i, 571).—Phenylated derivatives of the isooxazoline oxide previously obtained (*loc. cit.*) have now been prepared. These do not form additive compounds with water etc., and are not ruptured by strong bases, whilst acid chlorides and anhydrides only act as dehydrating agents. Phenylnitromethane and styryl methyl ketone condense in methyl-alcoholic sodium methoxide solution, giving  $\gamma$ -nitro- $\beta\gamma$ -diphenylpropiophenone,

$\text{NO}_2 \cdot \text{CHPh} \cdot \text{CHPh} \cdot \text{CH}_2\text{Bz}$ , in two stereoisomeric forms, m. p. 181—182° and 131—132°, the former predominating, especially in boiling solutions. Bromination of the isomeride, m. p. 181—182°, in chloroform solution yields two stereoisomeric  $\alpha$ -bromo derivatives, m. p. 185° and 162°, the isomeride of m. p. 131—132° similarly yielding two other isomeric  $\alpha$ -bromo derivatives, m. p. 155° and 125—127°. Bromination of the nitroketone in the presence of sodium methoxide yields  $\gamma$ -bromo- $\gamma$ -nitro- $\beta$ - $\gamma$ -diphenylpropionophenone in two stereoisomeric forms, m. p. 178—180° (decomp.) and 136—138°, differing from the  $\alpha$ -bromo compounds in their readier decomposition by heat and their stability towards potassium acetate. All four  $\alpha$ -bromo compounds lose hydrogen bromide when treated with methyl-alcoholic potassium acetate, yielding in the case of the isomerides from the nitroketone of m. p. 181—182° a single oxide, 4-benzoyl-2:3-diphenylisooxazoline oxide, m. p. 123° (+1MeOH, m. p. 93°), and, with the bromo derivatives of the lower-melting isomeride, a mixture of this oxide and an isomeric isooxazoline oxide, flat needles, m. p. 151°.

The former oxide yields a colourless sodium derivative (annexed formula), converted by benzoyl chloride into the benzoate,  $\text{C}_{29}\text{H}_{21}\text{O}_4\text{N}$ , needles, m. p. 190°. The sodium derivative gradually becomes yellow in dilute solution, but gives no copper derivative. When oxidised by sodium peroxide, the lower-melting oxide gives benzoic acid and the colourless sodium salt of the enolic form (m. p. 113°) of 2:3-diphenylisoxazol-4-one (copper derivative, deep blue). A boiling ethereal solution of the enol deposits the ketonic form in hard, lustrous tablets, m. p. about 150° (decomp.), the structure of which is established by its synthesis by the action of hydroxylamine hydrochloride on a methyl-alcoholic solution of methyl benzoylphenylacetate,  $\text{CHBzPh} \cdot \text{CO}_2\text{Me}$ , m. p. 75°, obtained by the alcoholysis of benzoylphenylacetonitrile. Solutions of the oxides in concentrated alkalis are colourless, but on dilution beyond a certain point turn yellow, through formation, together with isooxazole, of  $\alpha\gamma\delta$ -triphenylbutanetrione oxime,  $\text{HON} \cdot \text{CPh} \cdot \text{CHPh} \cdot \text{COBz}$ , by opening of the isooxazole ring.

The oxime, which is most conveniently obtained by the action of alcoholic alkali on the bromine compound, crystallises with 1 mol. of ether. The ether-free substance has m. p. 150°, decomposing immediately afterwards. It gives no copper derivative; strong bases convert it almost quantitatively into isooxazole, and oxidation with sodium peroxide yields benzoic acid and benzil  $\beta$ -monoxime, m. p. 118°. (Benzil  $\beta$ -monoxime, m. p. 113—114°, dissolved in sodium hydroxide and reprecipitated with hydrochloric acid, melts sharply at 118°.) The isooxazoline oxides on treatment with organic or inorganic bases or with acetyl chloride or phosphorus pentachloride readily lose water, giving the isooxazole. 4-Benzoyl-2:3-diphenylisooxazole, lustrous prisms, m. p. 167°, is most easily obtained by the action of ammonia on the lower-melting oxide in methyl-alcoholic solution. The structure of the isooxazole is deduced (1) from its reduction by zinc and acetic acid

to 2 : 3-diphenyl-4-(hydroxybenzyl)isooxazole, which is oxidised back to the ketone by chromic acid, and yields the corresponding tertiary alcohol, m. p. 145°, with magnesium ethyl bromide; and (2) from the behaviour of its oxime, m. p. 177°, which with phosphorus pentachloride in dry ether undergoes a Beckmann transformation, yielding the imide chloride,  $C_{15}H_{10}ON(CPh.NCl)$ , yellow prisms, m. p. 139°, and an anilide,  $C_{22}H_{16}O_2N_2$ , colourless prisms, hydrolysed by alcoholic potassium hydroxide to 2 : 3-diphenylisooxazole-4-carboxylic acid, thin plates, m. p. 170°. This acid gives an ozonide converted by water into oxalic acid and  $\beta$ -benzilmonoxime, m. p. 118°. On treatment with magnesium ethyl bromide etc., the isooxazoline oxide affords a tertiary alcohol, bunched needles, m. p. 168°, which with alcoholic potassium hydroxide gives the above tertiary alcohol (m. p. 145°). The same product is obtained when the reaction mixture is allowed to reach room temperature, boiled, and decomposed with acid, excess of Grignard reagent merely acting as a dehydrating agent and the system  $\cdot CPh.NO$  remaining unattacked, behaviour which shows that the isooxazoline oxides do not contain a nitro group.

R. B.

### Synthesis Reactions of Benzthiazole and its Derivatives.

G. BRUNI and T. G. LEVI (*Gazzetta*, 1924, **54**, 402—410; cf. A., 1921, i, 734; 1922, i, 466, 755).—Each of the following compounds yields (1) 1-anilinobenzthiazole when heated with sulphur and aniline at temperatures below 200°, and (2) 1-thiolbenzthiazole when heated with sulphur under pressure at above 260°: monophenylthiocarbamide, thiocarbanilide, *s*-phenyldimethylthiocarbamide, phenylguanidine, *s*-diphenylguanidine, monophenyldiguanide, phenylcyanamide. Benzthiazole itself is formed in such syntheses less frequently than its derivatives but is obtained in small proportion when methyleneaniline is heated with sulphur and aniline at temperatures below 200°; with sulphur under pressure above 300°, methyleneaniline reacts to form 1-thiolbenzthiazole.

T. H. P.

**Oxidation of Benzeneazoquinol.** D. BIGIARI and B. DE BENEDETTI (*Gazzetta*, 1924, **54**, 363—376).—To some extent benzeneazoquinol and the isomeric azoxy derivatives derived therefrom are subject to the influence of the 1 : 4-positions of the two hydroxyl groups. Thus, oxidation of benzeneazoquinol to the azoxy compounds by means of peracetic acid takes place only if one or both of the hydroxyls are protected by introduction of benzoyl or acetyl groups. Moreover, the action of bromine on  $\alpha$ -benzeneazoxyquinol does not lead to definite compounds, a bromine atom apparently entering the quinol nucleus and brominating the monobenzoyl derivative of the azoxy compound. This benzoyl derivative is converted into a nitro derivative by the action of nitrous acid, which, however, oxidises  $\alpha$ -benzeneazoxyquinol to  $\alpha$ -benzeneazoxyquinone. The latter exhibits certain properties of quinonoid compounds. Thus it is yellow, is readily prepared by the action of lead peroxide on the acetic acid solution of the corresponding quinol, is rapidly reduced to  $\alpha$ -benzeneazoxy-



quinol by phenylhydrazine or hydroxylamine, and liberates iodine from potassium iodide solution faintly acidified with acetic acid. On the other hand, it is non-volatile, is not reduced by sulphurous acid, and does not form with azoxyquinol compounds of the quinhydrone type.

Benzeneazobenzoylquinol, prepared by coupling diazobenzene with monobenzoylquinol, has the structure  $\text{OH} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \end{array} \text{OBz}$  and may

be regarded as an *o*-hydroxyazo compound. It is readily oxidised by peracetic acid, with formation of the two isomeric azoxy derivatives. Of these, the one which must be regarded as the  $\alpha$ -isomeride reacts with bromine to form first a monobromo derivative and ultimately a mixture of products difficult to separate and yielding aniline as sole volatile base on reduction. Unlike this  $\alpha$ -compound, the isomeric  $\beta$ -benzeneazoxybenzoylquinol does not react with nitrous acid.

*Benzeneazoquinol*, prepared by hydrolysis of benzeneazobenzoylquinol (cf. Witt and Johnson, A., 1893, i, 571), forms black crystals with cantharides-green reflection, or a garnet-red powder, m. p. 149°. With nitrous acid, it yields, not a nitro derivative but a compound,  $\text{C}_{12}\text{H}_8\text{O}_2\text{N}_2$ , which forms bright red crystals, blackening at 160°, m. p. 172°, and may be benzeneazoquinone or a polymeride thereof.

*Benzeneazobenzoylacetylquinol*,  $\text{OAc} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \end{array} \text{OBz}$ , obtained by

acetylating benzeneazobenzoylquinol, forms orange-yellow needles, m. p. 111°.

*Benzeneazodibenzoylquinol*,  $\text{C}_{28}\text{H}_{18}\text{O}_4\text{N}_2$ , separates in orange-yellow, crystalline globules, m. p. 153—155°, and *benzeneazodi-acetylquinol* in orange, crystalline granules, m. p. 112°.

$\alpha$ -*Benzeneazoxybenzoylquinol*,  $\text{O}:\text{NPh}:\text{N} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{OBz}$ , forms a pale yellow, crystalline powder, m. p. 167°, and dissolves slowly in alkali solution giving a violet-red liquid.  $\alpha$ -*Benzeneazoxybenzoylacetylquinol*,  $\text{O}:\text{NPh}:\text{N} \cdot \text{C}_6\text{H}_3(\text{OAc}) \cdot \text{OBz}$ , forms golden-yellow scales, transparent, red, rhombic crystals ( $+2\text{C}_2\text{H}_4\text{O}_2$ ), or white or pale yellow crystals, m. p. 133°.  $\alpha$ -*Benzeneazoxydibenzoylquinol* forms white crystals, m. p. 146—146.5°, and  $\alpha$ -*benzeneazoxydiacetylquinol* an almost white, crystalline powder, m. p. 111—113°.

$\alpha$ -*Benzeneazoxyquinol*,  $\text{O}:\text{NPh}:\text{N} \begin{array}{c} \text{HO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_3 \\ \diagdown \quad \diagup \\ \text{OH} \end{array}$ , forms golden-yellow

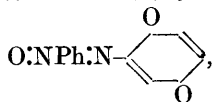
chips, blackening at about 162°, m. p. 166°, dissolves to a violet-blue solution in alkali hydroxide solution, and darkens on exposure to light.  $\alpha$ -*Benzeneazoxybenzoylbromoquinol* [ $\text{OH}:\text{Br}:\text{OBz}=2:3:5$ ], separates as a pale yellow, crystalline powder, m. p. 197°;  $\alpha$ -*benzeneazoxybromoquinol* forms yellowish-brown, silky needles, m. p. 188—191° (decomp.), and  $\alpha$ -*benzeneazoxybenzoylnitroquinol*, yellow globules, m. p. 149—150°.  $\alpha$ -*Benzeneazoxynitroquinol* forms rosettes of

*m m*\*

chestnut-yellow needles, darkening at 175°, m. p. 188° (slight decomp.), and dissolves to a blue liquid in alkali hydroxide or carbonate solution.

$\beta$ -Benzeneazoxybenzoylquinol,  $\text{NPh:NO}-\text{C}_6\text{H}_4-\text{OBz}$ , crystallises in

yellow needles, m. p. 120—121°.  $\beta$ -Benzeneazoxyquinol forms garnet-red crystals, m. p. 151°, and gives blood-red, ruby-red, and brownish-red solutions in alkali hydroxide solution, ammonia solution, and concentrated sulphuric acid respectively; in acetic acid solution, it reacts with lead peroxide, the product being apparently  $\beta$ -benzeneazoxyquinone, since by similar means  $\alpha$ -benzeneazoxyquinol is oxidised to  $\alpha$ -benzeneazoxyquinone,



which forms quinone-yellow, plush-like needles, m. p. 133° (decomp.), and colours alkali hydroxide solutions yellowish-brown when cold or violet-blue when heated.

T. H. P.

**Remarkable Reaction of Phenylhydrazine. Syntheses of Azo Dyes from 2-Methylated Quinolinium and Indolenium Salts.** E. ROSENHAUER (*Ber.*, 1924, 57, [B], 1192—1194).—The production of an azo dye from 2-bromomethylquinoline methobromide and phenylhydrazine (this vol., i, 768) is explained by the observation of the simultaneous formation of aniline and ammonia, the unstable hydrazo compound which is intermediately formed being reduced by the excess of phenylhydrazine. The tendency to form azo dyes in this manner is unusually pronounced, since they can also be produced from unsubstituted 2-methylquinolinium and -indolenium salts. Thus 1 : 2 : 3 : 3-tetramethylindolenium iodide and phenylhydrazine at about 120° yield 2-benzeneazomethylene-1 : 3 : 3-trimethylindoline hydriodide, decomp. 240°, from which the corresponding base, m. p. 106—107°, is prepared by the action of ammonia.

H. W.

**2-Hydrazinocymene and Other Compounds derived from 2-Aminocymene.** W. A. DEMONBREUN and R. E. KREMERS (*J. Amer. Pharm. Assoc.*, 1923, 12, 589—592).—2-Hydrazinocymene hydrochloride has m. p. 186—187°; acetyl derivative, m. p. 125—126°; dextrose compound, m. p. 92—93°; mannose compound, m. p. 110°; galactose compound, m. p. 149—150°. Cymylcarbamide has m. p. 162—163°; s-cymylphenylcarbamide has m. p. 192°.

CHEMICAL ABSTRACTS.

**Derivatives of p-Phenylenedihydrazine. (Preliminary Note.)** R. STOLLÉ and K. LEFFLER (*Ber.*, 1924, 57, [B], 1061—1063).—Attempts to obtain better yields of the additive compound from azodibenzoyl and dimethylaniline (*A.*, 1912, i, 920) by using a solvent were fruitless; the use of the more stable but

more unsaturated azodicarboxylic ester with aromatic hydrocarbons leads in the presence of sulphuric acid to derivatives of *p*-phenylenedihydrazine,  $C_6H_4[N(CO_2R) \cdot NH \cdot CO_2R]_2$ , the constitution of which follows from their decomposition to *p*-phenylenediamine and phenylhydrazine. Thus methyl azodicarboxylate and benzene yield *methyl p-phenylenedihydrazinetetracarboxylate* (m. p. 209°; yield 90%), this with sodium hydroxide yielding phenylhydrazine and *p*-phenylenediamine, with pyridine, *p*-phenylenediamine and a yellow substance, m. p. 235°, and with acetic acid *p*-phenylenediamine. *Ethyl p-phenylenedihydrazinetetracarboxylate*, m. p. 192°, is similarly obtained from ethyl azodicarboxylate and benzene, whilst toluene gives a resinous product yielding *p*-tolylhydrazine with sodium hydroxide, and bromobenzene gives a 70% yield of *p*-bromophenylhydrazine. R. B.

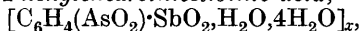
**Rate of Diazotisation of Amines.** M. L. WILLARD (*Textile Colorist*, 1924, 46, 164—165; cf. *ibid.*, 1924, 46, 22).—The rate of diazotisation of aniline and *p*-toluidine in *N*-solution is compared with that in solutions of 0.001*N* (Hantzsch and Schumann), 0.01*N* (Tassilly, A., 1914, ii, 42, 190, 256), and 0.1*N* concentration. Increased concentration of the amine accelerates the reaction but is less stable. At 20° the reaction with aniline is almost twice as fast as at 0°. The temperature effect on *p*- and *m*-toluidine was not quite so pronounced as with aniline. At higher temperatures, reaction is not quantitative, owing to decomposition, with the formation of tarry matter, and from most of the amines gas was evolved even at 20°. The reaction velocity of nitrous acid with amines containing negative radicals, anthranilic acid, and Schäffer's salt, as compared with those containing positive radicals, *p*- and *m*-toluidine, does not differ greatly, but as a whole indicates a slightly greater velocity for the negative amines. The position of the positive or negative radical with regard to the amine radical does not appreciably affect the reaction velocity.

CHEMICAL ABSTRACTS.

**Biological Standardisation of Salvarsan and Neosalvarsan.** G. B. ROTH (*U.S. Pub. Health Service, Hyg. Lab. Bull.*, 1924, No. 135, 13—32).—Salvarsan is about twice as toxic as neosalvarsan to the mouse, rat, and guinea pig.

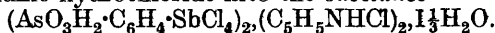
CHEMICAL ABSTRACTS.

**Aromatic Compounds containing Arsenic and Antimony.**  
**I. Phenylenearsinicstibinic Acids.** H. SCHMIDT (*Ber.*, 1924, 57, [B], 1142—1148).—Compounds containing the arsinic and stibinic acid residues attached to the same benzene nucleus can be obtained by treating diazotised aminophenylarsinic acids with antimony oxide or from arsenite and diazotised aminophenylstibinic acids. *p*-Phenylenearsinicstibinic acid,



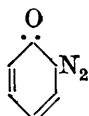
is a colourless powder prepared by the successive addition of solutions of tartar emetic and sodium hydroxide to a diazotised solution of *p*-aminophenylarsinic acid. It exhibits the phenomenon of gradual neutralisation with alkali hydroxide, the rate depending

on the concentration of the hydroxyl ions, the temperature, and the particular cation. The steps in the process of neutralisation are not sufficiently sharply differentiated to allow conclusions to be drawn as to the degree of polymerisation of the compound. The acid is converted by ammonium chloride in hydrochloric acid solution into the compound  $[\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Sb}(\text{OH})\text{Cl}_3]_3[\text{NH}_3]_2, 6\text{H}_2\text{O}$ , and by pyridine hydrochloride into the substance



**4-Hydroxyphenylene-3-stibinicarsinic acid** is a pale yellow powder which closely resembles the analogous compound described above.

Diazotisation of 3-amino-4-hydroxyphenylarsinic acid in 5*N*-hydrochloric acid solution causes the separation of the diazo compound (annexed formula), decomp. about 150°.



$\text{AsO}_3\text{H}_2$

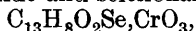
Analysis of the compounds is effected by boiling them with a mixture of concentrated sulphuric acid and nitric acid (*d* 1.49) and subsequent treatment of the solution with ammonium sulphate until the residual nitric acid is destroyed. Arsenic and antimony are then determined in the usual manner.

H. W.

**Organic Selenium Compounds. III. Preparation of a Selenium Derivative of Cinchophen Type.** M. T. BOGERT and H. H. HOPKINS (*J. Amer. Chem. Soc.*, 1924, **46**, 1700—1701).—6-Amino-2-phenylbenzoselenazole (A., 1922, i, 1182) has been converted by the Sandmeyer reaction into 6-cyano-2-phenylbenzoselenazole, a brown powder, decomp. 145—150°, which when hydrolysed with sulphuric acid yields 2-phenylbenzoselenazole-6-carboxylic acid, amorphous, decomp. 170—180° (methyl ester, crystals, m. p. 164.5—165.5°). The acid is a selenium derivative of the cinchophen (atophan) type and corresponds with 2-phenylbenzthiazole-6-carboxylic acid (A., 1922, i, 576).

R. B.

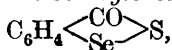
**Aromatic Compounds containing Selenium. VI.** R. LESSER and R. WEISS (*Ber.*, 1924, **57**, [B], 1077—1082; cf. A., 1914, i, 1083).—Selenoxanthone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{Se} \end{smallmatrix} \text{C}_6\text{H}_4$ , m. p. 191—192°, is readily prepared by the action of aluminium chloride on a solution of *o*-chloroselenobenzoyl chloride,  $\text{Cl} \cdot \text{Se} \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$ , in benzene; under similar conditions, toluene yields a methylselenoxanthone, m. p. 112—113°. The substance, m. p. 236—237°, obtained by the action of chromic acid on selenoxanthone is an additive compound of chromium trioxide and selenoxanthone oxide,



and not of selenoxanthone as considered previously (*loc. cit.*).

*o*-Chloroselenobenzoyl chloride is converted by ammonia into benzoyleneselenimide,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{Se} \end{smallmatrix} \text{NH}$ , which exists in two forms, needles or plates, m. p. 234—235° after previous softening; the alkali salts and the acetyl derivative, m. p. 172—174°, are described. The substance is converted by chromic acid into the additive compound,  $\text{C}_7\text{H}_5\text{ONSe} \cdot \text{CrO}_3$ . The corresponding methylimide, m. p.

159—160°, *ethylimide*, m. p. 102—103°, *phenylimide*, m. p. 182—183°, and *o-tolylimide*, m. p. 187—188°, are described; *methylene-dibenzoyleneselenimide*,  $\text{CH}_2(\text{C}_6\text{H}_4\text{ONSe})_2$ , has m. p. 331—332°, *o*-Chloroselenobenzoyl chloride is converted by sodium sulphide in the presence of acetone into *benzoyleneselenosulphide*,



m. p. 83—84°. *o*-Chloroselenobenzoyl chloride and hydrogen selenide yield *benzoylenediselenide*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{Se} \end{array} \text{Se}$ , m. p. 91—92°.

Dibenzylidiselenide is converted by nitric acid (*d* 1.4) into benzylselenious acid, m. p. 122—123°; the corresponding *barium* (+2H<sub>2</sub>O) and *calcium* (6H<sub>2</sub>O) salts are described. The acid is converted by phosphorus pentachloride into dibenzylselenide dichloride,  $(\text{CH}_2\text{Ph})_2\text{SeCl}_2$ , m. p. 134—135°. H. W.

**Direct Mercuration of Benzene and the Preparation of Mercury Diphenyl.** J. L. MAYNARD (*J. Amer. Chem. Soc.*, 1924, **46**, 1510—1512; cf. Roeder and Blasi, A., 1915, i, 331).—Phenylmercuric acetate is obtained in 80% yield by boiling benzene (80 c.c.), mercuric acetate (15 g.), and 95% alcohol (20 c.c.) for 55 hours, a further 20 c.c. of alcohol being added after the first 5 hours. A yellow precipitate, due to the alcoholysis of the mercuric acetate at the commencement of the reaction, is redissolved by the addition of a little glacial acetic acid. The acetic acid liberated during the reaction is removed by esterification with the alcohol, the consequent increase in yield of phenylmercuric acetate demonstrating the reversibility of the mercurisation reaction. Mercury diphenyl is obtained in 95% yield by the addition of alkaline sodium stannite solution to a well-stirred suspension of phenylmercuric acetate in cold water (cf. Dimroth, A., 1902, i, 849). F. G. W.

**Methylation of the Cerebrosides of Ox Brain.** J. PRYDE and R. W. HUMPHREYS (*Biochem. J.*, 1924, **18**, 661—664).—Kerasin and phrenosin undergo methylation unchanged. Kerasin takes up five methyl residues to form *pentamethylkerasin*, m. p. 73°. In the case of phrenosin methylation ceased at a stage intermediate between that required for a pentamethyl- and a hexamethyl-phrenosin, the product resembling pentamethylkerasin but having a lower melting point (35—40°). The possibility of the formation of a mixture of two compounds is suggested. The pentamethylkerasin was hydrolysed with acid methyl alcohol. Enough material was obtained to show that it is possible to separate in this way the methylated sugar residue. S. S. Z.

**Individual Blood Researches. II.** W. KÜSTER and H. OESTERLIN (*Z. physiol. Chem.*, 1924, **136**, 279—292).—In the blood of one ox used the  $\alpha$ -type of prosthetic group appeared to be preformed in the hæmoglobin, part of it remaining unchanged during the preparation of hæmin by the sulphuric acid-methyl alcohol process, the remainder being converted into the pseudo form of the  $\beta$ -type. In the blood of a second ox of similar age etc., the

pseudo form of the  $\alpha$ -type appeared to be present. It is considered that in the pseudo form the halogen is bound to nitrogen and not to iron, since it is completely removed by 5% sodium carbonate solution.

The degree of methylation of hæmin prepared from one source of blood was the same whether it was prepared from the whole blood or from the corpuscles. It appears to depend, however, on the amount of cholesterol in the blood. For etherification hydrobromic acid is as satisfactory as hydrochloric acid. O. O.

**Absorption of Violet Light by Organic Substances. IV.** L. MARCHLEWSKI and A. MOROZ (*Bull. Soc. chim.*, 1924, [iv], 35, 705—709).—Derivatives of hæmoglobin and chlorophyll show characteristic absorption bands in the violet part of the spectrum. Coefficients of extinction and absorption curves are given for oxyhæmoglobin, hæmin, hæmatoporphyrin, hæmatoporphyrin hydrochloride, mesoporphyrin hydrochloride, phyllocyanin, and phylloerythrin. R. B.

**Porphyrins. VII. Dibromohæmatoporphyrin Dimethyl Ether.** W. KÜSTER and H. OESTERLIN (*Z. physiol. Chem.*, 1924, 136, 235—242).—Hæmin is successively converted into chlorodimethylhæmin, *bromodimethylhæmin*, *bromodimethylhæmin dibromide*, and *dibromohæmatoporphyrin dimethyl ether*,  $C_{36}H_{42}O_6N_4Br_2$ . The last is a reddish-brown, amorphous material possessing no m. p. Its solution in hydrochloric acid showed two absorption bands at 540—568 and 590—600, the ethereal solution giving four bands at 483—520, 527—543, 568—589, 622—630. A compound with ammonia, a silver salt, a copper salt, and a dimethyl ester were prepared. From a study of the changes outlined in the scheme above it is concluded that one of the pyrrole nuclei in the porphyrin molecule must exist in the pyrroline form. O. O.

**Rational Systematic Classification of Proteins. I. Chromoproteins.** H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1924, 136, 75—81).—Hæmoglobin is resolved by the addition of a trace of hydrochloric acid into its component globin and hæmochromogen or hæmatin. The sodium derivative of hæmatin added to an aqueous solution of globin hydrochloride produces a reddish-brown precipitate which gives analytical figures corresponding with hæmoglobin, but which differs from the latter in solubility, a difference which is ascribed to changes in the globin residue. In aqueous suspension, it behaves to dilute acid as does hæmoglobin. The sodium derivative of hæmatin gives no precipitate with crystallised egg-albumin or globulin, with crystallised serum-albumin, or with protamine sulphate. The general conclusion drawn is that the chromoproteins are salt-like combinations of an acidic with a basic component. J. P.

**Rational Systematic Classification of Proteins. II. Chondroproteins.** T. TAKAHATA (*Z. physiol. Chem.*, 1924, 136, 82—88).—The potassium salt of chondroitin sulphuric acid added to clupein sulphate in aqueous solution produces a white precipitate of a protein, *chondroclupein*, containing 47.5% of chondroitin

sulphuric acid and 52.5% of clupein. Egg-albumin, edestin, and peptone give no precipitate with chondroitin sulphuric acid, but from collagen a gelatinous substance is obtained, composed of 82.5% of collagen and 17.5% of chondroitin sulphuric acid. The chondroproteins are therefore regarded as salt-like compounds (cf. preceding abstract). J. P.

**Solubility and Digestibility of Proteins.** Z. STARY (*Z. physiol. Chem.*, 1924, **136**, 160—172).—When the insoluble keratins are degraded into soluble products by heating with water under pressure or with dilute alkali, they give rise to soluble products called proto- and deuto-keratoses. These, when obtained by using alkali are extensively racemised. They can be easily salted out, but compared with the normal albumoses they are very resistant towards pepsin and trypsin. When keratins are heated with a mixture of glacial acetic acid and chloro- or bromo-acetic acid, they give rise, without any humin formation, to similar products, which are not racemised, are partly soluble in water and in alcohol, and are only very slightly affected by enzymes. If, however, a keratin such as human hair be treated with glacial acetic acid at the ordinary temperature in presence of an oxidising agent such as bromine, there is very little change in its outward appearance. The product after this treatment is readily soluble in very dilute alkali and is easily hydrolysed by trypsin. It therefore seemed that during this treatment certain reactions such as oxidation and substitution occur with certain groupings in the keratin molecule and alter its properties. With a view to ascertain whether by oxidation certain groups which hinder the action of enzymes are removed, the changes in the properties of keratins after treatment with oxidising agents such as hydrogen peroxide in acid solution and hypohalogen acids have been studied. By gentle oxidation, products result which are slightly soluble in alkali and are dissolved by trypsin. On further oxidation, the solubility in alkali decreases and on strong oxidation the  $-S-S-$  linking is attacked, with the formation of sulphuric acid, so that solubility and digestibility by enzymes scarcely seem to bear any relation to the  $-S-S-$  linking. D. R. N.

**Proteins. I. Behaviour on Solution in Phenols.** R. O. HERZOG and E. KRAHN (*Z. physiol. Chem.*, 1924, **134**, 290—295).—Gelatin in phenol solution was heated for varying periods and the product was precipitated with ether. It was found that the amino-nitrogen progressively diminished whilst the total nitrogen remained unchanged; this is interpreted as indicating the formation of diketopiperazines. When wool is treated similarly, a part of the original amino-nitrogen appears as ammonia-nitrogen in the product, and as much as two-thirds of the sulphur may be split off as hydrogen sulphide. C. R. H.

**Studies on Proteins. II. Determination of the Molecular Weight of Silk Fibroin.** R. HERZOG and M. KOBEL (*Z. physiol. Chem.*, 1924, **134**, 296—299).—The molecular weight of the

crystalline substance contained in silk fibroin was determined cryoscopically, using resorcinol as solvent. After preliminary exhaustive extraction of the silk fibroin with water or alcohol, values of about 200 were obtained; after extraction with boiling cresol, 314—380, and after solution in acid and subsequent neutralisation, 350—370. None of these methods of purification affected the nitrogen content of the material to a marked degree. C. R. H.

**Catalytic Effect exercised by certain Colloids, especially Glycogen, in the Hydrolysis of Proteins.** L. HUGOUNENQ and J. LOISELEUR (*Compt. rend.*, 1924, **179**, 86—87).—Without itself undergoing change, lecithin accelerates the hydrolysis of proteins by 0.3% hydrochloric acid, but colloidal silica, alumina, ferric oxide, arsenic sulphide, starch paste, etc. are without effect. Similar positive catalytic actions are exerted by colloidal sodium  $\alpha$ -thymonucleate, silver, gold, bismuth, and rhodium, and by glycogen on the hydrolysis by 0.3% sodium hydroxide solution of egg-albumin, fibrin, casein, and nucleoproteins derived from beer-yeast. The extent to which action increases becomes greater as the electric charge of the colloidal substance becomes more marked, and amounts to 30—33% with the colloidal metals. Pure glycogen is devoid of any effect, but becomes active on addition of 0.1% of its weight of an electrolyte such as sodium, potassium, rubidium, calcium, or magnesium chloride; the influence of glycogen increases also with the concentration of the alkali solution used to effect the hydrolysis.  
T. H. P.

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### Biochemistry.

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**Gas and Electrolyte Equilibria in Blood. VI. Acid Properties of Reduced and Oxygenated Hæmoglobin.** A. B. HASTINGS, D. D. VAN SLYKE, J. M. NEILL, M. HEIDELBERGER, and C. R. HARRINGTON (*J. Biol. Chem.*, 1924, **60**, 89—153).—The authors have determined directly the base-binding power and buffer value of oxyhæmoglobin and reduced hæmoglobin over the  $p_H$  range 6.8 to 7.6. The hæmoglobin was prepared by Heidelberg's method (A., 1922, i, 962) and the experimental technique was that described in the preceding papers of this series (A., 1922, i, 1207; 1923, i, 162, 163). The isoelectric point ( $I_E$ ) of reduced horse hæmoglobin was found to be at  $p_H$   $6.81 \pm 0.02$ . The molecular buffer value ( $\beta_E$ , cf. A., 1922, i, 893) of reduced hæmoglobin is nearly constant between the isoelectric point and  $p_H$  7.6 for a given solution, but increases from 2.6 for 30 mM cation concentration to 2.9 for 145 mM cation concentration. The buffer value of oxyhæmoglobin decreases steadily from  $p_H$  6.8 to 7.6 and the isoelectric point is estimated to be slightly below  $p_H$  6.7. The increase,  $\Delta[BHb]/\Delta[O_2Hb]$ , in base-binding power caused by oxygenation of hæmoglobin has a maximum value of about 0.7 equivalent of base per

mol. of hæmoglobin; the maximum value occurs at  $p_H$  7.6 in solutions of 30 mM cation concentration and at  $p_H$  7.3 in solutions of 145 mM cation concentration. This increase in base-binding power at varying  $p_H$  on oxygenation of reduced hæmoglobin is shown to follow quantitatively a curve consistent with Henderson's hypothesis (A., 1920, i, 403) that combination with a molecule of oxygen increases the dissociation constant of one acid hydrogen in the hæmoglobin molecule. The results do not follow the equation required by Hill's hypothesis (A., 1922, i, 193, 696; 1923, i, 398, 1144) that only one acid hydrogen in an aggregate of  $n$  hæmoglobin molecules, where  $n$  is the index in Hill's oxygen dissociation equation, has its dissociation constant affected by oxygenation and reduction. The relationships between base-binding power, reaction, and degree of oxygenation are expressed by the equation  $[BHb] = \beta_R[Hb](p_H - I_R) + [HbO_2](1/1 + 10^{pK' - p_H} - 1/1 + 10^{pK'' - p_H})$ , where  $[Hb]$  indicates total hæmoglobin in mols. of oxygen capacity and  $[HbO_2]$  the oxyhæmoglobin. This equation is more accurate than an earlier linear equation (A., 1923, i, 162). Values for the constants of this equation are given for three cation concentrations. E. M. C.

**Thermodynamic Relations of the Oxygen- and Base-combining Properties of Blood.** W. C. STADIE and K. A. MARTIN (*J. Biol. Chem.*, 1924, 60, 191—235).—The authors discuss the effect of temperature on the oxygen dissociation curve and base-combining properties of whole blood, and formulate a thermodynamical explanation of these changes. For the equations derived, reference should be made to the original paper. The heats of ionisation of carbonic acid and the hæmoglobin acids are calculated by means of the van't Hoff isochore. The molecular buffer value of hæmoglobin is shown theoretically and by experiment to be independent of temperature. Expressions are derived for the excess of base bound by oxyhæmoglobin over reduced hæmoglobin, and for the effect of temperature on the isoelectric point of a protein. The heats of ionisation of hæmoglobin both as base and acid are shown to be of the same order. It is concluded that, in contrast to its effect on the acid properties, oxidation has probably no effect on the basic properties of hæmoglobin. The magnitude of the heat of ionisation of hæmoglobin as an acid indicates that a small change in temperature produces a large change in the strength of hæmoglobin as an acid. This temperature effect is discussed in relation to fever and a temperature correction factor for  $p_H$  is derived. E. M. C.

**Applications of the Donnan Equilibrium to Human Blood-serum.** D. W. ATCHLEY, R. F. LOEB, and E. M. BENEDICT (*Proc. Soc. Exp. Biol. Med.*, 1923, 20, 238).—Dialysis of pure serum solutions and electrolyte solutions *in vitro* reproduced the conditions existing in the body, which are in the nature of the Donnan equilibrium. The serum solution contained less chlorine and more sodium than the fluid outside the collodion sac when potassium was absent; in the presence of potassium, the serum solution contained more potassium, less chlorine, and an equal amount of sodium. The

quantitative differences were proportional to the protein concentration in the serum. CHEMICAL ABSTRACTS.

**Solution of Fibrin and the Inhibition of Blood Clotting by Nicotine.** E. MANGOLD and N. KITAMURA (*Biochem. Z.*, 1924, **147**, 1—6).—In an ultramicroscopic preparation of rabbit or guinea-pig plasma showing formation of fibrin network, the addition of nicotine and its salts produces fibrinolysis. Direct addition of nicotine to the preparation before centrifuging retards or entirely inhibits the clotting and alters the typical form of the fibrin network. J. P.

**Increase of Uric Acid in the Blood during Prolonged Starvation.** W. G. LENNOX (*J. Amer. Med. Assoc.*, 1924, **82**, 602—604).—During starvation, the uric acid increased from 4 mg. to 10.7 mg. per 100 c.c. of whole blood. In some cases there was decreased excretion of uric acid, but without coincident retention of non-protein or urea nitrogen. CHEMICAL ABSTRACTS.

**Calcium in the Blood.** W. C. THRO and M. EHN (*Proc. Soc. Exp. Biol. Med.*, 1923, **20**, 313—315).—A low content of calcium in the blood, observed in furunculosis and in pneumonia in young children, is not always observed in tetany. CHEMICAL ABSTRACTS.

**Absence of Pyruvic Acid in Blood, Liver, and Muscle.** L. J. SIMON and E. AUBEL (*Bull. Soc. Chim. biol.*, 1924, **6**, 424—430).—When pyruvic acid is mixed with an extract of liver or fresh muscle no decrease is observed. When, however, it is injected into the liver *in vivo*, it disappears slowly, and after 1 hour it is possible to recover unaltered only about 40% of the original amount. Alanine, dextrose, and lactic acid under the same conditions do not give rise to pyruvic acid. D. R. N.

**Hippuric Acid Metabolism in Man.** J. SNAPPER (*Klin. Woch.*, 1924, **3**, 55—56; from *Chem. Zentr.*, 1924, i, 1225—1226).—After administration of 5 g. of sodium benzoate to healthy or diseased men with normal kidneys, 5 g. of hippuric acid are excreted in the urine within 12 hours. Normal kidneys can excrete urine containing up to 2% of hippuric acid. G. W. R.

**Transformations of Chlorophyll in the Animal Organism.** L. MARCHLEWSKI (*Bull. Soc. Chim. biol.*, 1924, **6**, 464—472).—The pigment termed cholehæmatin by MacMunn and bilipurpurin by Löbisch is shown to be identical with the author's phylloerythrin. It appears in the bile of herbivorous animals only when they are fed on fresh green grass. Cholehæmatin would therefore seem to be derived from chlorophyll, and not from hæmoglobin. D. R. N.

**Urine in Pernicious Anæmia.** H. REINWEIN and F. THIELMANN (*Arch. Exp. Path. Pharm.*, 1924, **103**, 115—126).—Histidine, methylguanidine,  $\gamma$ -butyrobetaine, *r*-lactic acid, and a base,  $C_7H_8O_2N_4$  (probably a dimethylxanthine) have been isolated from the urine in cases of pernicious anæmia and identified by analysis. J. P.

**Globulin and Albumin Content of the Plasma in Nephritis.**

G. C. LINDER, C. LUNDSGAARD, and D. D. VAN SLYKE (*Proc. Soc. Exp. Biol. Med.*, 1923, **20**, 320).—In most cases of glomerular nephritis examined, low protein concentrations of 3.5–5.5% were observed; in all cases the albumin:globulin ratios were less than 1:4. Cases of nephrosis gave similar results.

CHEMICAL ABSTRACTS.

**Relationship between the Calcium and Inorganic Phosphorus of the Serum in Rickets and Tetany.**

J. HOWLAND and B. KRAMER (*Monatsh. Kinderheilk.*, 1923, **25**, 279–293; from *Chem. Zentr.*, 1924, i, 1221; cf. Kramer, Tisdall, and Howland, A., 1923, i, 412).—In rickets, the phosphorus content of serum is decreased whilst the calcium content remains practically normal. In tetany, the phosphorus content remains normal and the calcium content is decreased. The occurrence of rickets is connected with the product of the calcium and potassium contents, expressed in mg. per 100 c.c. Rickets occurs when this is below 30 and may be excluded when it is above 40. In tetany, the product is generally 30 or slightly less.

G. W. R.

**Action of Alkali Iodides on Metabolism.**

E. HESSE (*Arch. Exp. Path. Pharm.*, 1924, **102**, 63–92).—Alkali iodide administered in considerable amount to dogs produces an increase in protein metabolism (nitrogen excretion) and in the gaseous exchange, the latter being conditioned chiefly by the former. In general, alkali iodides are regarded as increasing all chemical and enzymatic reactions in the organism, leading to breakdown of proteins, and possibly also to deamination of the hydrolysis products, more especially in the liver. The effect on protein metabolism of various iodinated fatty acid derivatives is compared with the action of potassium iodide. The action is similar, but may be more marked. Iodival (monoiodoisovalerylcarbamide) and alival (iododihydroxypropane) are toxic to dogs.

J. P.

**Mode of Action of Phosphorus.**

K. ENGEL (*Arch. Exp. Path. Pharm.*, 1924, **102**, 289–304).—Tonophosphan (an organic compound of phosphorous acid) stimulates the weakly beating mammalian or frog heart, and the surviving mammalian intestine, bladder, and uterus. From comparative experiments it is concluded that the action of tonophosphan is similar to that of sodium phosphite, but in higher concentrations the latter is more toxic than the former. Aqueous solutions of phosphorus act in a similar way to phosphite, but are still more toxic. Sodium hypophosphite is very much less toxic and has no stimulating action. The action of phosphate differs from that of phosphite.

J. P.

**Irreciprocal Permeability. IV. Salt Effect on the Living Membrane.**

E. WERTHEIMER (*Pflüger's Archiv*, 1923, **201**, 488–502; from *Chem. Zentr.*, 1924, i, 1207; cf. this vol., i, 686).—Basic dyes dissolved in distilled water or in isotonic solutions of non-electrolytes scarcely diffuse at all through the thoroughly washed membrane of frog's skin, although in electrolytic solu-

tions they diffuse readily. This electrolyte effect is not shown by acid dyes. The permeability of the membrane for sodium chloride is subject to the same salt effect. Sugar, amino-acids, and peptone can only diffuse when the inner side of the membrane is in contact with a non-electrolytic solution. The same effects are not observed with the outer side of the frog's skin, nor with dead membrane.

G. W. R.

**Permeability in Non-electrolytic Solutions.** K. HIRUMA (*Pflüger's Archiv*, 1923, **200**, 497—510; from *Chem. Zentr.*, 1924, i, 1220).—The absorption by red blood corpuscles of salicylate and thiocyanate is increased, and that of ammonium and alkaloids decreased by sucrose. With frog-muscle, sucrose causes increased absorption of basic dyes, alkaloid salts, iodine, acids, methylamine, salicylate, and thiocyanate. Amino-acids are not absorbed by blood-corpuscles.

G. W. R.

**Water-Salt Content of the Body in Relation to the Acid-Base Economy. I. Colloidal Chemical Basis of Purine Diuresis.** C. OEHME (*Arch. Exp. Path. Pharm.*, 1924, **102**, 40—62).—Oral administration of caffeine produces in adults a diuresis and an increased excretion of chlorides. Intravenous injection of theophylline-ethylenediamine (Euphyllin) produces a diuresis which progressively increases with increasing alkalinity. The action of purine diuretics cannot be ascribed to loss of water from serum proteins since the purines investigated do not lower the viscosity of serum-albumin until the  $p_H$  is raised to 9.

J. P.

**Fate of Morphine in the Animal Body. I. Excretion of Morphine in Warm-blooded Animals.** T. TAKAYANAGI (*Arch. Exp. Path. Pharm.*, 1924, **102**, 176—182).—Contrary to the findings of Faust (*ibid.*, 1900, **44**, 217), morphine is excreted almost wholly in the urine and but slightly in the faeces. It appears slowly in the former, and 2—3 days after administration its excretion reaches a maximum and then rapidly declines during the succeeding few days. In animals previously treated with morphine, the excretion of a subsequent dose is more rapid than that of the first dose.

J. P.

**Fate of Morphine in the Animal Body. II. Destruction of Morphine in the Body of Habituated and Non-habituated Rats.** T. TAKAYANAGI (*Arch. Exp. Path. Pharm.*, 1924, **102**, 183—187).—In confirmation of the observations of Rübsamen (*ibid.*, 1908, **59**, 227), rats become less susceptible to repeated doses of morphine. This is ascribed to an increased rate of destruction (and excretion, cf. preceding abstract) and an increased cell immunity to the alkaloid.

J. P.

**Intensity of Action on Nerve-endings of various Substituted Quaternary Aliphatic Ammonium Bases.** F. KÜLZ (*Arch. Exp. Path. Pharm.*, 1924, **102**, 283—288).—The paralyzing action of the halides of various alkyl and other substituted quaternary ammonium bases and of phenyltrimethylammonium chloride on the isolated nerve-muscle preparation of the frog is in the inverse order

of the solubilities of the corresponding perchlorates (cf. Hofmann, Höbold, and Quoos, A., 1912, i, 164), with the exception of glyceryltrimethylammonium chloride. A theoretical discussion is appended. J. P.

**Specific Rôle of Calcium in the Formation of Thrombin.** E. WÖHLISCH and K. PASCHKIS (*Klin. Woch.*, 1923, 2, 2319; from *Chem. Zentr.*, 1924, i, 1220).—Plasma from birds loses its coagulability with muscle extract after being dialysed against 1% sodium chloride solution. Coagulability is restored by addition of calcium. G. W. R.

**Theory of the Action of Thrombin.** E. WÖHLISCH (*Klin. Woch.*, 1923, 2, 1801—1802; from *Chem. Zentr.*, 1924, i, 1219—1220).—In opposition to the theory of Herzfeld and Klinger that thrombin acts by the removal of a stabilising adsorption layer from fibrinogen, the author holds that coagulation by thrombin is similar to spontaneous coagulation and that thrombin acts as a specific catalyst of the coagulation of fibrinogen. G. W. R.

**Cholesterogenic Function of the Spleen.** J. B. ABELOUS and L. C. SOULA (*Compt. rend.*, 1924, 178, 1850—1852).—The serum of a normal dog taken after the ingestion of fat and kept *in vitro* at the ordinary temperature increases in cholesterol content at the expense of the fatty acids present. In the case of dogs from which the spleen had been removed, the serum decreases in cholesterol content whilst the fatty acids and total lipoids increase. In the latter case, addition of extract of the spleen induces normal behaviour with the difference that neither total lipoids nor fatty acids decrease. The general conclusion is drawn that the spleen is of great importance in the metabolism of fats because of its cholesterogenic function. H. J. E.

**Method for Preserving Micro-organisms.** C. TRUCHE (*Ann. Inst. Pasteur*, 1924, 38, 516—519).—A modification of Ungermann's method for keeping cultures of pathogenic bacteria alive for considerable periods without sub-culturing is described. Tubes of Legroux's formalised serum, each covered with a layer of vaseline oil, are used. Many organisms such as meningococcus, gonococcus, cholera vibrio, etc., which are difficult to keep in the ordinary way without deterioration, have been preserved for periods from 4 months to 2 years. [Cf. B., 1924, 761.] C. T. G.

**Odour of Cultures of *Bacillus pyocyaneus*.** C. GESSARD (*Compt. rend.*, 1924, 178, 1857—1859).—The odour produced by cultures of *B. pyocyaneus* in the usual media is also obtained when using tryptophan in a decoction of seed of *Lupinus albus*, but only to a slight extent when the former is replaced by other amino-acids. When tryptophan is the sole organic constituent of the medium, the characteristic odour is also obtained. H. J. E.

**Anaërobic Bacteria. I. Growth and Biochemical Activities of *Bacillus botulinus*, *B. sporogenes*, and *B. tetani*.** E. WAGNER, C. C. DOZIER, and K. F. MEYER (*J. Infect. Dis.*, 1924, 34, 63—84).—*B. botulinus* and *B. sporogenes* show a similarity in

ammonia and amino-acid nitrogen accumulation; with *B. tetani*, the former was more marked towards the end of the experiment, and the latter was smaller. *B. tetani*, but not the other bacteria, utilised practically all the creatinine present and produced a greater accumulation of volatile acids; equal amounts of non-volatile acids were formed in the three cases. Under the conditions employed, Bengston's *B. botulinus*, type *C* (*U.S. Pub. Health Rept.*, 1923, **38**, 340), showed little chemical activity. CHEMICAL ABSTRACTS.

**Anaërobic Bacteria. II. Effect of Dextrose on the Biochemical Activities of *Bacillus botulinus*.** C. C. DOZIER, E. WAGNER, and K. F. MEYER (*J. Infect. Dis.*, 1924, **34**, 85—102).—Dextrose did not exert any effect on the production of toxin, which harmonises with the suggestion that the toxin is an autolytic product. CHEMICAL ABSTRACTS.

**Utilisation of Lævulosans by Organisms.** H. COLIN and V. ESTIENNE (*Bull. Soc. Chim. biol.*, 1924, **6**, 431—435).—Sucrose, which is the chief and the most common source of lævulose, is utilised by micro-organisms with great facility, although lævulosans, which are richer in lævulose and are just as sensitive towards acids as sucrose, are utilised imperfectly owing to the incapability of micro-organisms to hydrolyse them. The moulds, which are well-known for the diversity of their diastatic secretions, are only capable of attacking them with difficulty. In this respect, they may be classed with gums, mucilages, and pectins, with which they have in common certain physical characteristics. These substances are, however, capable of being utilised by the plants which elaborate them. D. R. N.

**Fermentation of Galactose by *Saccharomyces cerevisiæ*.** N. L. SOHNGEN and C. COOLHAAS (*J. Bact.*, 1924, **9**, 131—141).—The presence of *S. cerevisiæ* in a liquid medium containing galactose gives the newly-formed cells the property of fermenting this sugar, owing to the appearance of a new enzyme. This galactose zymase is more resistant than dextrose zymase, and remains, under favourable conditions, as a residue which is active after the stopping of growth. A high temperature will destroy dextrose zymase and leave galactose zymase. CHEMICAL ABSTRACTS.

**Fermentation of Rare Sugars by Plant Pathogenic Bacteria.** F. A. WOLF (*J. Elisha Mitchell Sci. Soc.*, 1922, **38**, 12—13).—*Bacillus tabacum* and *B. angulatum*, from tobacco, form acid from dextrose and sucrose but not from glycerol and lactose; the former, but not the latter, also attacks mannitol and galactose. A similar specialisation obtains with *B. glycineum* and *B. sojae*, from soja-bean. CHEMICAL ABSTRACTS.

**Acids produced by Hæmolytic and Non-hæmolytic *Streptococci*.** B. LANGWILL (*J. Bact.*, 1924, **9**, 79—94).—During the first 24 hours, the acid production, in a sucrose or lactose infusion broth, of non-hæmolytic *Streptococci* was nearly twice that of hæmolytic strains, but the eventual acidity produced was equal.

The non-volatile acid was almost entirely *dl*-lactic acid; the non-hæmolytic group produced formic, acetic, and a trace of butyric acids, whilst the hæmolytic group and *S. viridans* produced acetic and propionic acids, but not formic acid. CHEMICAL ABSTRACTS.

**Bacterial Association. I. Production of Lactic Acid.**

H. B. SPEAKMAN and J. E. PHILLIPPS (*J. Bact.*, 1924, 9, 183—198).—The characteristic production of large amounts of lactic acid by *Bacillus granulobacter pectinovorum* and *B. volutans* growing in association, in media containing carbohydrate, is due to a partial inhibition of the physiological processes of *B. granulobacter pectinovorum* by some factor produced in *B. volutans* cultures. The inhibitory factor is not characteristic of cultures of *B. volutans* grown for several generations in carbohydrate media. It is suggested that this substance may be a product of the nitrogen metabolism of *B. volutans* growing in media containing vegetable protein and only traces of carbohydrate. CHEMICAL ABSTRACTS.

**Quantitative Action of Enzymes of Seven Specific Organisms on the Proteins of Milk and on Gelatin.** E. H. PARFITT and G. SPITZER (*J. Bact.*, 1924, 9, 123—130).—The amount of peptone produced by the enzymes of different organisms is approximately four times greater in gelatin than in milk. The rate of peptonisation of gelatin is practically constant, being about 0.2% per hour except for *Bacillus mesentericus*, in which case it is slower. The digestive period was the same for casein and egg-albumin. CHEMICAL ABSTRACTS.

**Cystine in Bacterial Metabolism.** J. GORDON (*J. Path. Bact.*, 1924, 27, 123—124).—Organisms which form hydrogen sulphide from cystine, such as the colon-typhoid group and the anaërobes, can tolerate large concentrations of the substance. Exceptions are *Bacillus paratyphosus A*, and *B. dysentericæ*, Flexner. Cystine probably improved the growth of anaërobes. The delicate organisms do not split cystine and are highly sensitive to it. Perhaps serum in media acts as a protective colloid against toxic concentrations of amino-acids in the medium. In order to exert its effect on an organism, cystine must be in solution. This was done with a small amount of gelatin. CHEMICAL ABSTRACTS.

**Oxidation and Reduction by *Pneumococcus*. III. Reduction of Methylene-blue by Sterile Extracts of *Pneumococcus*. IV. Oxidation of Hæmotoxin in Sterile Extracts of *Pneumococcus*. V. Destruction of Oxyhæmoglobin by Sterile Extracts of *Pneumococcus*.** O. T. AVERY and J. M. NEILL (*J. Exp. Med.*, 1924, 39, 543—552, 745—755, 757—775).—III. Peroxide formation and methylene-blue reduction are believed to be functions of the same or closely-related systems.

IV. The destruction of hæmotoxin in extracts capable of undergoing autoxidation is probably due to a peroxide.

V. The mechanism of, and conditions for, the conversion of oxyhæmoglobin into methæmoglobin are discussed.

CHEMICAL ABSTRACTS.



**Correlation of Citrate Utilisation by Members of the Colon-Aerogenes Group with other Differential Characteristics and with Habitat.** S. A. KOSER (*J. Bact.*, 1924, 9, 59—78).—*Bacillus coli* of faecal origin is unable to utilise sodium or potassium citrate when supplied as the sole source of carbon, whereas the aerogenes-cloacæ group, which formed the largest section of soil cultures, all utilised citrate readily.

CHEMICAL ABSTRACTS.

**Radioactivity and Nitrogen-fixing Bacteria.** E. KAYSER and H. DELAVAL (*Compt. rend.*, 1924, 179, 110—112; cf. Stoklasa, A., 1913, i, 1421).—A radioactive uranium mineral (60% uranium oxide) is able to produce increased nitrogen fixation by various nitrogen-fixing bacteria. The bacteria which have been grown in media containing small quantities of the radioactive substance are more elongated and of greater mobility than the normal strain. The addition of 15 mg. of the radioactive mineral per litre of culture media produces a 67% increase in the amount of nitrogen fixed in 40 days at 26° in the case of *Azotobacter chroococcum*, 250% increase with “*Azotobacter de la Comore*,” and 35% with *A. agile*, whilst for the addition of 30 mg. per litre the corresponding increases are 78%, 506%, and 56%. It is suggested that by the production of successive generations of the bacteria in the presence of an optimum quantity of the radioactive substance, a strain with much greater power of nitrogen fixation in liquid media or in the soil may be obtained.

J. W. B.

**Decomposition Products of Spore-bearing Bacilli in Heated Milk.** H. LISK (*J. Bact.*, 1924, 9, 1—12).—Aërobic spore-bearing bacilli showed a progressive increase in ammonia formation with a similar but larger increase in amino-nitrogen. Formation of indole and hydrogen sulphide, but not of mercaptan, was sometimes observed.

CHEMICAL ABSTRACTS.

**Mode of Action of Bismuth Derivatives in Spirillosis and Trypanosomiasis.** C. LEVADITI (*J. State Med.*, 1924, 32, 62—81; cf. *Compt. rend.*, 1922, 176, 1189).—The physiological action of bismuth appears to depend on its conversion into “bismoxyl” by a partly thermostable, colloidal, organic substance (“bismogene”) in the cellular extracts. Contact between “bismogene” and a bismuth derivative gives rise to flocculation of protein colloids, accompanied by spirillicidal and trypanocidal activity; “bismoxyl,” composed of bismuth and a protein flocculated colloidal complex, is relatively thermostable, and does not pass through porcelain filters. The bismuth content of the complex is not constant. Bismuth is a more effective spirillicidal agent than arsenic.

CHEMICAL ABSTRACTS.

**Action of Potassium and Copper Dichromates on the Growth of *Phytophthora infestans*.** A. and R. SARTORY (*Compt. rend.*, 1924, 179, 69—70).—Copper dichromate is twice as toxic as potassium dichromate to *P. infestans*.

T. H. P.

**Hormone of the Placenta and of the Corpus Luteum and the Lipoids of the Corpus Luteum.** O. O. FELLNER (*Biochem. Z.*, 1924, **147**, 185—186).—A claim of priority in relation to the citation by Fränkel and Fonda (*A.*, 1923, **i**, 1257) of Hermann's work on the placental hormone (*Zentr. allgem. Pathol.*, 1912, **23**). The author states that the hormone does not survive the vacuum distillation employed by Fränkel and Fonda as a method of isolation, but that it is readily purified by extraction with 75% alcohol, in which the accompanying impurities are insoluble. J. P.

**Catalytic Action of Minute Amounts of Copper in the Destruction of Antiscorbutic Vitamin in Milk.** A. F. HESS and M. WEINSTOCK (*J. Amer. Med. Assoc.*, 1924, **82**, 952—956).—Antiscorbutic vitamin is readily destroyed by oxidation, particularly when heated, and in presence of small quantities of copper. Vitamin-A is also very sensitive to the destructive effect of oxidation. The amounts of copper concerned are considerably less than those showing a toxic effect.

CHEMICAL ABSTRACTS.

**Presence of Insulin-like Substance in Gastric and Duodenal Mucosa, and its Relation to Gastric Secretion.** A. C. IVY and N. F. FISHER (*Amer. J. Physiol.*, 1924, **67**, 445—450).—Using Fisher's method (*J. Amer. Med. Assoc.*, 1923, **81**, 920), a substance was obtained from the gastric and duodenal mucosa of the hog which produced an insulin-like effect in a diabetic dog. The method also extracts gastric secretin which, however, is not precipitated with insulin by half-saturation of an acid aqueous solution with ammonium sulphate.

CHEMICAL ABSTRACTS.

**Preparation of Insulin.** T. B. ROBERTSON and A. B. ANDERSON (*Med. J. Australia*, 1923, **2**, 189—191).—Four-fifths of the water contained in the extract containing 50% of ethyl alcohol is removed by means of anhydrous sodium sulphate.

CHEMICAL ABSTRACTS.

**Influence of Insulin on Normal Metabolism in Man.** C. H. KELLAWAY and T. A. HUGHES (*Brit. Med. J.*, 1923, **I**, 710—711).—The results afford evidence of the combustion of dextrose, and of the transformation of dextrose into a complex poorer in oxygen.

CHEMICAL ABSTRACTS.

**Factors Influencing the Production of Insulin.** F. G. BANTING and S. GAIRNS (*Amer. J. Physiol.*, 1924, **68**, 24—30).—High blood-sugar acts as a stimulus to the normal pancreas leading to the production of insulin adequate to reduce the blood-sugar to its normal level.

CHEMICAL ABSTRACTS.

**Insulin-like Compounds.** I. T. BRUGSCH and H. HORSTERS (*Biochem. Z.*, 1924, **147**, 150—162).—An investigation by the blood-sugar test of substances, resembling insulin either physico-chemically or physiologically, isolated from various organs, by processes used in preparing the pancreatic hormone. Such substances are called "raw insulin" irrespective of their action on the blood-sugar. Thyroid extract and extract of epithelial material had practically

no effect; suprarenal material gave results complicated by the presence of adrenaline; liver extracts caused a slight increase in blood-sugar; spleen extract produced a very slight and temporary fall. The human placenta yielded a "raw insulin," resembling that of the pancreas in physical and chemical properties, which caused a slight fall of blood-sugar. Alcoholic placental extracts proved very toxic to rabbits, producing spasms followed by death. Yeast yielded an "insulin" which is thought to differ from that of the pancreas. Sodium hydrogen phosphate and phosphite depressed the blood-sugar; an organic phosphorus compound (tonophosphan) had no effect; atophan and atoxyl produced increases in blood-sugar. J. P.

**Reaction of Living Protoplasm.** R. SCHAEDE (*Ber. deut. bot. Ges.*, 1924, **42**, 219—224).—The plasma of the bulb scales of the onion absorbs methyl-red strongly. Small pieces were floated on an aqueous solution of methyl-red (0.004%) rendered just definitely acid and observed under the microscope. Within 5 to 10 minutes, the plasma of the upper epidermis was definitely coloured yellow, followed later by the plasma of the under epidermis. The cell-sap was strongly coloured red. Various organic and mineral acids were used for the preliminary acidification, and it was shown that neither the methyl-red nor the acids at the concentration used were poisonous to the plasma. Dead plasma under the same conditions is coloured red. Methyl-red therefore indicates that living plasma is alkaline in reaction.

C. T. G.

**Mechanism of Photosynthesis.** J. PEKLO (*Chem. News*, 1924, **129**, 90—94).—Experiments on the poisoning of living cells by various compounds support Willstätter's theory of the formation of a formaldehyde-peroxide complex as an intermediate product of photosynthesis.

A. A. E.

**Absorption of Ions from the Soil through the Root System of Plants.** J. STOKLASA (*Ber. deut. bot. Ges.*, 1924, **42**, 183—191).—Determinations are recorded of (1) the  $p_H$  of the sap in the roots of various cultivated plants, (2) the amount of carbon dioxide excreted per unit weight of the roots, (3) the numbers of bacteria in the soil in the neighbourhood of the roots, and (4) the amount of carbon dioxide respired per unit weight of the soil by the bacteria present. Contrary to the results of other workers, the hydrogen-ion concentration of the sap of the roots of plants grown in normally aerated soil was in no case found to be sufficiently high to account for the absorption of mineral constituents from the soil. The  $p_H$  figures varied only from 6.2 for buckwheat to 6.9 or 7.0 for wheat, barley, and potatoes. The amount of carbon dioxide excreted by the roots varied with different plants, but had no relation to the  $p_H$  of the sap. By growing plants in an artificial soil under sterile conditions and supplied with nitrogen in the form of ammonium salts, it was shown that the various species used possessed characteristic powers of preferential absorption of anions

or cations, *e.g.*, cereals and buckwheat take up anions (phosphate) more readily than cations (potash), whilst beet and potatoes absorb more cations than anions. The yield from such cultures was much increased on inoculation with active bacteria from soil surrounding the roots of the same species of plant, indicating the important part played by bacteria in the absorption of mineral materials by the roots. The number of bacteria found in the neighbourhood of the roots is different for different species of plants grown in the same soil; and these differences are reflected in the amount of carbon dioxide respired by the soil. No appreciable differences were noticed in the  $p_H$  of the soil near the roots of the various plants. It is concluded that the absorption of difficultly soluble mineral nutrients by the root system of plants is brought about entirely by the action of carbon dioxide excreted by the roots and by carbon dioxide and organic acids produced by bacteria.

C. T. G.

**Occurrence of Inulin in the Leaves of *Marcgraviaceae*.** H. MELCHIOR (*Ber. deut. bot. Ges.*, 1924, **42**, 198—204).—The cells of certain small swellings on the leaves of dried specimens of *Marcgravia macroscypha* from S. America were found to be filled with inulin. No starch was present in the leaf. The localisation of the inulin in special areas was probably due to the preliminary preservation of the specimens in alcohol. Inulin was also recognised in the fresh leaves of other species of *Marcgravia*, and again no starch was present. Experiments indicated that in plants of this genus inulin takes the place of starch as a primary product of assimilation.

C. T. G.

**Chemical Composition of the Green Fruit of Vanilla and Mode of Formation of the Perfume of Vanilla.** A. GORIS (*Compt. rend.*, 1924, **179**, 70—72).—Green vanilla fruit contains three glucosides: glucovanillin, which has been isolated; glucovanillic alcohol, which is characterised by the formation of vanillic alcohol on hydrolysis; and a glucoside, not yet isolated, but yielding, on hydrolysis, an ester having the odour of vanilla which gives a crystalline acid and an alcohol when treated with alcoholic sodium hydroxide. The glucovanillic alcohol probably gives rise to glucovanillin and then to vanillin, on oxidation.

T. H. P.

**Composition of the Turpentine Oils from *P. Laricio Austriaca* and *P. Laricio* of Spain.** G. DUPONT and M. BARRAUD (*Bull. Soc. chim.*, 1924, [iv], **35**, 784—792).—Turpentine oil obtained from *P. Laricio Austriaca* consists of 96% of *l*-pinene, about 1% of a dextrorotatory hydrocarbon, *d*-limonene (?), 1% of a sesquiterpene (hydrobromide, m. p. 115—115.5°), and 2% of esters and oxidation products. The turpentine oil obtained from the *P. Laricio* of Spain contains about 90% of *l*-pinene, 4% of *l*-limonene, 1.5% of a sesquiterpene, and 4.5% of oxidation and other products. The pinene obtained from the Spanish turpentine has a lower rotatory power than that from *P. Laricio Austriaca*. The two sesquiterpenes are not identical, since their hydrobromides have

different melting points, although both terpenes with acetic anhydride, or acetic acid, and sulphuric acid give similar colour reactions. The higher-boiling fractions of both essences contain a strongly dextrorotatory constituent. R. B.

**Elementary Composition of the Corn [Maize] Plant.** W. L. LATSHAW and E. C. MILLER (*J. Agric. Res.*, 1924, **27**, 845—860).—Five Pride of Saline maize plants have been analysed at a stage when it could be assumed that the maximum amount of minerals had been removed from the soil. The average dry weight was distributed as follows: leaves, 28.10%; stem, 24.02%; grain, 31.26%; cob, 9.37%; roots, 7.25%. Of the total dry weight approximately 4% was mineral, 1.47% nitrogen, and 94.34% consisted of carbon, hydrogen, and oxygen. The variation in the amount of the different elements and their removal from the soil is discussed. O. O.

**Sulphur Content of the Tomato.** R. S. MARSH (*Amer. Soc. Hort. Sci. Proc.*, 1922, **19**, 83—84).—An increase of the sulphur content occurs with advancing age of the tissue; a high sulphur content is associated with a low phosphorus content. It is suggested that sulphur may liberate phosphorus from the older tissue for translocation to the younger tissue. Phosphate-fertilised plants show a marked increase in sulphur and phosphorus content, particularly near the blossoms. CHEMICAL ABSTRACTS.

**Carbohydrate Reserves of Young Apple Trees as influenced by Winter Storage.** P. T. BLOOD (*Amer. Soc. Hort. Sci. Proc.*, 1922, **19**, 33—35).—The total carbohydrates, including hydrolysable material, are approximately equal in the autumn in the trunks, branches, and roots, but the roots contained 25% less reducing sugar and 3 times as much starch as the trunks and branches. In the spring, a marked reduction in the total carbohydrates was observed; sucrose was then practically absent from the branches and trunks. The effect of the conditions of storage on the magnitude of the changes is recorded.

CHEMICAL ABSTRACTS.

**Effect of Ringing a Stem on the Upward Transfer of Nitrogen and Ash Constituents.** O. F. CURTIS (*Amer. J. Bot.*, 1923, **10**, 361—382).—Ringing twigs and small branches of peach and other trees, either in the spring before the leaves are formed or in the summer when the leaves are fully-developed, affects adversely the movement of nitrogen and ash constituents into the leaves above the ring. When a dressing of sodium nitrate was given immediately after ringing, the nitrogen and ash constituents of the leaves from unringed stems and of the stems themselves increased to a much greater extent than did those of the leaves and stem when ringed. Experiments on privet indicated that the reduced nitrogen content above a ring is not caused by a lowering of transpiration and is independent of its effect on the carbohydrate

content. The data afford strong, although not conclusive, evidence that nutrients are carried chiefly in the phloem. C. T. G.

**Course of Acidity changes during the Growth Period of Wheat with Special Reference to Stem Rust Resistance.** A. M. HURD (*J. Agric. Res.*, 1924, 27, 725—735).—Examination of the expressed juice of a number of varieties of wheat plants showed a general sequence of acidity changes through the period of growth. There was an initial decrease in titratable acidity during the first 2—6 weeks, followed by a period of low acidity which was maintained until the plants began to mature. From this time, the acidity increased fairly regularly to the ripening stage. The hydrogen-ion concentration did not show markedly the initial decrease, but rose considerably during the later stages of the plants' development. External conditions affected both hydrogen-ion concentration and titratable acidity. No correlation was apparent between acidity and susceptibility to stem rust, and resistant varieties showed the same sequence of acidity changes as non-resistant ones. A. G. P.

**Daily Variation of the Carbohydrates in the Leaves of Corn [Maize] and the Sorghums.** E. C. MILLER (*J. Agric. Res.*, 1924, 27, 785—807).—Portions of the leaves of maize and sorghum plants were examined at 2-hourly periods. The amount of dry matter per unit leaf area was always greater in the sorghum than in the maize. From daylight until about 4 p.m. there was a steady increase and later a steady decline until the following daybreak. The amount of water in unit leaf area was always greater in maize, and seemed to become a limiting factor in the production of dry matter when reaching a minimum of 112 g. per sq. metre of leaf. No such limitation occurred in the case of sorghum. The quantity of sugars in the leaves was at a minimum at daybreak and reached a maximum at from midday to 5 p.m. The insoluble carbohydrates reached a maximum later than the sugars and did not decrease appreciably in quantity until after midnight, after which there was a steady decline till daybreak. Non-reducing sugars were usually predominant, increasing during the day and declining at night. Reducing sugars varied to a much smaller extent, and were present in irregular amounts at different times of the day. A. G. P.

**Effect of Nitrate Applications on the Hydrocyanic Acid Content of Sorghum.** R. M. PINCKNEY (*J. Agric. Res.*, 1924, 27, 717—723).—Pot experiments with sorghum showed that nitrate additions to soil in which the plants were grown improved the size and colour of the plants and also increased their hydrocyanic acid content. The latter effect was roughly proportional to the dose of nitrate applied and continued beyond the stage when increased nitrate ceased to affect the size or colour of the plant. In general, lighter coloured plants contained less hydrocyanic acid than darker ones and more was present in the leaf than in the stems. The possibility of utilising sorghum as an indicator plant in soil-nitrogen experiments is noted. A. G. P.

**Action of Dicyanodiamide and Guanylcarbamide Sulphate on Plant Growth.** A. F. McGUINN (*Soil Sci.*, 1924, **17**, 487—500).—Pot and water culture experiments with dicyanodiamide and guanylcarbamide sulphate showed that neither of these substances retards seed germination when applied in small quantities. In large amounts, dicyanodiamide was slightly toxic and very stable in soil. Guanylcarbamide sulphate showed no toxicity and was slowly decomposed to ammonia. Small doses of dicyanodiamide inhibit nitrification, but guanylcarbamide sulphate exerts only a slightly retarding action. Neither substance affects ammonification or the numbers of bacteria and fungi in soil. Urea has a fertilising value approximately equal to that of sodium nitrate, and its value does not diminish if 10% of its nitrogen is in the form of dicyanodiamide and guanylcarbamide sulphate. A. G. P.

**Influence of Silica, Lime, and Soil Reaction on the Availability of Phosphates in Highly Ferruginous Soils.** W. T. McGEORGE (*Soil Sci.*, 1924, **17**, 463—468).—In a number of Hawaiian sugar-cane soils examined, high phosphate availability—as determined by extraction with 1% citric acid—was generally accompanied by high silica availability. Response to phosphate fertilisers was usually more marked in soils of low  $p_H$  value and those having smaller proportions of easily soluble calcium salts (carbonate, sulphate, and silicate). Relationships were traced between available phosphate and silicate, reaction, and soluble calcium, and the phosphate content of the cane juice. A. G. P.

**Influence of Varying Ratios of Phosphoric Acid and Potash on Crop Yield and Nitrogen Recovery.** A. W. BLAIR and A. L. PRINCE (*Soil Sci.*, 1924, **17**, 327—330).—A continuation of earlier work (cf. Lipman and Blair, *N.J. Agr. Expt. Sta.*, 44th *Ann. Rept.*, 1923). Maize was grown in cylinders, with fertilisers applied in various ratios, and harvested green as a forage crop. A ratio of 1 : 2 for nitrogen and phosphoric acid gave somewhat better yields than a ratio of 1 : 1 or 1 : 3. The form in which the nitrogen was used did not affect the percentage of nitrogen in the dry matter, but it influenced the yield and hence the nitrogen recovered in the crop. The recovery was on an average 43% from sodium nitrate, about 30% from ammonium sulphate, and just over 20% from dried blood. The amount of phosphoric acid in the fertiliser did not influence the percentage of nitrogen in the dry matter. C. T. G.

**Mutual Effects on Soil and Plant Induced by Added Solutes.** J. S. BURD and J. C. MARTIN (*Calif. Agr. Exp. Sta. Tech. Paper*, 1923, No. 13).—Treatment of soil with solutions of salts causes a substantial increase in water-extractable materials. The changes are ascribed to added solutes, chemical replacements of solid material, fixation by the solid phase, and increased solubility of solid material in the new soil solution. Addition of nitrate did not prevent the practical disappearance of that ion at the height of the growing season. Some irregular results are ascribed to the defects of water-extraction as a measure of the soil solution, or to the influence

of changed concentrations of other constituents on the absorption of a given element by the plant. CHEMICAL ABSTRACTS.

**Nitrification in Sudan Soils.** F. J. MARTIN and R. E. MASSEY (*Wellcome Trop. Res. Lab., Khartoum, Chem. Sect. Publ.*, 1923, No. 29, 29 pp.).—In field experiments on irrigated soils at Shambat it was found that nitrates accumulated in considerable quantities in the tops of the ridges in irrigated land and in land carrying cotton. The nitrates disappeared from land in dry fallow. The accumulation of nitrate was ascribed to nitrogen fixation, and not to concentration of the soil solution by evaporation, since other soluble salts were washed down and tended to accumulate in the lower subsoil. The amount of nitrate in the surface of the ridge was many times greater than that in the furrows or the subsoil. It is suggested that this accumulated nitrate is not available for the crop. Flooding of the ridges in order to wash the nitrate into the soil was tried with some success. Ammonium sulphate gave the greatest crop increases for wheat and cotton when applied 6 to 8 weeks after sowing. E. M. C.

**Nitrification. V. Mechanism of Ammonia Oxidation.** A. BONAZZI (*J. Bact.*, 1923, 8, 343—363).—Using an active form of *Nitrosococcus*, grown in Omeliansky culture solution, it was found that three atoms of oxygen were utilised by the organisms for each atom of nitrogen oxidised. The bacterium is able to cause the breakdown of hydrogen peroxide; but no peroxide-oxygen could be detected in the cultures. The changes undergone by the iron present in the nitrifying cultures were studied, and it is suggested that the iron acts as an oxygen carrier forming an intermediate ferrous oxide-peroxide from which the bacterial cells are able to obtain active oxygen. Thus, in the actual process of ammonia oxidation, iron plays the part of a peroxide and activates the inert oxygen of the air. The mechanism itself appears to be intracellular.

The presence of ammonium iodide had no harmful effect on the process of ammonia oxidation and no appreciable oxidation of the iodine to iodate was observed. C. T. G.

**Chemical Factors in Denitrification.** G. J. FOWLER and Y. N. KOTWAL (*J. Indian Inst. Sci.*, 1924, 7, 29—37).—The stability of dilute solutions of ammonium nitrite under conditions likely to occur in sewage purification is investigated; and it is concluded that any loss of gaseous nitrogen in the operations of agriculture and sewage purification due to purely chemical causes is negligible. [Cf. *B.*, 1924, 728.] C. T. G.

**Microbiological Analysis of Soil as an Index of Soil Fertility. IX. Nitrogen Fixation and Mannitol Decomposition.** S. A. WAKSMAN and P. D. KARUNAKAR (*Soil Sci.*, 1924, 17, 379—393; cf. *B.*, 1924, 106, 143, 394).—The nitrogen-fixing powers or mannitol-decomposing powers of soils from several experimental plots have been compared by four methods. The importance of phosphorus for the nitrogen-fixing organisms makes it possible to obtain in this



way an indication of the amount of available phosphorus in the soil. The determination of the increase in total nitrogen following the addition of mannitol to the soil is untrustworthy owing to the lack of sensitiveness in the determination of total nitrogen. The increase of total nitrogen in a standard mannitol solution after inoculation with the soil sample and incubation serves as an index of the nitrogen-fixing flora of the soil and to some extent of the microbiological condition of the soil. The nitrogen fixation in a sterilised mixture of mannitol solution and soil, after inoculation with *Azotobacter* and incubation, can serve as an index of the available phosphate in the soil. Christensen's method of incubating the soil with mannitol and determining at intervals of 5 days the residual soluble organic matter, by oxidation with potassium permanganate, can serve as an index of the nitrogen-fixing flora and of the amount of phosphorus available in the soil. E. M. C.

**Value of Soil Analysis when Limited to an Intensive Single Cropping System.** W. T. McGEORGE (*Soil Sci.*, 1924, 17, 457—462).—The value of weak acid solvents, notably 1% citric acid, in determining the availability of potash and phosphate in sugar-cane soils is discussed. Under these limited conditions, the citric acid extract proved of considerable value in arriving at fertiliser requirements. Certain general relationships between availability and soil type are noted. A. G. P.

**Intensity of Assimilation of Atmospheric Nitrogen by Forest Soils.** A. NÉMEC and K. KVAPIL (*Bull. Soc. Chim. biol.*, 1924, 6, 515—520; cf. *Compt. rend.*, 1923, 176, 260).—A comparison of the amounts of nitrogen fixed under similar conditions in the presence of samples of both the humus and the lower mineral soil, from forests of various types and with different species of trees. G. M. B.

**Sulphofication in Pure and Mixed Cultures, with Special Reference to Sulphate Production, Hydrogen-ion Concentration, and Nitrification.** H. D. BROWN (*J. Amer. Soc. Agron.*, 1923, 15, 350—382).—No nitrogen was lost from soil in which large amounts of sulphur were oxidised. A close inter-relation existed between sulphofication, nitrification, and soil reaction. With the oxidation of sulphur, the hydrogen-ion concentration increased and nitrification was depressed. Liming increased both sulphofication and nitrification. E. M. C.

**Toxic Organic Soil Constituents and the Influence of Oxidation.** O. SCHREINER (*J. Amer. Soc. Agron.*, 1923, 15, 270—276).—The author reviews earlier work on the isolation from unproductive soils of harmful substances, such as picolincarboxylic acid, dihydroxystearic acid, oxalic acid, salicylaldehyde, and vanillin. Toxic substances, especially aldehydes, are formed under conditions of imperfect aëration and oxidation. Such infertile soils are improved by the changed biochemical processes resulting from drainage, liming, rotations, green manuring, and fertilisation. E. M. C.

## Organic Chemistry.

### Methylethylisopropylmethane and Diisopropylmethane.

G. CHAVANNE and H. DE GRAEF (*Bull. Soc. chim. Belg.*, 1924, **33**, 366—375).—Methylethylisopropyl carbinol [ $\beta\gamma$ -dimethylpentan- $\gamma$ -ol], prepared by the action of magnesium isopropyl iodide on methyl ethyl ketone, and of magnesium ethyl bromide on methyl isopropyl ketone, has b. p.  $42\text{--}43^\circ/11$  mm.,  $139.4\text{--}139.9^\circ/760$  mm. (slight decomp.),  $d_4^{15}$  0.8445,  $n_D^{20}$  1.4280. It is converted by *p*-toluenesulphonic acid into two isomeric dimethylpentenes, probably  $\beta\gamma$ -dimethyl- $\Delta^2$ -pentene and  $\beta\gamma$ -dimethyl- $\Delta\gamma$ -pentene, b. p.  $92^\circ$  and  $96\text{--}97^\circ$  respectively, which are catalytically reduced in acetic acid to methylethylisopropylmethane [ $\beta\gamma$ -dimethylpentane], b. p.  $89.9\text{--}90.1^\circ/760$  mm.,  $d_4^{15}$  0.6991,  $d_4^{20}$  0.6950,  $n_D^{20}$  1.3918, separation point from aniline,  $68.1 \pm 0.1^\circ$ .

isoButyl bromide is best prepared by the action of gaseous hydrogen bromide on cold isobutyl alcohol, the yield being 80%. Dimethylisobutyl carbinol [ $\beta\delta$ -dimethylpentan- $\beta$ -ol], obtained by the action of magnesium isobutyl bromide on acetone, has b. p.  $42\text{--}43^\circ/11$  mm.,  $132.8\text{--}133.4^\circ/760$  mm. (slight decomp.),  $d_4^{15}$  0.8168,  $n_D^{20}$  1.4172. The carbinol when dehydrated with *p*-toluenesulphonic acid gives dimethylisopropylethylene [ $\beta\delta$ -dimethyl- $\Delta^2$ -pentene], b. p.  $83.1\text{--}83.3^\circ/760$  mm.,  $d_4^{15}$  0.6994,  $n_D^{20}$  1.4016, the constitution of which is confirmed by oxidation with chromic acid to acetone and isobutyric acid. Reduction in the presence of platinum converts it into diisopropylmethane [ $\beta\delta$ -dimethylpentane], b. p.  $80.7\text{--}80.9^\circ/760$  mm., m. p.  $-119.4^\circ$ ,  $d_4^{15}$  0.6769,  $n_D^{20}$  1.3814, separation point from aniline,  $78.6 \pm 0.1^\circ$ .

F. G. M.

**Pyrogenic Dissociation of Hexadecene.** H. GAULT and Y. ALTCHIDJIAN (*Compt. rend.*, 1924, **178**, 2092—2095).—The decomposition products consist of hydrogen, paraffins, and ethylenic hydrocarbons. The percentage of the last-named increases with temperature to a maximum of 67—68; further increase in temperature brings about a decrease in this yield. There is a corresponding minimum point for paraffins. The percentage of hydrogen increases slowly with rise of temperature. The authors have employed the apparatus previously described (Gault, Hessel, and Altchidjian, this vol., i, 701) and their results indicate that the size of the furnace used, whilst not altering the general results, shifts the temperature range over which they are obtained; e.g., the maximum production of ethylenic hydrocarbons occurs at  $570^\circ$  with a 64 cm. furnace but at  $685^\circ$  with one of 16 cm.

H. J. E.

**Pyrogenic Dissociation of Hexadecane.** H. GAULT and F. A. HESSEL (*Compt. rend.*, 1924, **179**, 171—173; cf. this vol., i, 701).—The pyrogenic decomposition of hexadecane at various temperatures and in furnaces of various lengths has been investig-

ated. The formation of saturated hydrocarbons and of hydrogen in the gaseous products increased and that of unsaturated hydrocarbons decreased with increase of temperature from 600° to 815°; acetylene was detected in the products at 615° and in some cases at lower temperatures. Figures are given for the iodine absorption, density, and refractive index of the liquid products; except in one instance, these contained no aromatic hydrocarbons when tested by the solubility in methyl sulphate. F. G. M.

**Catalytic Activation of Ethylene by an Organo-nickelic Compound.** A. JOB and R. REICH (*Compt. rend.*, 1924, 179, 330—332).—On addition of successive small quantities of pure, powdered nickel chloride to an ethereal solution of magnesium phenyl bromide in the presence of pure, dry ethylene (the temperature being maintained strictly at 6°) the gas is rapidly absorbed, the rate being proportional, not to the amount of nickel chloride added, but to the quantity of the magnesium phenyl bromide employed. By the action of water on the very complex solution obtained, the main product is ethane, mixed with smaller quantities of liquid hydrocarbons, ethylbenzene, styrene, diphenyl, and some hydrocarbons of b. p. above 270°. The action of carbon dioxide yields a mixture of acids, among which formic, propionic, and phenylpropionic acids are identified. The catalyst is probably an organo-nickelic compound, the magnesium acting as the acceptor.

J. W. B.

**Tautomerism of Dyads. II. Acetylene and its Halogen Derivatives.** (MRS.) E. H. INGOLD (*J. Chem. Soc.*, 1924, 125, 1528—1537).—The presence of small proportions of isoacetylene,  $\text{CH}_2\text{:C}$ , in acetylene is indicated by the thermodynamic method for the detection of tautomeric equilibria in very mobile systems (T., 1922, 121, 1604) and by the formation of keten when the gas is very cautiously oxidised.

Chloroacetylene exists in two phases at the ordinary temperature, since  $\alpha$ -chloro- $\beta\beta$ -di-iodoethylene is produced by passing the gas into a solution of iodine in benzene, whereas exposure of the gas, mixed with nitrogen, to bright light results in the isolation of *s*-trichlorobenzene. Further, the action of hypobromous acid leads to the formation of chloroacetic acid and chlorodibromoacetaldehyde, one derived from each of the two isomerides originally in equilibrium. Bromoacetylene also displays this dual chemical character. The dihalogen-acetylenes show no tendency to pass into halogenated benzenes; all the evidence supports the isoacetylene structure, and no fact is known which needs an assumption of the structure  $\text{CBr:CCBr}$ . A. C.

**Explosion of Acetylene and Nitrogen. III. Effect of the Addition of Oxygen on the Production of Hydrocyanic Acid.** W. E. GARNER and S. W. SAUNDERS (*J. Chem. Soc.*, 1924, 125, 1634—1641; cf. T., 1921, 119, 1903; 1922, 121, 1729).—The relation  $K_1^{\text{II}} = [\text{HCN}]/[\text{C}][\text{N}_2]^{0.37}$ , which gives constant values for explosive mixtures of nitrogen and acetylene alone and when

admixed with helium or hydrogen, no longer holds when oxygen is present. The production of hydrocyanic acid in explosive mixtures of acetylene, nitrogen, and oxygen, in which the content of nitrogen is kept constant at about 22% and the proportions of oxygen and acetylene are varied, increases with the proportion of oxygen, reaches a maximum in mixtures containing about 37% of oxygen, and then falls to zero. If the ratio of oxygen to acetylene exceeds 1:1, no hydrocyanic acid is found amongst the products; with mixtures richer in oxygen, appreciable amounts of carbon are not liberated at the temperature of the explosion and hence hydrocyanic acid cannot be formed.

C. J. S.

**Transformation of Acetylenic Hydrocarbons by means of Sodamide.** BOURGUEL (*Compt. rend.*, 1924, **178**, 1984—1986; cf. Meunier and Desparmet, this vol., i, 701).—The action of sodamide at 110° on acetylenic hydrocarbons of the type  $CR:CMe$  results in the quantitative formation of the sodium derivatives of hydrocarbons,  $CH_2R \cdot C:CH$ , with the evolution of an equimolecular quantity of ammonia. The action is more rapid than when sodium alone is used (cf. Faworsky, A., 1888, 1168), and none of the hydrocarbon is reduced. A similar transformation from  $CR:Cet$  into  $CH_2R \cdot CH_2 \cdot C:CH$  occurs, but the reaction is much slower.

H. J. E.

**Decomposition of Ethylene Bromide by Potassium and Sodium Iodide Solutions.** T. S. PATTERSON and J. ROBERTSON (*J. Chem. Soc.*, 1924, **125**, 1526—1527).—Ethylene is evolved and iodine is liberated when mixtures of potassium iodide, water, and ethylene bromide are gently boiled.

S. B.

**Preparation of  $\alpha\alpha$ -Dichloro- $\beta$ -bromoethylene.** H. VAN DE WALLE (*Bull. Acad. Roy. Belg.*, 1924, [v], **10**, 94—108).—This compound (cf. Denzel, A., 1879, 368) may be prepared according to the scheme:  $CH_2Cl \cdot CH_2Cl \rightarrow CH_2:CHCl \rightarrow CH_2Cl \cdot CHCl_2 \rightarrow CH_2 \cdot CCl_2 \rightarrow CH_2Br \cdot CCl_2Br \rightarrow CHBr \cdot CCl_2$ . Repetition of the procedure given by Mouneyrat (A., 1899, i, 470) failed to yield  $\alpha\beta$ -tetrachloroethane, but treatment of  $\alpha\beta$ -dichloroethane with alcoholic potassium hydroxide gives chloroethylene, which is converted by passage through cooled antimony pentachloride into  $\alpha\alpha\beta$ -trichloroethane. Treatment of the latter with alcoholic potassium hydroxide in a current of nitrogen yields  $\alpha\alpha$ -dichloroethylene, which is readily brominated to  $\alpha\alpha$ -dichloro- $\alpha\beta$ -dibromoethane, b. p. 175° (decomp.), 65°/13 mm., 70°/18 mm., m. p. —66–85°,  $d_4^{15}$  2.2695,  $n_D^{15}$  1.55930. Treatment with alcoholic potassium hydroxide solution then forms  $\alpha\alpha$ -dichloro- $\beta$ -bromoethylene, b. p. 107—108°, m. p. —88.5°,  $d_4^{15}$  1.9053,  $n_D^{15}$  1.52028, which yields with alcohol an azeotropic mixture, b. p. 77.25°, containing 60.5% of alcohol.  $\alpha\alpha$ -Dichloro- $\alpha\beta\beta$ -tribromoethane, obtained by addition of bromine to the preceding compound (cf. Städel, A., 1879, 368; Denzel, *loc. cit.*), has b. p. 210° (decomp.), 106°/16 mm., m. p. 16–80°,  $d_4^{15}$  2.6315,  $n_D^{30}$  1.60035.  $\alpha\beta$ -Dichloro- $\alpha\alpha\beta$ -tribromoethane (cf. Swarts, A., 1899, i, 725) has b. p. 210° (decomp.), 112°/16 mm.,

n n 2

m. p.  $5.95^{\circ}$ ,  $d_4^{25}$  2.6346,  $n_D^{15}$  1.60846. The melting-point curve for mixtures of these two isomerides has a minimum at  $4.20^{\circ}$ , the crystalline phases being solid solutions having a gap between 80% and 100% of  $\alpha\beta$ -dichloro- $\alpha\alpha\beta$ -tribromoethane. T. H. P.

**Action of Light on Solutions of certain Organic Substances in Chloropicrin.** A. PIUTTI and P. BADOLATO (*Atti R. Accad. Lincei*, 1924, [v], 33, i, 475—479).—Investigation of the compounds formed when solutions in chloropicrin of acetic acid, ethyl succinate, methyl salicylate, toluene, naphthalene, phenol,  $\psi$ -cumene, or *o*-, *m*-, or *p*-xylene were exposed to light for several months showed that, although chloropicrin is stable in the dark, it decomposes in the light into products having a chlorinating, oxidising, or substituting action on the solute. In some instances, the nitro group underwent reduction to the ammonium group, which separated as chloride or oxalate. T. H. P.

**Halogenation of s.-Dipotassium Tetranitroethane.** L. HUNTER (*J. Chem. Soc.*, 1924, 125, 1480—1484).—The action of chlorine on a solution of s.-dipotassium tetranitroethane and sodium acetate in water results in the precipitation of s.-dichlorotetranitroethane,  $\text{CCl}(\text{NO}_2)_2 \cdot \text{CCl}(\text{NO}_2)_2$ , m. p.  $107^{\circ}$  after incipient decomposition at  $60$ — $65^{\circ}$ . Boiling water causes it to decompose into carbon dioxide, oxides of nitrogen, hydrochloric acid, and dichlorodinitromethane. It shows the usual reactions of "positive" halogen, characteristic of the *gem*-halogen-nitroparaffins. With 50% potassium hydroxide solution it is reconverted into s.-dipotassium tetranitroethane. Potassium iodide solution gives the same result, iodine being precipitated. Vigorous reaction takes place with potassium cyanide: cyanogen chloride is evolved and a black powder separates, whilst the filtrate contains carbonate, nitrite, and chloride.  $\alpha\beta$ -Tribromo- $\alpha\beta\beta$ -trinitroethane (cf. Scholl and Brenneisen, A., 1898, i, 345), when treated with potassium iodide, also gave s.-dipotassium tetranitroethane, the potassium nitrite formed by a side decomposition acting as nitrating agent. Attempts to prepare the bromine analogue of s.-dichlorotetranitromethane resulted in the formation of dibromodinitromethane,  $\text{CBr}_2(\text{NO}_2)_2$ . Although s.-dipotassium tetranitroethane is stable towards iodine as illustrated in the preparation of this salt from bromopicrin and potassium iodide (Hunter, T., 1923, 123, 543), attempts to increase the yield by addition of potassium nitrite resulted in a diminished yield and production of *potassium iodonitromethane* as a by-product, orange leaflets, exploding at  $154$ — $156^{\circ}$ , silver salt, explosion point  $104$ — $106^{\circ}$ . Salts other than potassium nitrite failed to effect this change. A. C.

**Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. V. Preparation of Primary Alcohols by Catalytic Hydrogenation of Aldehydes.** W. H. CAROTHERS and R. ADAMS.—(See i, 968.)

**Action of Aluminium Sulphide on certain Organic Compounds [Ethyl Alcohol].** G. R. LEVI and G. NATTA.—(See i, 952.)

**Dehydration of Alcohol. The System: Water-Alcohol-Hydrocarbon-Potassium Carbonate. Equilibrium between the Three Liquid Phases.** L. GAY, P. MION, and SERVIGNE (*Chim. et Ind.*, May 1924 [special number], 286—295).—The equilibrium between water, liquid hydrocarbons (both pure and mixed), alcohol, and potassium carbonate is theoretically examined, the general conclusions being confirmed experimentally. The amount of alcohol in the hydrocarbon layer is independent of the potassium carbonate concentration in the lower, aqueous layer, provided this concentration is below 30%. Potassium carbonate is not sufficiently soluble at 20° to render alcohol and hydrocarbon miscible at this temperature. A good dehydrating agent must, in aqueous solution, have negligible solubility in the hydrocarbon-alcohol mixture, or the alcohol must be practically insoluble in the solution of the dehydrating agent. A sufficiently concentrated potassium carbonate solution, containing about 45% of the salt, fulfils these conditions. S. K. T.

**Rotatory Dispersive Power of Organic Compounds. XII. Octyl Alcohol and Octyl Oxalate.** T. M. LOWRY and E. M. RICHARDS (*J. Chem. Soc.*, 1924, 125, 1593—1597).—Determinations of the rotatory dispersion of *sec.*-octyl alcohol for 19 wave-lengths by the visual method and 6 other wave-lengths by the photographic method have shown that the results can be expressed by one term of Drude's equation. The dispersion of octyl oxalate over a range of 27 wave-lengths is more complex and can be expressed neither by the one-term equation nor by Biot's law, although the results approximate to the latter. C. J. S.

**Trimethylethylglycerol [ $\beta\delta$ -Dimethylhexane- $\beta\gamma\delta$ -triol].** PASTUREAU and H. BERNARD (*Compt. rend.*, 1924, 179, 181—184; cf. A., 1922, i, 717; 1923, i, 646).—Magnesium ethyl bromide reacts with the chlorohydrin of mesityl oxide to give  $\gamma$ -chloro- $\beta\delta$ -dimethylhexane- $\beta\delta$ -diol, m. p. 35—37°, b. p. 105—110°/5 mm., which, on treatment with potassium carbonate, gives  $\beta\delta$ -dimethylhexane- $\beta\gamma\delta$ -triol, m. p. ca. 75°. Magnesium ethyl bromide and mesityl oxide give  $\beta\delta$ -dimethyl- $\Delta^{\beta}$ -hexan- $\delta$ -ol, b. p. 45—47°/9 mm., which reacts vigorously with hypoiodous acid; the resulting iodohydrin is too unstable to be isolated (cf. A., 1923, i, 891). F. G. M.

**Ethers of Polysaccharides with Hydroxy-acids.** J. K. CHOWDHURY (*Biochem. Z.*, 1924, 148, 76—97).—By the action of chloroacetic acid on polysaccharides in the presence of concentrated aqueous sodium hydroxide, ethers are obtained which, when thoroughly dried, are insoluble in water and in organic solvents. In the case of the cellulose ethers of glycollic acid the preparation with the lowest content of acid had one molecular proportion of the latter to three glucose residues, whilst that with the highest acid content had three molecules in each glucose residue. By the action of phosphorus tri-iodide and water on the cellulose glycollic acid ethers, cellulose and glycollic acid were obtained. In the cases of starch and inulin the highest degrees of substitution attained were respectively 2 mols. and 2½ mols. of acid per glucose residue.

The more highly substituted derivatives form insoluble salts with the alkaline-earth metals, and may be separated from the less highly substituted compounds of which the corresponding salts are soluble in water. The monosubstituted cellulose derivative exists as a lactone, that of starch as a mixture of free acid and lactone. The partly substituted cellulose derivatives may be methylated by means of methyl sulphate and sodium hydroxide, the carboxyl groups of the acid residues undergoing a partial methylation. The resulting product is soluble in cold, but insoluble in hot water. In the case of starch the carboxyl group does not undergo esterification and the product, which is soluble in both cold and hot water, shows a combined acid and methoxyl content corresponding with a substitution of  $2\frac{1}{3}$  of the three available hydroxyl groups in each glucose residue. By the action of chloropropionic acid and sodium hydroxide on cellulose, lactic acid ethers were obtained in small yields, but the formation of similar products was not observed using chloro- and bromo-malonic acids. J. P.

**Methylations. Hydrolysis of Methyl Sulphate.** H. F. LEWIS, O'N. MASON, and R. MORGAN (*Ind. Eng. Chem.*, 1924, **16**, 811—812).—The reaction,  $\text{Me}_2\text{SO}_4 + \text{H}_2\text{O} = \text{MeHSO}_4 + \text{MeOH}$ , is complete within 3 mins. at  $95^\circ$  in mixtures of methyl sulphate and water containing from 0.5 to 75.0% of the former. The hydrolysis of the methyl hydrogen sulphate is considerably slower with concentrations of methyl sulphate up to 5%, thereafter increasing rapidly with increase in concentration of the latter, a mixture containing 75% of methyl sulphate being hydrolysed to the extent of 96% in 3 mins. In mixtures containing 1% of methyl sulphate, the presence of 1% of sulphuric or hydrochloric acid produces an initial decrease, and subsequent increase in the rate of hydrolysis as compared with water alone, these variations being less marked with 25% sulphuric acid. In mixtures containing 25% of methyl sulphate, the presence of any acid decreases the rate of hydrolysis, whilst in mixtures containing 1 or 25% of methyl sulphate, the presence of 25% of acetic acid affords almost complete resistance to hydrolysis of the methyl hydrogen sulphate. The hydrolysis is depressed by alkalis and salts, potassium hydroxide showing greater hydrolytic activity than sodium hydroxide with low concentrations of methyl sulphate, whilst potassium chloride is a stronger depressant than sodium chloride. F. G. W.

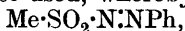
**Autoxidation of Organic Sulphur Compounds.** M. DELÉPINE (*Bull. Soc. chim. Belg.*, 1924, **33**, 339—365).—A lecture delivered before the Chemical Society of Belgium.

F. G. M.

**Method of Preparing Sulphinones.** L. BERT (*Compt. rend.*, 1924, **178**, 1826—1828).—*Di-n-butyl sulphite*, a colourless liquid, b. p.  $230^\circ$  (slight decomp.),  $111^\circ/15\text{ mm.}$ ,  $d^{20}_4$  1.001,  $n^{20}_D$  1.435, was prepared by the action of sulphur chloride on butyl alcohol at  $100^\circ$ . When 1 mol. is added to 2 mols. of an organo-magnesium compound of the type  $\text{MgRX}$ , the corresponding sulphinone  $\text{R}_2\text{SO}$  is obtained.

H. J. E.

**Action of Diazo Salts on Methanesulphonamide.** P. K. DURR (*J. Chem. Soc.*, 1924, **125**, 1463—1465; cf. T., 1921, **119**, 2088).—Methanesulphonamide, m. p. 84—85°, was prepared by slowly dropping methyl sulphate into a mixture of a solution of sodium sulphite and boiling methyl alcohol and treating the sodium methanesulphonate (yield *ca.* 94%) successively with phosphoryl chloride and dry ammonia. When it is dissolved in sodium hydroxide and mixed with a solution of benzenediazonium chloride, a yellow solid appears which quickly decomposes and produces phenylazoimide. After the removal of the latter, the aqueous portion is treated with a second portion of benzenediazonium chloride equal to that first used, whereby the compound,



yellow needles, m. p. 71—72° (decomp.), is produced. The substance,  $\text{Me}\cdot\text{SO}_2\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_7$ , prepared similarly from *p*-toluenediazonium chloride, has m. p. 112—113° (decomp.). The interaction of toluene-*o*-sulphonamide with benzenediazonium chloride gave a tarry product from which only phenylazoimide could be isolated. The stability of these diazoamines appears to depend on some influence at present unknown. A. C.

**Thermal Decomposition of some Pure Metallic Acetates.** W. KRÖNIG (*Z. angew. Chem.*, 1924, **37**, 667—672).—The dried acetates of lithium, sodium, potassium, copper, magnesium, calcium, barium, lead, and manganese, when gradually heated to 500°, appear normally to break down directly into acetone, metal oxide, and carbon dioxide, the last two then combining to a greater or less extent. The best yield of acetone is given by lithium acetate, the residue being almost pure lithium carbonate. Sodium, potassium, calcium, and barium acetates also give a residue consisting essentially of metallic carbonate, but the distillate from the first two contains a large amount (37% and 52%, respectively) of an oily condensation product, insoluble in water. The decomposition of copper acetate resembles that of silver acetate, the residue comprising the metal (with a small quantity of oxide) and carbon, and the distillate nearly pure acetic acid. Magnesium and manganese acetates yield mainly the metallic oxide, acetone, and carbon dioxide. With lead acetate, the lead oxide first formed oxidises a portion of the acetone, and the residue consists of nearly pure lead. An examination of the thermal decomposition of zinc acetate was impossible owing to excessive sublimation. The yield of acetone from metallic acetates appears to be related to the basicity of the metal. W. T. K. B.

**Hydrates in Aqueous Solution. II. Citrate, *d*-Tartrate, Acetate, and Oxalate Ions.** R. FRICKE and H. SCHÜTZDELLER (*Z. anorg. Chem.*, 1924, **136**, 295—304).—Determinations of the viscosity, freezing point, and density of aqueous solutions of the neutral potassium salts of citric, *d*-tartaric, acetic, and oxalic acids of varying concentrations indicate that the anions, especially the first three, are strongly hydrated. Hofmeister's series of



decreasing hydration—citrate, tartrate, sulphate, acetate—is true only if solutions of equimolar concentration are compared; it does not hold for solutions of equal normality. The molar depression of the freezing point of solutions of potassium oxalate or tartrate falls continuously with increasing dilution, whereas that of solutions of potassium citrate or acetate has a minimum value. Normal potassium citrate (+H<sub>2</sub>O) has  $d_4^{18}$  1.995 and fused potassium acetate  $d_4^{18}$  1.519.

A. R. P.

**Marine Animal Oils. Identity of Phocenic and Valeric Acids.** E. ANDRÉ (*Bull. Soc. chim.*, 1924, [iv], **35**, 857—868).—Phocenic acid, derived from dolphin's head or whale oil by hydrolysis, is shown to be identical with valeric acid. The author thus refutes the suggestions made both by Lewkowitsch ("Chemical Technology of Oils, Fats and Waxes," 5th ed., p. 152) and Fryer and Weston ("Technical Handbook of Oils, Fats and Waxes," 3rd ed., p. 37) that the oil consists of a mixture of the glycerides of *n*-butyric and hexoic acids.

A. E. C.

**Oil from *Mimusops Hexandra* : Rayan Oil.** C. K. PATEL (*J. Indian Inst. Sci.*, 1924, **7**, 71—80).—Rayan seeds yield 24.6% of an edible oil which is equivalent to a yield of 47.2% on the kernels. The oil,  $d_{15}^{15.5}$  0.914,  $n_D^{20}$  1.4528, saponification value 190, iodine value 65, has a faint odour, is nearly colourless, is readily refined by alkali, and is easily hydrolysed by castor-seed lipase. The curve relating iodine value with refractive index is exactly similar to those for mohua, cotton-seed, and cashew-kernel oils. The fatty acids obtained by hydrolysis are palmitic, stearic, and oleic, with very small amounts of lignoceric and linolic, and the unsaponifiable matter consists of a liquid with a high refractive index and a sterol, probably ergosterol. The oil also contains a small quantity of a bitter principle soluble in water, probably a saponin.

P. M.

**Dehydrogenating Action of Nickel-Copper Catalysts.** G. KITA, T. MAZUME, and K. KINO (*Chem. Umschau*, 1924, **31**, 165—167).—Catalysts were used containing 16.9% of Ni and 3.1% of Cu; 14.0% of Ni and 6.0% of Cu; and 10.5% of Ni and 9.5% of Cu on kaolin. Stearic acid at 300—310° does not undergo dehydrogenation, but ketonic decomposition takes place, the amount increasing with increase of copper in the catalyst. With herring oil, dehydrogenation of the fatty acid takes place at 200° and at 170° with those catalysts containing more copper, and hydrogenation with those containing only nickel or nickel and a little copper. The catalyst containing little copper shows slight dehydrogenation at 100°. The temperature of reduction of the catalyst has an important effect; that reduced at 340—350° shows some dehydrogenating activity even at 100°, but that reduced at 220—230° shows none at any of the temperatures employed.

P. M.

**Wool Fat.** F. GRASSOW (*Biochem. Z.*, 1924, **148**, 61—75).—By hydrolysis of wool fat with *N*/2-potassium hydroxide, cerotic acid,

$C_{27}H_{54}O_2$ , m. p.  $78^\circ$ , was obtained and identified by comparison, together with its derivatives (methyl, ethyl, and cholesteryl esters, amide, *anilide*, m. p.  $97^\circ$ ) with a corresponding preparation from beeswax. The *menthyl* ester, m. p.  $43-44^\circ$ , and the *phenyl* ester, plates, m. p.  $59^\circ$ , are described. *Methyl* and *benzyl lanocerinates*, m. p.  $79-80^\circ$  and  $80^\circ$ , respectively, are also described. By the action of benzoyl chloride on the silver lanocerate, the mixed *anhydride*,  $C_{29}H_{57}(OH)_2 \cdot CO \cdot OBz$ , m. p.  $76^\circ$ , was obtained.

J. P.

**Decomposition of Animal Wax.** A. MAILHE (*Compt. rend.*, 1924, **179**, 184—185).—A mixture of 300 g. of beeswax, m. p.  $64^\circ$ , and 50 g. of anhydrous magnesium chloride was cautiously heated. At the beginning of the reaction the gas evolved contained  $CO_2$  39%, CO 25.5%,  $CH_4$  9%, and  $H_2$  26.5%. As the temperature rose to  $500^\circ$ , about 215 g. of distillate were collected, whilst a sample of the gas evolved contained  $CO_2$  14.5%, CO 22.4%, olefines 23.5%, methane 17.4%, other paraffins 18%, and  $H_2$  4.2%. The distillate, when freed from acids, had b. p.  $55-350^\circ$ , and contained paraffins, olefines, and an unidentified ketone, white needles, m. p.  $53-54^\circ$ . Zinc, calcium, and barium chlorides and metallic oxides gave similar results.

F. G. M.

**Action of Halogens on Unsaturated Aliphatic Compounds.** J. J. CERDEIRAS (*Bull. Soc. chim.*, 1924, [iv], **35**, 902—904).—Wijs' reagent is 3—4 times more reactive than iodine in acetic acid solution towards olive and linseed oils, and 2—3 times as reactive towards oleic and linolenic acids. In each case, the reaction with Wijs' reagent is practically complete after 40 mins.

A. E. C.

**Natural Soaps in Soja Bean.** S. MURAMATSU (*J. Chem. Soc. Japan*, 1923, **44**, 1035—1049).—When powdered soja bean, after being freed from fats and free acids, is extracted with warm alcohol (80%), the amount of soaps dissolved in the case of different species of the bean (even when unripe) is 1.44—1.86% of the dried bean. The total acids of the soap are composed of fatty and hydroxy-acids. The mixed fatty acids have acid value 177.1; mean mol. wt. 316.9. They can be separated into liquid acids, m. p.  $38^\circ$  (29.31% of the total organic acid), and solid acids, m. p.  $55^\circ$  (4.63%). The purified hydroxy-acid,  $C_{34}H_{68}O_{17}$ , white crystals, m. p.  $224^\circ$ , is named *hispidic acid*. It gives a *hexa-acetyl* derivative, m. p.  $155^\circ$ . The alkali salts of hispidic acid easily give a viscous, aqueous solution, which has marked foam-forming and detergent powers. K. K.

**Relation between the Iodine Values and Refractive Indices of Hardened Oils.** II. H. E. WATSON and J. J. SUDBOROUGH (*J. Indian Inst. Sci.*, 1924, **7**, 81—95).—Iodine values and refractive indices for oils of different degrees of hydrogenation are recorded for argemone, English mustard, Indian rape, cashew kernel, soja bean, poppy-seed, rayan, olive, seal, and cod-liver oils. Rocket, mustard, and rape oils have higher refractive indices for a given

 $n_{D^{20}}$

iodine value than all the other oils examined except castor and argemone oils, this being attributed to the presence of glycerides of erucic acid. The high ratio of refractive index to iodine value for argemone oil is not due to glycerides of erucic acid, but to diglycerides and glycerides of hydroxy-acids. The refractive index for completely hardened olive oil ( $n_D^{60}$  1.4463) agrees very closely with that of the purest tristearin (1.4462). Most of the curves are approximately parallel, but that for seal oil is exceptional and crosses most of the others. P. M.

**Theory of Polymerisation in Fatty Oils. II.** R. S. MORRELL (*J. Oil and Colour Chem. Assoc.*, 1924, 7, 153—160).—The degree of polymerisation of fatty oils is not accurately indicated by the determination of the iodine value on account of the depolymerising action of some of the components of Wijs' solution. The molecular weight of these oils cannot be satisfactorily determined with benzene as a solvent, as esters show a tendency to combine with the solvent, and association occurs if acids be present. The polymerisation of linseed oil may be extramolecular as well as intramolecular, and it must be viewed from a colloidal as well as from a strictly chemical aspect. The ethyl esters derived from linseed and tung oils show a greater gain in weight in "drying" than do the glycerides, but the resulting films are liquid, and not solid as in the latter case, where polymerisation followed by gelation takes place. There is absorption of oxygen in both cases. P. M.

**Equilibrium between Lactic Acid and its Anhydrides.** G. I. THURMOND and G. EDGAR (*Ind. Eng. Chem.*, 1924, 16, 823—826).—In a mixture of lactic acid, lactic anhydride, and lactide, the free acid is determined by direct titration of an alcoholic solution of the mixture with 0.3*N*-sodium hydroxide, and the total of the three constituents by the consumption of alkali when the mixture is heated for 15 mins. with excess of the reagent. When warmed in alcoholic solution with zinc carbonate, the free acid and anhydride are precipitated as zinc lactate, the unattacked lactide being then determined in the evaporated and filtered solution by warming with excess of standard alkali, adding a known excess of standard acid and a little potassium ferrocyanide to precipitate the last traces of zinc, and titrating back. The presence of zinc interferes with the end-point of this titration, and the amount of zinc held in solution varies with the amount of lactide present. Lactic acid, lactide, and water form an equilibrium mixture, the position of the equilibrium being the same at 155°, for which  $C_{\text{lactide}} \times C_{\text{H}_2\text{O}}^2 / C_{\text{acid}}^2 = 0.0567$ . Anhydride is present in such mixtures in amount varying with the previous history of the sample, and not depending on the amount of water present, an effect ascribed to the colloidal nature of the anhydride. F. G. W.

**Spontaneous Oxidation of Lactic Esters and Alanine in Presence and in Absence of Catalysts.** L. J. SIMON and L. PIAUX (*Bull. Soc. Chim. biol.*, 1924, 6, 412—423).—Lactic esters

are oxidised spontaneously in contact with air or oxygen with the formation of acetaldehyde, ethyl pyruvate, and carbon dioxide. The oxidation is accelerated by warming and agitation, but it is not influenced by light. Alanine, on the other hand, is not spontaneously oxidised except in the presence of sodium hydroxide and finely-divided metallic copper, when it gives rise to pyruvic acid and acetaldehyde. If pyruvates in alkaline solution are agitated in presence of oxygen, a decrease in the quantity of pyruvic acid is observed. The production of pyruvic acid does not necessarily precede the formation of acetaldehyde, which may be derived from  $\alpha$ -hydroxyacrylic acid.

D. R. N.

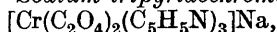
**Synthesis of Oxalic Acid.** C. MATIGNON and C. FAURHOLT (*Compt. rend.*, 1924, 179, 271—274).—The synthesis of potassium oxalate by the action of carbon monoxide under pressure on potassium carbonate is described. The reverse action, viz., the decomposition of the oxalate in a vacuum, is observed at  $370^{\circ}$ , is distinct at  $420^{\circ}$ , and reaches a practicable velocity at  $430$ — $440^{\circ}$ ; for the synthesis it is therefore necessary to employ at least this temperature and a pressure of carbon monoxide greater than that calculated either by the  $Q/T$  relation or the Nernst formula from the equation  $\text{CO} + \text{K}_2\text{CO}_3 = \text{K}_2\text{C}_2\text{O}_4 + 19.8$  cals. At the necessary temperature in the absence of catalysts, the decomposition of the carbon monoxide into carbon dioxide is negligibly small, so that at  $470^{\circ}$  and with a pressure of 243 atm. of carbon monoxide, potassium carbonate to which is added 2.5% of animal charcoal as a catalyst, is converted in  $2\frac{1}{2}$  hours into a product containing 29% (optimum) of potassium oxalate. Under the same conditions, but in the absence of animal charcoal, the yield is only 9.7%. No oxalate is produced under similar conditions using sodium carbonate, since the thermal effect necessitates the use of a much higher pressure.

J. W. B.

**Complex Compounds of Chromium and Cobalt with Aliphatic and Aromatic Amines. IV. Stereochemistry of Saturated Tervalent Nitrogen.** J. MEISENHEIMER (*Annalen*, 1924, 438, 217—278).—[With L. ANGERMANN and H. HOLSTEN].—*Pyridochromidioxalates*. *trans*-Pyridinium diaquochromidioxalate,  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]\text{H}_5\text{C}_5\text{H}_5\text{N}$ , (I), fine, lilac crystals, is obtained by double decomposition of the sodium salt with pyridinium nitrate, the *cis* salt being present in the mother-liquors. The *cis* salts of this series are transformed into the *trans* salts in dilute hydrochloric acid solution, the reverse change being brought about by dilute alkalis. Compound (I) is converted into *trans*-pyridinium mono-aquomonopyridochromidioxalate,  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})\text{Py}]\text{H}_5\text{C}_5\text{H}_5\text{N}$ , reddish-violet crystals, by the action of cold aqueous pyridine, the *cis* isomeride being obtained if excess of pyridine, with only a trace of water, is used. The *dipyridochromidioxalates*,  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{C}_5\text{H}_5\text{N})_2]$ , are obtained from the diaquo salts when the latter are boiled with pyridine, *cis-trans* isomerism not being observed in this series, the following members of which are described: *potassium*, pale rose needles ( $+3\text{H}_2\text{O}$ ) or octahedra ( $+2\text{H}_2\text{O}$ ); *pyridinium* ( $+2\frac{1}{2}\text{H}_2\text{O}$ );

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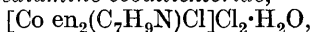
sodium (+1H<sub>2</sub>O); barium and calcium (+6H<sub>2</sub>O); cinchonine, and strychnine salts. Sodium tripyridochromidioxalate,



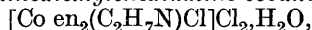
bluish-red, cubic crystals (anhydrous) or prisms (+3½H<sub>2</sub>O), is obtained by boiling the dried diaquo salts with anhydrous pyridine. The complex aniline and cinchonine salts are described.

*Dimethylethylenediaminechromidioxalates.* Ethylene di-*p*-toluenesulphonamide, prisms, m. p. 162—163°, was treated with methyl sulphate and sodium hydroxide to form ethylene di-*p*-toluenesulphonmethylamide, needles, m. p. 167—168°, the latter yielding dimethylethylenediamine on hydrolysis with 70% sulphuric acid. Potassium dimethylethylenediaminechromidioxalate was isolated in the form of a double salt with potassium iodide,  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{C}_4\text{H}_{12}\text{N}_2]\text{K}, \text{KI}, 2\text{H}_2\text{O}$ , small, dark red crystals, by the action of the base on an aqueous solution of *cis* potassium diaquochromidioxalate at 70°, potassium iodide being added when reaction was complete. The potassium nitrate double salt,  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{C}_4\text{H}_{12}\text{N}_2]\text{K}, \text{KNO}_3, 2\text{H}_2\text{O}$ , dark red plates or prisms, the silver salt,  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{C}_4\text{H}_{12}\text{N}_2]\text{Ag}, \text{H}_2\text{O}$ , bluish-red plates, and the strychnine salt, bluish-red needles, are described.

[With E. KIDERLEN.]—Chloroaminediethylenediaminecobalti salts. Praseo-dichloroethylenediaminecobalti salts react in cold aqueous solution with primary aliphatic and aromatic amines, one of the inner halogen atoms being replaced by the amine. The violeo salts yield identical products, but the reaction is much slower. Chloroanilinediethylenediaminecobaltichloride,  $[\text{Co en}_2, \text{Ph} \cdot \text{NH}_2, \text{Cl}]\text{Cl}_2, \text{H}_2\text{O}$ , reddish-violet, hexagonal prisms; bromide (+½H<sub>2</sub>O), similar; iodide, chloride-dithionate, violet-pink prisms; nitrate, dark red crystals; chloride-nitrate, violet-pink needles; and d- $\pi$ -bromocamphorsulphonate are described. The *p*-toluidine derivatives of this series decompose more readily than those of aniline. Chloro-*p*-toluidine diethylenediaminecobaltichloride (+H<sub>2</sub>O), bromide (+H<sub>2</sub>O), iodide, dithionate, chloride-nitrate, and d- $\pi$ -bromocamphorsulphonate are described. The tendency of primary amines to enter the complex ion increases with increasing basicity, aliphatic amines reacting more rapidly than aromatic. Chloroallylamine diethylenediaminecobaltichloride,  $[\text{Co en}_2(\text{C}_3\text{H}_7\text{N})\text{Cl}]\text{Cl}_2, \text{H}_2\text{O}$ , bromide, iodide, dithionate, and d- $\pi$ -bromocamphorsulphonate (+2H<sub>2</sub>O), are described. The latter could not be resolved by fractional crystallisation. Chlorobenzylaminediethylenediaminecobaltichloride,

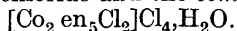


violet-red needles (anhydrous, lustrous pink plates), bromide (+½H<sub>2</sub>O), iodide, chloride-dithionate, nitrate, and d- $\pi$ -bromocamphorsulphonate, m. p. 183—185° (decomp.), are described. The latter was separated into the inactive (*trans*) form and *d*- and *l*-(*cis*) forms. Chloro-ethylaminediethylenediaminecobaltichloride,

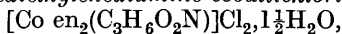


and iodide (anhydrous) were also prepared. The action of benzylamine and ethylamine on the violeo salts yields hydroxo-aquo salts. Diethylamine and methylbenzylamine react with praseochloride with formation of transchlorohydroxodiethylenediaminecobaltichloride,  $[\text{Co en}_2(\text{OH})\text{Cl}]\text{Cl}, \text{H}_2\text{O}$ , dove-grey crystals (an-

hydrous, paler and greenish). This yields, on solution in hydrochloric acid, *transchloroaquodithylenediamine cobaltchloride*,  $[\text{Co en}_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , dirty, greyish-green needles; on warming with aqueous potassium bromide, *hydroxaquodithylenediamine cobaltbromide*,  $[\text{Co en}_2(\text{OH})(\text{H}_2\text{O})]\text{Br}_2$ ; and on precipitation from warm aqueous solution with alcohol, *diaquodithylenediamine cobaltchloride*,  $[\text{Co en}_2(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ , short, red, hexagonal prisms. Dimethylethylenediamine converts the *praseo-chloride* into triethylenediamine cobaltchloride, whilst methylaniline converts it into the *violet-chloride* and the *complex salt*,



[With L. ANGERMANN and H. HOLSTEN.]—*Glycine and sarcosine diethylenediamine cobalti salts*. *Glycinediethylenediamine cobaltchloride*,  $[\text{Co en}_2(\text{C}_2\text{H}_4\text{O}_2\text{N})]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , yellowish-red prisms, is obtained by the action of glycine on *praseo-chloride* in presence of sodium carbonate. The *d-π-bromocamphorsulphonate*, thick red prisms, yields the *l-complex d-bromocamphorsulphonate* on repeated crystallisation from alcohol and water. The *l-iodide* and *l-dithionate* are described; *Sarcosinediethylenediamine cobaltchloride*,



strawberry-red plates, is obtained similarly, using sodium hydroxide in place of the carbonate. The *iodide* ( $+1\text{H}_2\text{O}$ ) and *dithionate* ( $+1\text{H}_2\text{O}$ ) were also prepared. The *d-bromocamphorsulphonate* forms pale red needles or garnet-red prisms containing alcohol and water of crystallisation, or pink needles of the heptahydrate. The latter can be obtained in two forms of  $[M]_D -923^\circ$  and  $+2020^\circ$ , respectively, the optical activity of the complex ion being due to the cobalt atom alone, the asymmetric nitrogen atom of the sarcosine being inactive. When the mother-liquors from the above salts were concentrated, a *tetrahydrate* separated as a pale red powder, the freshly prepared solution of which had  $[M]_D +2290^\circ$ , the value rapidly falling to  $+2020^\circ$ , the increased activity being due to the nitrogen atom. The remaining isomerides were only obtained in an impure condition. The *d- and l-iodides* ( $+1\frac{1}{2}\text{H}_2\text{O}$ ), red prisms,  $[M]_D +1485^\circ$  and  $-1530^\circ$ , and *dithionates* ( $+1\frac{1}{2}\text{H}_2\text{O}$ ),  $[M]_D +1530^\circ$  and  $-1555^\circ$ , are described. The action of phenylglycine, *o*-carboxyphenylglycine, and anthranilic acid on the *praseo-chloride* did not proceed analogously to that of the above bases. F. G. W.

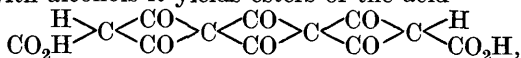
**Ethyl-*n*-hexylbarbituric Acid and other Derivatives of *n*-Hexylmalonic Acid.** A. W. Dox (*J. Amer. Chem. Soc.*, 1924, 46, 1707—1711).—*n*-Hexyl bromide condenses with ethyl malonate in the presence of sodium ethoxide, giving *ethyl n-hexylmalonate*, b. p.  $268-270^\circ/749$  mm., from which *n-hexylmalonic acid*, m. p.  $105-106^\circ$  (*amide*, m. p.  $208^\circ$ , *anilide*, m. p.  $156^\circ$ ), is obtained by hydrolysis with potassium hydroxide. On heating with carbamide and sodium ethoxide at  $104^\circ$ , ethyl hexylmalonate yields *n-hexylbarbituric acid*, m. p.  $216^\circ$ . Methylcarbamide similarly yields *1-methyl-5-n-hexylbarbituric acid*, m. p.  $68^\circ$ . *1-Phenyl-5-n-hexylbarbituric acid*, m. p.  $141^\circ$ , and *1-o-tolyl-n-hexylbarbituric acid*, m. p.  $118^\circ$ , were similarly prepared. *Ethyl ethyl-n-hexylmalonate*,

b. p. 280—282°/755 mm., from ethyl ethylmalonate and hexyl bromide, yields *ethyl-n-hexylmalonic acid*, m. p. 75°, decomp. at 140°. The ester is converted by carbamide and sodium ethoxide into *ethyl-n-hexylbarbituric acid*, small, white crystals, in 96% of the theoretical yield. Ethyl-*n*-hexylbarbituric acid is a somewhat more effective hypnotic than "luminal," being more rapid in its action and less toxic, although the effect is of shorter duration. 1-Methyl-5-hexylbarbituric acid is inert and 1-phenyl-5-hexylbarbituric acid is toxic without hypnotic action. R. B.

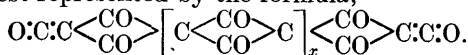
**Carbon Suboxide.** O. DIELS, R. BECKMANN, and G. TÖNNIES (*Annalen*, 1924, **439**, 76—96).—Carbon suboxide was prepared by a modification of the method of Ott and Schmidt (cf. A., 1922, ii, 641) which increased the yield from 40 to 55—60%. The hypothesis of Ott and Schmidt that the lack of stability of carbon suboxide, prepared by means of phosphoric oxide, is due to the presence of phosphorus compounds is shown to be incorrect, since specimens prepared from diacetyltartaric anhydride were found to polymerise as rapidly as those obtained by the older method, the stability of Ott and Schmidt's specimens more probably being due to the careful removal of other substances, *e.g.*, acetic acid. By the action of carbon suboxide on acetic acid, a product is obtained which, by loss of acetic anhydride, yields not malonic anhydride as previously suggested (cf. A., 1908, i, 929), but a *mixed anhydride* of acetic and malonic acids,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{OAc}$ . With oxalic acid in acetone solution, carbon suboxide yields the  $\beta$ -lactone of  $\beta$ -hydroxyisopropylmalonic acid (cf. Meldrum, T., 1908, **93**, 601), carbon dioxide and carbon monoxide also being evolved. Malonic acid in ether or ethyl acetate solutions reacts with 3 mols. of carbon suboxide, probably first to yield a mixed anhydride of keten character, which then reacts with the remaining 2 mols. of the suboxide to yield an exceedingly hygroscopic, yellow *substance* (decomp. 60°) to which the formula

$$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{OC}\begin{matrix} \text{H} \\ \diagup \end{matrix}\text{C}\begin{matrix} \text{CO} \\ \diagdown \end{matrix}\text{C}\begin{matrix} \text{CO} \\ \diagdown \end{matrix}\text{C}\begin{matrix} \text{CO} \\ \diagdown \end{matrix}\text{C}\begin{matrix} \text{CO} \\ \diagdown \end{matrix}\text{C}\begin{matrix} \text{H} \\ \diagup \end{matrix}\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$$

is given. It reacts with water, yielding carbon dioxide and malonic acid and with alcohols it yields esters of the acid



together with the corresponding dialkyl esters of malonic acid and acetonedicarboxylic acid (the latter by profound alcoholysis); the *methyl*, m. p. 183·5° (decomp.); *ethyl*, m. p. 150—151° (decomp.); *propyl*, m. p. 132—133°, esters are described. Molecular-weight determinations agree with the suggested formula, and hence the constitution of the corresponding red polymeride of carbon suboxide is probably best represented by the formula,



The reaction of carbon suboxide with hydrogen sulphide depends largely on the proportions of the reactants employed. With excess of hydrogen sulphide, thioacetic acid and carbonyl sulphide are formed, dithiomalonic acid probably being an intermediate product.

In equimolecular proportion, the reaction yields *bi(?)molecular malonic thioanhydride*,  $\text{H}_2\text{C} \begin{smallmatrix} \text{CO} \cdot \text{S} \cdot \text{CO} \\ \text{CO} \cdot \text{S} \cdot \text{CO} \end{smallmatrix} \text{CH}_2$ , m. p. 120—125°, its very slight solubility in all solvents precluding the determination of its molecular weight. With ammonia, it yields the *ammonium* salt of *thiomalonamic acid*, but with aniline yields only malonanilide, hydrogen sulphide being evolved. Heating in a high vacuum at 200° yields carbonyl sulphide and thioacetic acid. Thermal decomposition in the presence of phosphoric oxide yields carbon suboxide, hydrogen sulphide, carbonyl sulphide, carbon subsulphide, and the *unimolecular malonic thioanhydride*,  $\text{CH}_2 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{S}$ , dark golden, very unstable crystals, m. p. 60°. It has a distinct acid character and reacts with dimethylaniline in dry benzene with evolution of heat, and is therefore probably *ketenthiocarbonic acid*,  $\text{CO} \cdot \text{CH} \cdot \text{CO} \cdot \text{SH}$ . With water, much heat is evolved and malonic acid is formed with evolution of hydrogen sulphide, but if the mixture be kept cool in ice no hydrogen sulphide is formed and *monothiomalonic acid*, a crystalline compound, is produced. This on heating with water yields malonic acid and hydrogen sulphide.  
J. W. B.

**Configuration of  $\alpha\alpha'$ -Dibromodibasic Acids. II. Derivatives of Adipic Acid.** A. W. BERTON, H. R. ING, and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1924, 125, 1492—1502).—Isomeric ethyl and methyl  $\alpha\alpha'$ -dibromoadipates have been prepared and condensed with ethyl sodiomalonate and similar compounds to form *cyclopentanes*. Further evidence is adduced in support of the contention (cf. T., 1921, 119, 1393) that the  $\alpha\alpha'$ -dibromoadipic acid of m. p. 193° is the *dl*- or racemic modification and that of m. p. 139° the *meso*-isomeride. The liquid isomeride of ethyl  $\alpha\alpha'$ -dibromoadipate on condensation with ethyl sodiomalonate yielded ethyl *cyclopentane*-1 : 2 : 2 : 3-tetracarboxylate, which on hydrolysis gave a solid, m. p. 184°, identical with the *cyclopentane*-1 : 2 : 3-tricarboxylic acid obtained by Perkin and Robinson (*loc. cit.*) from the solid isomeride. The tribasic acid when treated successively with thionyl chloride and concentrated ammonia gave the *triamide*, m. p. 274°. The solid and liquid isomerides of methyl dibromoadipate on condensation with ethyl sodiomalonate formed (in each case) *methyl cyclopentane*-1 : 2 : 2 : 3-tetracarboxylate, m. p. 82—84°. Hydrolysis with methyl-alcoholic potassium hydroxide gave *trans*- (m. p. 184°), and with boiling hydrochloric acid a mixture (m. p. ca. 154°) of *cis*- and *trans*-*cyclopentanetricarboxylic acids*. *Ethyl 2-acetylcyclopentane*-1 : 2 : 3-tricarboxylate, b. p. 181—190°/16 mm., was obtained on condensing the solid isomeride of ethyl dibromoadipate with ethyl sodioacetoacetate; on hydrolysis, it yielded *trans*-*cyclopentane*-1 : 2 : 3-tricarboxylic acid. Ethyl sodiobenzoylacetate and the solid isomeride yielded *ethyl 2-benzoyl cyclopentane*-1 : 2 : 3-tricarboxylate, an oil, b. p. 235—242°/14 mm.; hydrolysis with cold methyl-alcoholic potassium hydroxide gave the *trans*-*cyclopentane*-1 : 2 : 3-tricarboxylate (the benzoyl group hav-



ing been eliminated); the liquid isomeride gave the same products. Both isomerides of methyl  $\alpha\alpha'$ -dibromoadipate react with methyl sodiocyanoacetate to form methyl 2-cyanocyclopentane-1:2:3-tricarboxylate, rhombic prisms, m. p. 83—84°, b. p. 192—196°/12 mm. Cold concentrated hydrochloric acid converts this into the dimethyl cyclopentanetetracarboxylate, m. p. 115°. With boiling acid, a mixture of the *cis* and *trans* forms of the cyclopentane-1:2:3-tricarboxylic acid was obtained. The liquid isomeride of methyl  $\alpha\alpha'$ -dibromoadipate (cf. Stephen and Weizmann, T., 1913, **103**, 271), b. p. 169—170°/14 mm., is converted to the extent of about 50% into the higher melting isomeride during distillation; the change takes place very gradually at the ordinary temperature. The liquid isomeride of ethyl dibromoadipate behaves similarly, but the conversion is more rapid. Sodium ethoxide or methoxide readily brings about the transformation. Two isomeric methyl  $\alpha\alpha'$ -di-iodoadipates, m. p. 63° and 112°, respectively, were prepared by boiling the dibromo compounds with sodium iodide in methyl-alcoholic solution. The former was almost immediately changed to the latter variety when its solution in methyl alcohol was shaken with 2 mols. of sodium methoxide. Potassium hydroxide in alcohol acts equally well, but the change was much more gradual in the presence of alcoholic ammonia. The di-iodo ethyl esters interacted much less readily with ethyl sodiomalonate than the corresponding dibromo esters. Prolonged boiling of the low-melting isomeride of methyl di-iodoadipate with methyl sodiocyanoacetate gave a small yield of methyl 2-cyanocyclopentane-1:2:3-tricarboxylate, and the methyl di-iodoadipate which was recovered had been transformed into a variety of high m. p. The diamide of  $\alpha\alpha'$ -di-iodoadipic acid, m. p. 238° (decomp.), was obtained by the action of concentrated methyl-alcoholic ammonia on methyl di-iodoadipate. Both isomerides of methyl dibromoadipate gave the diamide of  $\alpha\alpha'$ -dibromoadipic acid, m. p. 196°. A. C.

**Compounds of Malic Acid and Copper.** E. DARMOIS (*Compt. rend.*, 1924, **178**, 1981—1983).—Addition of copper hydroxide to solutions of malic acid resulted in formation of two well-defined salts,  $\text{Cu}(\text{C}_4\text{H}_4\text{O}_5)_2 \cdot 2\text{H}_2\text{O}$ , sky-blue crystals, and  $3\text{CuO} \cdot 2\text{C}_4\text{H}_6\text{O}_5 \cdot 4\text{H}_2\text{O}$ ,

green crystals. In the attempt to obtain other salts, some physical properties of the solutions obtained by adding various proportions of copper hydroxide to malic acid were studied, and details of the values obtained are given. H. J. E.

**Rotatory Dispersive Power of Organic Compounds. XI. Molecular Weight of Ethyl Tartrate and the Origin of Anomalous Rotatory Dispersion in Tartaric Acid and its Derivatives.** T. M. LOWRY and J. O. CUTTER (*J. Chem. Soc.*, 1924, **125**, 1465—1470).—Measurements of molecular weight and optical rotation of ethyl tartrate in various solvents did not show any parallelism between the rotation and the degree of association of the solute. The authors therefore criticise the suggestion of

Astbury (A., 1923, i, 178) that the dextrorotatory component of tartaric acid is a single molecule, whilst the levorotatory component is a polymeride in which the structure of the crystal is in part maintained. Anomalous rotatory dispersion is ascribed to intramolecular changes. S. B.

**Optical Superposition. V. *d*-sec.-Octyl *i*-Tartrate.** T. S. PATTERSON and C. BUCHANAN (*J. Chem. Soc.*, 1924, 125, 1475—1476).—*d*-sec.-Octyl *i*-tartrate has b. p.  $208^{\circ}$ /about 4 mm., m. p.  $33^{\circ}$ ,  $[\alpha]_D^{25} +0.42^{\circ}$ . This value of the specific rotation is in contradiction to the principle of optical superposition. S. B.

**Dithioformic Acid.** T. G. LEVI (*Gazzetta*, 1924, 54, 395—397).—From potassium dithioformate solution, prepared by the action of potassium sulphide on chloroform (cf. Cambi, *R. Ist. Lomb. Sci. Lett.*, 1910, 43, II), the corresponding silver,  $\text{H}\cdot\text{CS}_2\cdot\text{Ag}$ , and lead salts may be obtained as comparatively stable, orange-yellow precipitates; the former begins to darken at  $95$ — $100^{\circ}$  and the latter at  $130$ — $135^{\circ}$ . The zinc salt is yellowish-white and the cobalt salt, deep reddish-brown. The disulphide,  $(\text{H}\cdot\text{CS}_2\cdot\text{CS}_2\cdot\text{H})_x$ , obtained on cautious addition of alcoholic iodine solution to potassium dithioformate dissolved in alcohol, forms a reddish-yellow precipitate, decomp. above  $200^{\circ}$ . T. H. P.

**Preparation of Thioacetic Acid.** H. T. CLARKE and W. W. HARTMAN (*J. Amer. Chem. Soc.*, 1924, 46, 1731—1733).—Acetic anhydride or acetyl chloride alone does not react with hydrogen sulphide, but on passing the gas into acetic anhydride containing about 2% of acetyl chloride absorption takes place to the extent of 80% of the quantity calculated on the equation:  $(\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{S} = \text{Me}\cdot\text{CO}\cdot\text{SH} + \text{Me}\cdot\text{CO}_2\text{H}$ , and a 70% yield of thioacetic acid, b. p.  $88$ — $91.5^{\circ}$ , is obtained. Hydrogen chloride and concentrated sulphuric acid also catalyse the reaction, the latter acid also tending to oxidise the hydrogen sulphide, but acetyl bromide is a more effective catalyst than acetyl chloride (cf. Orton, Watson, and Bayliss, T., 1923, 123, 3081). The reaction proceeds in two stages, the first of which (20—30% absorption) requires only one-tenth of the amount of catalyst required for completion of the reaction. R. B.

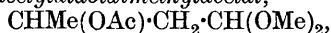
**Sulphide Acids. II. *iso*Butyl Ether of Thioglycollic Acid [*iso*Butylthiolacetic Acid].** Y. UYEDA and J. KAMON (*J. Chem. Soc. Japan*, 1923, 44, 1061—1070).—*iso*Butylthiolacetic acid,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , a pale yellow liquid, b. p.  $244^{\circ}$ ,  $d^{25}_4$  1.0685,  $n^{25}_D$  1.4750, is obtained by boiling a solution of the sodium salt of *isobutyl* mercaptan with sodium chloroacetate. The strontium ( $+1.5\text{H}_2\text{O}$ ), nickel ( $+2\text{H}_2\text{O}$ ), cobalt ( $+2\text{H}_2\text{O}$ ), cadmium ( $+ \text{H}_2\text{O}$ ), copper ( $+2\text{H}_2\text{O}$ ), and silver salts are described. It gives a chloride, b. p.  $104$ — $105^{\circ}$ /13—15 mm.,  $d^{25}_4$  1.1034,  $n^{25}_D$  1.4780; an amide, m. p.  $49^{\circ}$ ; an ethyl ester, b. p.  $209^{\circ}$ ,  $d^{25}_4$  0.9848,  $n^{25}_D$  1.4550; a propyl ester, b. p.  $228^{\circ}$ ,  $d^{25}_4$  0.9648,  $n^{25}_D$  1.4550; an *isobutyl* ester,

b. p. 234°,  $d_4^{25}$  0.9526,  $n_D^{25}$  1.4530; and a *butyl* ester, b. p. 245°,  $d_4^{25}$  0.9577,  $n_D^{25}$  1.4515. K. K.

**Catalytic Action. VII. Catalytic Action of Reduced Copper on Acetaldehyde.** S. KOMATSU and M. KURATA (*Mem. Coll. Sci. Kyoto*, 1924, 7, 293—295).—Acetaldehyde, when passed over reduced copper heated at 300°, is partly converted into crotonaldehyde, paraldehyde, and metaldehyde. F. G. M.

**Polymerisation of Aldols.** M. BERGMANN and E. KANN (*Annalen*, 1924, 438, 278—293).—*Acetylcycloaldol* (*paraldol di-*

*acetate*),  $\text{CH}_3\text{—}\overset{\text{O}}{\text{—CH—CH}_2\text{—CH—OAc}}$ , b. p. 156—158°/12 mm.,  $n_D^{20}$  1.4425,  $d_4^{20}$  1.100, is obtained by the action of cold acetic anhydride on acetaldo in presence of pyridine. It remains associated to the bimolecular form in benzene, phenol, or glacial acetic acid, but the vapour dissociates gradually at 140° and rapidly at 180°. It does not react with methyl orthoformate, but yields a colourless, viscous *oxime*, b. p. 120—122°/12 mm.,  $n_D^{20}$  1.4500. Aldoldimethylacetal affords, similarly, *acetyldimethylacetal*,



b. p. 84—86°/13 mm., which is hydrolysed by cold N/1-sulphuric acid to *γ-acetoxy-n-butaldehyde*, sour-smelling, mobile liquid, b. p. 72—76°/12 mm. The latter reacts with methyl orthoformate, yielding the dimethylacetal again, and forms the same *oxime* as the above *acetylcycloaldol*. The dimethylacetal is also obtained by the action of methyl orthoformate on *paraldol*. *Hydracetylacetone monoacetate*, b. p. 84°/12 mm. (*phenylhydrazone*, hexagonal plates, m. p. 115°); *acetopropyl acetate*,  $\text{CH}_3\text{·CO·CH}_2\text{·CH}_2\text{·CH}_2\text{·OAc}$ , b. p. 91°/12 mm.,  $n_D^{14}$  2.4295,  $d_4^{14}$  1.0186; and *acetobutyl acetate*, b. p. 114—116°/12 mm.,  $n_D^{13.5}$  1.4336,  $d_4^{13.5}$  1.002, none of which is associated in solution, are described. *γ-Methylglucoside*, tetra-methyl-*γ-methylglucoside*, *tetra-acetyl-γ-methylglucoside*, a pale yellow syrup, b. p. 156°/0.3 mm., and tetra-acetyl-*β-methylglucoside* are unimolecular in solution. The tendency to polymerisation of the aldol *cycloacetates* is ascribed to the unsaturated affinity of the bridge-oxygen, and is greater the nearer the two carbon atoms thereby connected. F. G. W.

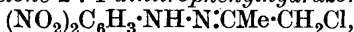
#### Action of Calcium Hydride on certain Organic Compounds.

**I. Acetone.** C. PORLEZZA and U. GATTI (*Gazzetta*, 1924, 54, 491—509).—The condensation of acetone in presence of calcium hydride yields *α-* and *β-isoxylitones* (cf. Knoevenagel and Blach, A., 1906, i, 964; Knoevenagel and Beer, *ibid.*) and other apparently analogous compounds. In presence of calcium or its oxide, acetone undergoes a condensation which is similar, at least qualitatively, to that effected by the hydride, but the latter acts more energetically in this respect. Under no conditions was it found possible to obtain the compound, b. p. 226—236°, described by Reich and Serpek (A., 1920, i, 249). T. H. P.

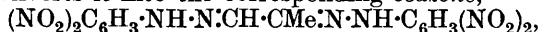
#### Reactions of Chloroacetone 2 : 4-Dinitrophenylhydrazones.

C. BÜLOW and F. SEIDEL (*Annalen*, 1924, 439, 48—58).—The con-

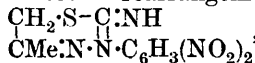
condensation of chloroacetone with 2:4-dinitrophenylhydrazine at first gives *chloroacetone 2:4-dinitrophenylhydrazone*,



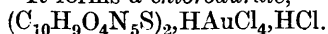
yellow needles, m. p. 124—125.5°. Prolonged boiling in alcoholic solution converts it into the corresponding *osazone*,



m. p. 298°. The chlorine atom of the hydrazone has a greatly increased reactivity and reacts with a large number of amines. One mol. of ammonia condenses with 2 mols. of the phenylhydrazone to yield the *imine*,  $\text{NH}[\text{CH}_2\cdot\text{CMe}\cdot\text{NR}]_2$ , where R is the hydrazone residue, m. p. 215°, and methylamine yields the corresponding *methylimine*, microscopic yellow needles, m. p. 222°. Camphylamine yields a *camphylimino* derivative, m. p. 184—185°, pyridine a quaternary *pyridinium* salt,  $\text{CMe}\cdot\text{NR}\cdot\text{CH}_2\cdot\text{NC}_5\text{H}_5\text{Cl}$ , greenish-yellow, becoming red at 180—190°, m. p. 201—203°. Piperidine yields a *tertiary base*, m. p. 200° (decomp.), whilst quinoline yields a *compound* analogous to that obtained with pyridine, but which retains 1 mol. of water of crystallisation very tenaciously and is isolated as the *osazone*, m. p. 295° (much decomp.). The action of phenylhydrazine on chloroacetone 2:4-dinitrophenylhydrazone yields the *mixed osazone*, carmine-red needles, m. p. 232°. By the action of sodium acetate in alcoholic solution on chloroacetone 2:4-dinitrophenylhydrazone, the corresponding *phenylhydrazone of acetonyl acetate* (cf. Henry, A., 1873, 379), long, flat, yellow tablets, m. p. 106—107°, is obtained, whilst by the action of potassium thiocyanate the corresponding *thiocyanoacetone 2:4-dinitrophenylhydrazone*, golden, iridescent crystals, m. p. 127—128°, is formed. By intramolecular rearrangement this compound forms a cyclic compound,



as its *hydrochloride*. It forms a *chloroaurate*,



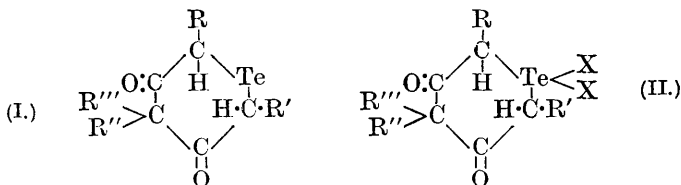
With potassium xanthate in the cold, chloroacetone 2:4-dinitrophenylhydrazone forms a *xanthate*,  $\text{CMe}(\cdot\text{NR})\cdot\text{CH}_2\cdot\text{S}\cdot\text{CS}\cdot\text{OEt}$ , fine needles, m. p. 77—78° (cf. this vol., i, 573). J. W. B.

**Special Examples of Grignard's Reaction.** H. GOUDET and H. PAILLARD.—(See i, 1055.)

**Dehydration of some new Pinacones.** R. LOCQUIN and L. LEERS (*Compt. rend.*, 1924, 178, 2095—2098).—Dehydration of a series of pinacones, as in the case of those already studied (Meerwein, A., 1913, i, 485; Locquin and Sung, this vol., i, 613), results in formation only of  $\text{CRMe}_2\cdot\text{CO}\cdot\text{Me}$  from  $\text{CRMe}(\text{OH})\cdot\text{CMe}_2\cdot\text{OH}$ ; the alternative transformation into  $\text{CMe}_2\cdot\text{CO}\cdot\text{R}$  does not appear to occur. This was shown both by oxidation of the resulting ketone to the corresponding acid and by comparison with the latter type of ketone prepared by condensation of pivaloyl chloride with organo-zinc compounds of the type  $\text{R}\cdot\text{Zn}\cdot\text{I}$ . The following are described:  $\gamma\gamma$ -Dimethylhexan- $\beta$ -one, b. p. 149°/745 mm.,  $d_4^{20}$  0.838, semicarbazone, m. p. 119.5°, oxime, m. p. 58°, b. p. 100—101°/12 mm.;

$\alpha\alpha$ -dimethylpentoic acid, b. p. 98—99°/9 mm., chloride, b. p. 45°/10 mm., methyl ester, b. p. 144—145°;  $\beta\gamma$ -dimethylheptane- $\beta\gamma$ -diol,  $\gamma\gamma$ -dimethylheptan- $\beta$ -one, b. p. 169·5°/735 mm.,  $d_4^{25}$  0·834, semicarbazone, m. p. 130—131°;  $\alpha\alpha$ -dimethylhexoyl chloride, b. p. 56°/10 mm., amide, m. p. 92°;  $\beta\beta$ -dimethylheptan- $\gamma$ -one, b. p. 164°/735 mm.,  $d_4^{25}$  0·823, semicarbazone, m. p. 142—143°;  $\gamma\gamma$ -dimethyloctan- $\beta$ -one, b. p. 75°/10 mm.,  $d_4^{25}$  0·843, semicarbazone, m. p. 106°;  $\alpha\alpha$ -dimethylheptoic acid, b. p. 130°/12 mm., chloride, b. p. 74—75°/10 mm., amide, m. p. 101—102°;  $\beta\beta$ -dimethyloctan- $\gamma$ -one, b. p. 72°/10 mm.,  $d_4^{25}$  0·834, semicarbazone, m. p. 139—140°. H. J. E.

**cycloTelluropentanediones and cycloTelluripentanedione Dihalides.** G. T. MORGAN and H. D. K. DREW (*J. Chem. Soc.*, 1924, 125, 1601—1607).—The behaviour of a series of tellurium  $\beta$ -diketones towards hydroxylamine shows that these compounds are diketonic in structure, since they yield dioximes as well as monoximes. It is concluded that the cyclic tellurium  $\beta$ -diketones and their corresponding dihalides belong to two new types of cyclic organometalloidal compounds, that represented by (I) being



designated cyclotelluropentane-3:5-diones and (II) cyclotelluripentane-3:5-dione-1:1-dihalides; X may be Cl, Br, or I, and R, R', etc. may stand for hydrogen atoms or similar or dissimilar alkyl or arylalkyl (*e.g.*, benzyl) groups, but not for phenyl or other purely aromatic groups. cycloTelluri-4:4-dimethylpentane-3:5-dione-1:1-dichloride, m. p. 194°, prepared by refluxing a chloroform solution of dimethylacetylacetone with tellurium tetrachloride, was converted by aqueous potassium metabisulphite into cyclotelluro-4:4-dimethylpentane-3:5-dione, m. p. 124—125°. Oximation of tellurium acetylacetone gave cyclotelluropentane-3:5-dionedioxime, m. p. indefinite; similarly, tellurium ethyl acetylacetone yielded cyclotelluro-4-ethylpentane-3:5-dionedioxime (decomp. 192° after darkening at 173°). Steric hindrance manifests itself as substitution proceeds, monoximes being formed when oximation is conducted in presence of dilute acetic acid, and dioximes under more drastic conditions in alkaline solution. cycloTelluro-4:4-dimethylpentane-3:5-dione-5-monoxime has m. p. 183—184° or 180° when crystallised from benzene or alcohol, respectively; the corresponding dioxime decomposes at 235°. cycloTelluro-2:4-dimethylpentane-3:5-dione-5-monoxime and the corresponding dioxime decompose respectively at 168° and 198°.

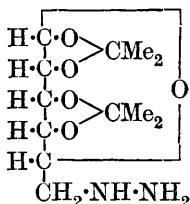
Derivatives of tellurium *n*-butyrylacetone exhibit isomerism of the Hantzsch-Werner type and two isomeric dioximes have been isolated which are provisionally designated as  $\alpha$ - and  $\beta$ -forms, and

may have respectively the *syn*- and *anti*-configurations.  $\alpha$ -cyclo-Telluro-2-ethylpentane-3:5-dionedioxime, m. p. 149°, and its  $\beta$ -isomeride, m. p. 183°, are produced in the ratio of 5 : 1 by oximation in alkaline solution.

Three dynamic isomerides of  $\beta$ -diketones exist as evidenced by the interaction of acetylacetone and its homologues with metallic compounds and selenium and tellurium tetrachlorides. (1) A *trans*-monoenolic form reacts in the case of the formation of derivatives of Cu, B, Si, Ge, Ti, Sn, and Zr. (2) A *cis*-monoenolic form takes part in condensation with  $\text{SeCl}_4$ . (3) A diketonic form interacts with  $\text{TeCl}_4$  to form a six-membered ring in which enolisation can only occur under conditions of strain tending to disrupt the ring. C. J. S.

**The Anthocyanin Pigment of *Ipomæa hederacea*.** Y. YAMAGUCHI (*Ber. deut. bot. Ges.*, 1924, 42, 144—147).—The anthocyanin was extracted from the flowers of *Ipomæa hederacea* by treatment with methyl alcohol containing 3% of hydrochloric acid and precipitated with ether. A very small yield of reddish-brown, rhombic crystals was obtained by mixing the crude product with 1% hydrochloric acid and a large volume of 1.5% picric acid solution at 50° and allowing to stand for 2 months. The anthocyanin is tentatively named hederacein. The sugar obtained on acid hydrolysis of the crude product and removal of the anthocyanidin was almost certainly dextrose and not galactose. C. T. G.

**Nitrogenous Derivative of Diacetoneglucose.** E. MERCK CHEMISCHE FABRIK (D.R.-P. 382913; from *Chem. Zentr.*, 1924, i, 1591).—*Hydrazinediacetoneglucose* (annexed formula), from toluene-*p*-sulphonyldextrosediacetone and hydrazine, has m. p. 96—97°,  $[\alpha]_D + 83^\circ$ . It forms an *isopropylidene compound*, and a *benzylidene compound*, m. p. 99—100°,  $[\alpha]_D + 144^\circ$  in *s*-tetrachloroethane. G. W. R.



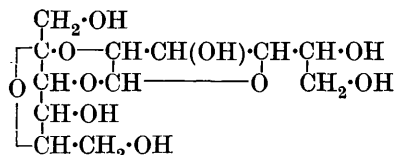
**Mechanism of the Oxidation of Lævulose in Phosphate Solutions.** O. MEYERHOF and K. MATSUOKA (*Biochem. Z.*, 1924, 150, 1—11).—

The spontaneous oxidation of lævulose in concentrated phosphate solutions, described by Warburg and Yabusoe (this vol., i, 713), is shown to be due to the catalytic action of a metal, since the reaction is inhibited by the presence of potassium cyanide and of sodium pyrophosphate, which would lead to the formation of stable complex salts; it is accelerated by the addition of copper, iron, and manganese, this acceleration being abolished by the simultaneous addition of cyanide, and it takes place equally well in solutions of arsenates. C. R. H.

**Action of Heat on Sucrose.** A. PICTET and N. ANDRIANOFF (*Helv. Chim. Acta*, 1924, 7, 703—707; cf. this vol., i, 499).—When sucrose (m. p. 183°) is heated at 185—190°/10—15 mm. until it has lost 5% of its weight, isosaccharosan,  $\text{C}_{12}\text{H}_{20}\text{O}_{10}$ , is obtained, which, when precipitated from methyl-alcoholic solution by addition

of acetone, forms a white, hygroscopic, amorphous powder with a bitter taste, m. p. 94—94·5°,  $[\alpha]_D^{25} + 64\cdot0^\circ$ ; it rapidly undergoes hydrolysis to dextrose and lævulose in aqueous solution. The *hexa-acetate* forms colourless prisms, m. p. 79—80°. If the heating be continued until the sucrose has lost 10% of its weight, caramelan,  $C_{24}H_{36}O_8$  (cf. Cunningham and Dorée, A., 1917, i, 513), is obtained as a pale yellow, hygroscopic, amorphous substance, much purer than when produced in an open vessel. It has m. p. 144—145°,  $[\alpha]_D^{25} + 80\cdot0^\circ$ . Further heating of sucrose, until 15% of the weight has been driven off, leaves caramelen,  $C_{36}H_{50}O_{25}$ , a brown, non-hygroscopic powder, m. p. 204—205°,  $[\alpha]_D^{25} + 65\cdot4^\circ$ . W. A. S.

**Constitution and Synthesis of isoSaccharosan.** A. PICTET and P. STRICKER (*Helv. Chim. Acta*, 1924, 7, 708—713).—*isoSaccharosan* (cf. preceding abstract) reduces Fehling's solution to half the extent that it should do if the reduction depended on hydrolysis to a mixture of dextrose and lævulose. Moreover, *isosaccharosan* yields an *osazone*,  $C_{24}H_{32}O_9N_4$ , m. p. 124—125°, in addition to glucosazone, which is the chief product of the reaction. These results indicate that the substance is not a simple anhydride of sucrose, a constitution for which would be difficult to frame. Sucrose is converted at its melting point without loss of weight (cf. Gelis, *Ann. Chim.*, 1859, [iii], 57, 234) into a mixture of dextrose and lævulosan; in accordance with this it is found that *isosaccharosan* is formed when a mixture of lævulosan and dextrose is heated at 185°/15 mm. until 5% of the total weight is lost. Likewise, if a mixture of glucosan and lævulosan be similarly heated, *isosaccharosan* is formed, no loss of weight taking place in this case. To *isosaccharosan* is attributed the constitution:



Preliminary experiments indicated that by treating *isosaccharosan* with cold 5% ammonia, *isosucrose* could be obtained. W. A. S.

**Glycogen. I. Partial Methylation, and the Isolation of Methylated Glucoses.** A. K. MACBETH and J. MACKAY (*J. Chem. Soc.*, 1924, 125, 1513—1521).—Glycogen was alkylated by the repeated action of methyl sulphate in the presence of sodium hydroxide. After three methylations, the product contained 26·7% OMe. Methyl alcohol was then used to keep the product in solution, whereby ultimately a compound with more than 36·4% OMe, corresponding with an introduction of 2—3 methyl groups for each glucose residue, was isolated. Either steric hindrance or physical condition hinders further alkylation. A product containing 36·4% OMe had  $[\alpha]_D + 179\cdot83^\circ$  in chloroform. Hydrolysis with methyl-alcoholic hydrogen chloride yielded (a) almost pure tri-

methyl methylglucoside, which on treatment with methyl iodide and silver oxide was converted into 2 : 3 : 5 : 6-tetramethyl methylglucoside and therefore contained the butylene oxide linking. Hydrolysis with 6% hydrochloric acid changed it to 2 : 3 : 6-trimethylglucose with constants in good agreement with those of the crystalline 2 : 3 : 6-trimethylglucose from cellobiose, cellulose, and starch; (b) a dimethyl methylglucoside belonging to the butylene oxide series which was hydrolysed to a dimethylglucose differing from the 2 : 3-compound described by Irvine and Scott (T., 1913, 103, 575) and possibly a 2 : 5-derivative, and (c) a probable mixture of mono- and di-methyl methylglucosides. It was possible to use glycogen possessing a fairly high nitrogen content in the above methylations; the nitrogen disappeared in the early stages and the products did not differ from those in which rigorously purified material was used. The close agreement between starch and glycogen on methylation and the similarity of the products on hydrolysis, indicates that the polysaccharides are built up from the same basal unit, and that the various formulæ proposed for starch may also be applied to glycogen. A. C.

**Redetermination of the Heat of Combustion of Glycogen with Special Reference to its Physiological Importance.** W. K. SLATER (*Biochem. J.*, 1924, 18, 621—631).—The heat of combustion of glycogen monohydrate in dilute solution is 3836 cal. per gram. S. S. Z.

**Cellulose Nitrate and Camphor.** J. B. NICHOLS.—(See i, 972.)

**Soluble Cellulose Esters of Higher Ethylenic Fatty Acids.** H. GAULT and [MLLE.] M. URBAN (*Compt. rend.*, 1924, 179, 333—334).—In continuation of previous work (cf. Gault and Ehrmann, A., 1923, i, 757), *cellulose triundecylenate*, m. p. (indef.) above 190°, has been prepared by allowing undecylenyl chloride to act, in toluene, on hydrocellulose, previously saturated with a mixture of toluene and excess of pyridine, at 110—120° for 2 hours. The ester is hydrolysed only with great difficulty, and it is therefore not possible to determine the corresponding acid in this manner. J. W. B.

**A Substance giving a Blue Colour with Iodine in the Asci of Lichens (*isoLichenin*).** H. ZIEGENSPECK (*Ber. deut. bot. Ges.*, 1924, 42, 116—119).—A compound, giving a blue coloration with iodine, to which the name *isolichenin* is given, has been isolated from an extract of the apothecia of the lichen *Xanthoria parietina* and also from other species. It is a carbohydrate, related to starch, stable towards diastase, and giving dextrose and a little methylpentose on complete hydrolysis with sulphuric acid. It has been detected in the vegetative thallus of only one species—*Cetraria islandica*; in the hymenium of several, and in the young asci of a large number of species. It occurs in the asci until they are almost fully developed, but disappears with the development of the spores, being converted into glycogen. *isoLichenin* is considered to have the function of a reserve food material. C. T. G.

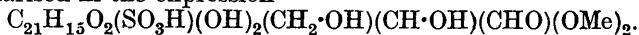


**Hydrocellulose.** H. GAULT and B. C. MUKERJI (*Compt. rend.*, 1924, **179**, 402—405).—The formation of hydrocellulose by the action of dilute sulphuric acid on cellulose has been studied systematically, the increase in the copper number, determined by the method previously described (this vol., ii, 280), giving a measure of the degradation. The rate of formation of hydrocellulose varies directly with the strength of the acid, the time and temperature of immersion, and the temperature of drying. With 5% sulphuric acid, the degradation begins to be appreciable only at 70°. Hauser and Herzfeld's observation (*A.*, 1915, i, 941) that the copper number of hydrocellulose falls to that of pure cellulose on prolonged extraction with boiling water was not confirmed. R. B.

**Action of Aqueous Sulphurous Acid on Lignocellulose.** C. F. CROSS and A. ENGELSTAD (*J. Soc. Chem. Ind.*, 1924, **43**, 253—257r).—The process for the manufacture of cellulose from wood by digestion with a 7% solution of sulphurous acid, free from sulphuric acid (*Brit. Pat.* 202016, 1922), proves that sulphonation is a direct reaction of sulphurous acid with certain groups of the lignone complex. The secondary effects which differentiate the products of the sulphurous acid process from those of the bisulphite process are the degree of sulphonation, deoxidation of CO groups, and condensation of the sulphonated complex. Analogous reactions are observed with cinnamaldehyde under the same treatment, but not with benzaldehyde or dextrose. Dextrose, however, is partly broken down with formation of acetic acid and caramel, whilst elementary sulphur and sulphur-oxygen by-products are detected. Digestion of oil of turpentine with aqueous sulphurous acid also forms small quantities of sulphur. Digestion of cotton cellulose with pure aqueous sulphurous acid leads to a pronounced degradation of the cellulose, indicating the necessity for synchronising the exposure of the wood cellulose by removal of lignone with the substantial exhaustion of the free sulphurous acid in the digestion liquor. One of the characteristic features of this process is the production of sulphuric acid as the result of deoxidation of certain groups of the lignone, and the conditions have been studied for limiting this phase of the reaction. Chemical attack on the cellulose is considerably promoted by fine subdivision of the raw material without a corresponding intensification of the reaction with the lignone. J. F. B.

**Lignosulphonic Acid obtained by the Action of Sulphurous Acid on Spruce Wood.** C. DORÉE and L. HALL (*J. Soc. Chem. Ind.*, 1924, **43**, 257—263r).—The liquor obtained by digestion of wood with free sulphurous acid differs from that of the ordinary digestion with calcium hydrogen sulphite in its lower degree of sulphonation, its tanning qualities, and its capacity to form gels, these pronounced colloid qualities being associated with the lower temperature of digestion, viz., 100—110°. The lignosulphonic acid has been separated by prolonged dialysis and contains only 5.5% of sulphur as against 7.3% for the bisulphite product. Its empirical formula is  $C_{26}H_{30}O_{12}S$ , and according to its reactions with  $\alpha$ -naphthylamine

it consists practically entirely of a substance of Klason's  $\alpha$  (aldehydic) type of lignone. The characterised groups in this complex are summarised in the expression



On heating with 5% nitric acid, these groups are respectively changed with the following result,



the nature of the modification of the changed methoxyl group being unexplained. The reactions of this nitro compound on reduction, giving with loss of ammonia a nitrogen-free ketone with three CO groups, show no analogy with the aromatic type and the behaviour of the system generally recalls that of certain unsaturated terpenes of the cholesterol series. Further oxidation by 32% nitric acid gives oxalic acid and a substantial yield of an acid,  $\text{C}_{20}\text{H}_{24}\text{O}_{12}(\text{CO}_2\text{H})_6(\text{NO}_2)_2$ . The persistence of the  $\text{C}_{26}$  complex through all these reactions with a resistant nucleus of the order of  $\text{C}_{20}$  suggests that the nucleus of lignone is hydroaromatic in character, consisting of a complex of reduced rings somewhat resembling the reduced benzophenanthrene hydrocarbon formulated by Schrauth (A., 1923, i, 443). This involves the general absence of oxygen linkings, the direct attachment of the side groups, including the CHO group, to the carbon atoms of the ring, and the presence of double linkings in the reduced ring.

J. F. B.

**Preparation of  $\alpha\beta\gamma$ -Triaminopropane and Formation of Complex Metallic Derivatives.** W. J. POPE and F. G. MANN (*Compt. rend.*, 1924, 178, 2085—2086; cf. Curtis and Hesse, A., 1901, i, 70).—From citric acid the following substances were successively prepared: Acetonedicarboxylic acid, diisonitrosoacetone, diaminoacetone, diacetyldiaminoacetoxime,  $\alpha\beta\gamma$ -triaminopropane. The yield at each stage is stated to be satisfactory. The base is converted into *cobaltiditriaminopropane chloride* and *rhodiditriaminopropane chloride*.

H. J. E.

**Preparation of a Derivative of Hexamethylenetetramine.** R. WOLFFENSTEIN (D.R.-P. 382904; from *Chem. Zentr.*, 1924, i, 968).—*Hexamethylenetetramine formate* is crystalline and has m. p. about 60°.

G. W. R.

**Synthesis of Hydroxyamines by the Curtius Method.** P. A. LEVENE and J. SCHEIDEGGER (*J. Biol. Chem.*, 1924, 60, 179—181).—Ethyl  $\beta$ -hydroxybutyrate is converted successively into  $\beta$ -hydroxybutyrihydrazide, m. p. 119—120°,  $\beta$ -hydroxybutyrazide, and di- $\beta$ -hydroxypropylacetamide (*picrate*, m. p. 118—119°). The latter is hydrolysed to  $\beta$ -hydroxypropylamine (*chloroplatinate*, m. p. 210° after softening at 205°).

C. T. G.

**Formation of Bismuthamines.** A. C. VOURNAZOS (*Compt. rend.*, 1924, 178, 2089—2092).—A brief description of a series of bismuthamines (cf. A., 1923, i, 759) with their formulæ; these substances have been prepared by combination of halides of tervalent bismuth with salts of ammonium, of various types of amines and of alkaloids. Bismuth nitrate and sulphate also yield similar

products. The co-ordination number of the bismuthomonoamines is 4, whilst that of the triamines is 6. The compounds resulting from the action of a bismuth halide,  $\text{BiX}_3$ , on an amine salt,  $\text{RNH}_3\text{Z}$ , are identical with those derived from  $\text{BiZ}_3$  and  $\text{RNH}_3\text{X}$  if the affinity of bismuth for X is greater than that for Z. H. J. E.

**N-Alkylamino Fatty Acids and their N-Acyl Derivatives.** H. SCHEIBLER (D.R.-P. 386743; from *Chem. Zentr.*, 1924, i, 1592—1593; cf. Scheibler and Baumgarten, A., 1922, i, 655).—The following new compounds are mentioned: *ethyl cyanobenzyl- $\alpha$ -aminopropionate*; *benzylidenealanine*; *N-benzylalanine hydrochloride*, m. p. 258°. G. W. R.

**Chain-forming Reactions of the Amides of  $\alpha$ -Hydroxyacids.** A. SCHMUCK (*Biochem. Z.*, 1924, 147, 193—202).—The amides of glycollic and lactic acids, obtained by treating the corresponding cyclic anhydrides with ammonia, yield, when heated in a stream of ammonia at 160—200°, *amidides* or *oxyamidides*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , hygroscopic crystals, m. p. 86°, and  $\text{CHMe}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}_2$ , small, hygroscopic tables, m. p. 52°, respectively, which give the biuret and alkaloidal precipitation reactions and are closely related to peptides. The compound thus prepared from lactamide yields on hydrolysis with 5% hydrochloric acid, alanine and lactic acid. In the case of glycollamide, the yield of amidide is small, and an amorphous substance,  $\text{C}_4\text{H}_6\text{O}_2\text{N}_2$ , containing 3.77% of amide nitrogen, is also obtained.

J. P.

**Relation between Crystal Structure and Constitution of Carbon Compounds. II. Crystallography of further Simple Substitution Products of Methane.** I. E. KNAGGS (*J. Chem. Soc.*, 1924, 125, 1441—1444).—A crystallographic description is given of chlorobromoacetomethylamide, chlorobromoacetoethylamide, dichloroacetoethylamide, dichloroacetomethylanilide, and dichloroacetoethylanilide (cf. McKie, this vol., i, 715). S. B.

**Action of Hydroxylamine on Ethyl Tartrate.** A. J. A. GUILLAUMIN (*Compt. rend.*, 1924, 178, 1986—1988).—An alcoholic solution of ethyl tartrate ( $\frac{1}{2}$  mol.) to which hydroxylamine (2 mols.) has been added, when kept at the ordinary temperature, deposits crystals of *tartramhydroxamic acid*,  $\text{CO}(\text{NH}_2)\cdot[\text{CH}\cdot\text{OH}]_2\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH}$ , m. p. 170—172° (decomp.),  $[\alpha]_D^{18}$  96° 30', *tetra-acetyl* derivative, m. p. 105°, *tribenzoyl* derivative, m. p. 203°. The substance exhibits mutarotation and, unlike other hydroxamic acids, forms no precipitate with copper acetate; further, ferric chloride gives with it a red coloration on standing. The structure is thus probably of the type  $\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$ , which is rearranged as above on solution in water.

H. J. E.

**Heat of Formation of Calcium Cyanamide.** N. KAMEYANA (*J. Faculty Eng., Tokyo Imp. Univ.*, 1923, 13, 61—71).—The author criticises the calculations of the heat of formation of calcium cyanamide given by Thompson and Lombard (*Met. Chem. Eng.*, 1910, 8, 682) and Dolch (A., 1921, ii, 17).

E. M. C.

**Behaviour of Calcium Cyanamide when Heated in Nitrogen at High Temperatures.** N. KAMEYANA (*J. Faculty Eng., Tokyo Imp. Univ.*, 1923, **13**, 75—102).—On heating calcium cyanamide in nitrogen to temperatures above 1250°, considerable loss occurred with evolution of nitrogen and severe corrosion of the porcelain reaction tube over a considerable distance. It is suggested that the calcium cyanamide sublimed at this temperature and that the vapour reacted with the porcelain. E. M. C.

**Preparation of Guanidinium Salts from Calcium Cyanamide.** J. S. BLAIR and J. M. BRAHAM (*Ind. Eng. Chem.*, 1924, **16**, 848—852).—A cold, filtered, aqueous extract of calcium cyanamide is neutralised with sulphuric acid, and evaporated below 80° to a cyanamide content of 165 g. per l. Ammonium nitrate (2 mols. per mol. of cyanamide) is added, and the solution heated slowly to 155°, this temperature being maintained for 3 hours. The hot solution is filtered, the guanidine nitrate crystallising on cooling the filtrate. About 80% of the cyanamide is converted into guanidine. [Cf. *B.*, 1924, 806.] F. G. W.

**Peralkylated Guanidines. II.** H. LECHER and F. GRAF (*Annalen*, 1924, **438**, 154—169; cf. *A.*, 1923, i, 761).—Pentamethylguanidine combines with ethyl iodide in ether solution to form *pentamethylethylguanidinium iodide*, colourless crystals, which unites with iodine to produce the corresponding *tri-iodide*, m. p. 58—59°. *NNS-Trimethyl-N'-ethyl-ψ-thiocarbamide*,  $\text{NM}_2\text{C}(\text{NEt})\cdot\text{S}\cdot\text{Me}$ , an oil, b. p. 69.2—69.5°/12 mm., is obtained by treating *NN*-dimethyl-*N'*-ethylthiocarbamide (Billeter, *A.*, 1893, i, 575) with methyl sulphate; when it is heated at 100° with dimethylamine in presence of mercuric chloride, *NNN'N'-tetramethyl-N'-ethylguanidine*, an oil, b. p. 55.5°/11 mm., is obtained. The latter combines with methyl iodide to give the same pentamethylethylguanidinium iodide as before; addition therefore takes place in both cases at the imino group, and presumably salt-formation takes place in the same way, not, as hitherto supposed, at one of the amino groups.

*Guanidinium iodide*, prepared by dissolving the carbonate in hydriodic acid, does not form a tri-iodide. *Pentamethylguanidinium* and *hexamethylguanidinium iodides* were obtained in a similar way; the latter yields a *tri-iodide*, red leaflets, m. p. 118—120°. *Hexamethylguanidinium hydroxide* can be obtained only in aqueous solution, best by treating the iodide with thallium sulphate and the resulting sulphate with barium hydroxide. A dilute solution is tolerably stable, but decomposition takes place when it is boiled alone or when sodium hydroxide is present, or even when it is concentrated under diminished pressure, the products of the decomposition being tetramethylcarbamide and dimethylamine.

Guanidinium hydroxide and its alkyl derivatives are bases comparable in strength with the alkali hydroxides. Pentamethylguanidinium hydroxide precipitates from solutions of their salts the hydroxides of the alkaline-earth and heavy metals. W. A. S.

**Constitution of Thiocarbamide and "Thiuronium" Salts.** H. LECHER and C. HEUCK (*Annalen*, 1924, **438**, 169—184).—It is

suggested that the salts of carbamide and of thiocarbamide be termed "uronium" and "thiuronium" salts, respectively. When thiocarbamide forms a salt, the hydrogen of the acid attaches itself to the sulphur atom because pentamethylthiuronium iodide (tetramethylthiocarbamide methiodide, Delépine, A., 1911, i, 23) may be obtained by combining with methyl iodide either *NNN'N'*-tetramethylthiocarbamide or *NNN'S*-tetramethyl- $\psi$ -thiocarbamide. In the first case, reaction proceeds rapidly in ethereal solution; in the second, the two reagents were mixed without a solvent, as it was found that in ethereal solution only 10% of the product had separated after two days. The two products were proved to be identical by converting them into the corresponding *picrate*, m. p. 92—93.5°.

*NN*-Dimethylthiocarbamyl chloride (Billeter, A., 1893, i, 575) interacts with diethylamine in hot benzene to yield *NN*-dimethyl-*N'N'*-diethylthiocarbamide, an oil, b. p. 119—120°/10 mm. Methylthiocarbimide and diethylamine unite in aqueous suspension to form *N*-methyl-*N'N'*-diethylthiocarbamide,  $\text{NHMe}\cdot\text{CS}\cdot\text{NEt}_2$ , m. p. 36—37.5°; when the latter is treated in hot methyl alcohol with methyl sulphate, *NS*-dimethyl-*N'N'*-diethyl- $\psi$ -thiocarbamide,  $\text{NMe}\cdot\text{C}(\text{SMe})\cdot\text{NEt}_2$ , an oil, b. p. 79—80°/10—11 mm., is obtained. When *NN*-dimethyl-*N'N'*-diethylthiocarbamide or *NS*-dimethyl-*N'N'*-diethyl- $\psi$ -thiocarbamide is treated with methyl iodide, or when *NNS*-trimethyl-*N'*-ethyl- $\psi$ -thiocarbamide is treated with ethyl iodide, *NNS*-trimethyl-*N'N'*-diethylthiuronium iodide,  $\text{SMe}\cdot\text{C}(\text{NEt}_2)\cdot\text{NMe}_2\text{I}$ , m. p. 94—95°, is obtained. The three products were conclusively proved to be identical by preparing from each the corresponding *picrate*, m. p. 80—83°. These results need further investigation. Pentamethylthiuronium hydroxide solutions, obtained by treating the iodide with sodium hydroxide, decompose even at room temperature, tetramethylcarbamide and methyl mercaptan being formed. The base was found to be comparable in strength with the alkali hydroxides. W. A. S.

**Chemical Behaviour of  $\alpha$ - and  $\beta$ -Hydroformamine Cyanides (Methyleneaminoacetoneitriles).** H. W. RINEHART and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1924, 46, 1653—1661; cf. this vol., i, 625).—Although  $\alpha$ -hydroformamine cyanide, m. p. 129°, yields the hydrochloride of ethyl aminoacetate on hydrolysis with alcoholic hydrogen chloride (Jay and Curtius, A., 1894, i, 162; 1899, i, 9; Klages, A., 1902, i, 354), the  $\beta$ -compound, m. p. 86°, merely decomposes to ammonium chloride and a nitrogen derivative of unknown constitution. When hydrolysed in alkaline solution the  $\alpha$ -isomeride yields ammonia equivalent to one-half of its nitrogen, whilst the  $\beta$ -compound readily gives off two-thirds of its nitrogen as ammonia. Hydrolysis is less ready with sulphuric acid and the amount of ammonia produced is less, but, in the case of the  $\beta$ -isomeride, increases with the concentration of the acid. Both isomerides are slowly hydrolysed in boiling aqueous solution, the  $\alpha$ -compound giving off ammonia rapidly at first, but the rate of production rapidly falls off, whilst the  $\beta$ -compound gives off

ammonia slowly at a nearly constant rate up to 17% of its nitrogen, as compared with 40% for the  $\alpha$ -isomeride.  $\alpha$ -Hydroformamine cyanide yields with hydrogen sulphide and alcoholic ammonia a white, crystalline substance,  $C_8H_{12}N_5 \cdot CS \cdot NH_2$ , m. p. 152—153° on rapid heating, 125—140° (decomp.) in the ordinary way, prolonged treatment giving dithiopiperazine or a thiopolypeptide.  $\beta$ -Hydroformamine cyanide similarly yields a colourless, crystalline substance,  $C_7H_{12}N_4(CS \cdot NH_2)_2$ , m. p. 148° (decomp.). An examination of the absorption spectra of the two isomerides in acetone solution supports the view that neither substance contains free ethylenic linkings.

R. B.

**Butenonitriles. IV.** P. BRUYLANTS (*Bull. Soc. chim. Belg.*, 1924, **33**, 331—338).—During the preparation of vinylacetonitrile by the interaction of allyl bromide and cuprous cyanide (A., 1922, i, 817, 924), diallyl is sometimes produced, but the cause is unknown. Vinylacetonitrile is converted into an equilibrium mixture of crotono- and isocrotono-nitriles by sodium phenoxide in the presence of phenol, and by aliphatic mono- and di-amines, but not by acidic reagents. Aqueous  $N/10$ -sodium hydroxide solution also converts vinylacetonitrile into a mixture of the two crotononitriles and some crotonamide, whereas  $N/2$  ethyl-alcoholic sodium hydroxide transforms it almost quantitatively into  $\beta$ -ethoxybutyronitrile, whilst an  $N/4$ -sodium hydroxide solution in alcohol-water (3 : 1 by vol.) gives a mixture of the two isomeric crotononitriles and  $\beta$ -ethoxybutyronitrile. Vinylacetonitrile, when treated with 1 mol. of sulphuric acid, gives a 50% yield of vinylacetic acid, b. p. 72.6—72.8°/13 mm., 169—169.2°/764.3 mm., m. p. —38.2°,  $d_4^{20}$  1.0091,  $n_D^{20}$  1.4252, together with traces of crotonic acid and amide; the vinylacetic acid is identified by conversion into  $\beta\gamma$ -dibromobutyric acid, and by the close similarity of its absorption spectrum curve with that of vinylacetonitrile. Vinylacetic acid when heated under reflux for 24 hours is converted into crotonic acid, which probably contains some isocrotonic acid. Sodium vinylacetate is stable in aqueous solution, but in sodium hydroxide solution is partly converted into sodium crotonate. Both isomeric crotononitriles are converted by concentrated sulphuric acid into the same (solid) crotonic acid.

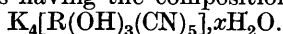
F. G. M.

**Phase Rule Study of the Cupro-, Argento-, Auro-, and Thallo-cyanides of Potassium.** H. BASSETT and A. S. CORBET (*J. Chem. Soc.*, 1924, **125**, 1660—1675).—The curves obtained for the system  $KCN-CuCN-H_2O$  at 25° indicate the existence of four complex cyanides, and these have been isolated.  $KCu_2(CN)_3 \cdot H_2O$ , monoclinic scales, was prepared in small quantity by boiling an excess of cuprous cyanide with 10% aqueous solution of potassium cyanide; on concentrating the mother-liquor, there were first deposited crystals (hexagonal plates or needles) of  $KCu(CN)_2$ , and, later, prismatic crystals of  $K_3Cu(CN)_4$ . Colourless rhombohedral crystals of the compound  $K_3Cu(CN)_4 \cdot H_2O$  were obtained by evaporating a solution containing potassium and cuprous cyanides in the molecular ratio of 3 : 1.

In the system  $\text{KCN-AgCN-H}_2\text{O}$  at  $25^\circ$ , the compounds  $\text{KAg(CN)}_2$ ,  $\text{K}_3\text{Ag(CN)}_4\cdot\text{H}_2\text{O}$ , and  $\text{KAg}_2(\text{CN})_3\cdot\text{H}_2\text{O}$  can exist in contact with the solution. The complex,  $\text{K}_3\text{Ag(CN)}_4\cdot\text{H}_2\text{O}$ , was obtained as large, colourless, tabular prisms on evaporating a solution containing potassium and silver cyanides in the ratio 3:1. The salt,  $\text{KAg}_2(\text{CN})_3\cdot\text{H}_2\text{O}$ , forms minute needles.

No evidence was obtained for the existence of potassium aurocyanides other than  $\text{KAu(CN)}_2$ . One thallocyanide,  $\text{KTI(CN)}_2\cdot\text{H}_2\text{O}$  (rectangular prisms), is capable of existence in the system  $\text{KCN-TICN-H}_2\text{O}$ .  
C. J. S.

**Decomposition of the Octacyanides of Quadrivalent Molybdenum and Tungsten by Sunlight.** I. O. COLLENBERG (*Z. anorg. Chem.*, 1924, **136**, 245—251).—Sulphuric acid solutions of compounds of the type  $\text{K}_4\text{R(CN)}_8$ , where  $\text{R}=\text{Mo}$  or  $\text{W}$ , are pale yellow in colour, but, on exposure to bright sunlight, they turn, in succession, reddish-brown, dark brown, and eventually green, whilst a brown, flocculent precipitate forms. No definite compounds could be isolated from the decomposed solution. The corresponding octacyanides in *N*-potassium hydroxide solution undergo a change on exposure to bright sunlight involving the replacement of four cyano groups successively by hydroxyl, and the colour of the solution passes through brown to violet. From the violet solutions addition of excess of potassium hydroxide precipitates, in the cold, crystalline substances having the composition



The tungsten compound is yellowish-brown in colour and gives violet solutions. The molybdenum compound exists in two forms, one, yellow-brown in colour, crystallising from hot solutions, and the other, reddish-violet in colour, from cold; both give deep blue solutions in water.  
A. R. P.

**Preparation of Hydroxyethylarsinic Acid.** LES ÉTABL. POULENC FRÈRES and C. OECHSLIN (*Brit. Pat.* 206143).—An ethylene dihalide is heated with an aqueous solution of an alkali arsenite; the resulting mixture is neutralised with hydrochloric acid and hydrogen peroxide is added to convert any free arsenious into arsenic acid, which is removed with magnesium oxide.

W. T. K. B.

**Preparation of Magnesium Methyl Chloride for the Grignard Reaction.** H. SCHMALFUSS (*J. pr. Chem.*, 1924, [ii], **108**, 88—90).—The reaction between magnesium and gaseous methyl chloride is greatly accelerated by a catalyst formed by mixing in a flask the magnesium, some ethyl bromide, a few crystals of iodine, and a very little ether. The catalyst is formed at once, dry ether is added, and a stream of dry methyl chloride gas is passed into the boiling ether as fast as it can be absorbed. Using the magnesium-methyl chloride thus prepared, 98% of the theoretical yield of diphenylmethylcarbinol was obtained from benzophenone.

E. H. R.

**Valency Requirements of Organic Radicals.** K. VON AUWERS (*Ber.*, 1924, **57**, [B], 1051—1056).—A theoretical survey of results obtained by Meerwein (A., 1920, i, 2; this vol., i, 188, 191), von Braun (A., 1923, i, 1193; this vol., i, 632), Skraup (A., 1919, i, 598), Steinkopf (A., 1922, i, 994), and Schonberg (this vol., i, 520) in relation to observations of the author and Zincke on  $\psi$ -phenols (A., 1900, i, 159), *p*-hydroxybenzylpiperidines (A., 1906, i, 258), phenyl benzyl ethers (A., 1900, i, 168; 1902, i, 212; 1906, i, 347; 1907, i, 1033), *o*- and *p*-hydroxybenzyl bromides (A., 1900, i, 154), and *pp'*-dihydroxydiphenylmethanes (A., 1906, i, 263; 1907, i, 919). The relative tenacity of the radicals is not under all conditions a measure of their valency requirements, since other factors, such as steric hindrance and ionisation, may come into play. R. B.

**Isomerisation due to the Action of Zinc Dust and Alcohol on the Stereoisomeric Dibromodimethylcyclohexanes.** A. USPENSKI (*Trans. Inst. Chem. Reagents, Moscow*, 1923, No. 2, 5—9).—When the solid *cis*-3:5-dibromo-1:1-dimethylcyclohexane (A., 1923, i, 666) is reduced by means of zinc dust and alcohol, the product is the pure bicyclic hydrocarbon (*loc. cit.*), b. p. 114—114.1°/740 mm.,  $d_4^{20}$  0.8131,  $n_D^{20}$  1.4350; if the liquid isomeride, consisting mainly of the *trans*-form, is employed a mixture is obtained, b. p. 115.5°/740 mm.,  $d_4^{20}$  0.7885,  $n_D^{20}$  1.4337, which contains only small quantities of the above hydrocarbon, the greater part consisting of the unsaturated isomeride, as evidenced by the high molecular refractivity and its reaction with permanganate. G. A. R. K.

**Refractive Index of Benzene and Carbon Tetrachloride in an Electric Field.** PAUTHENIER.—(See ii, 582.)

**Sulphonation of Benzene.** A. W. HARVEY and G. STEGEMAN (*Ind. Eng. Chem.*, 1924, **16**, 842—845).—When benzene vapour is passed through sulphuric acid (93.2%) at 130—170°, the concentration of the sulphuric acid falls, first rapidly, then more slowly, until a limiting value (0.6% at 170°) is reached. The concentration of benzenesulphonic acid shows a corresponding increase, but reaches a maximum (88—92%) before the limiting sulphuric acid concentration is attained. This point corresponds with the commencement of the formation of diphenylsulphone, according to the equations  $2\text{PhSO}_3\text{H} = \text{Ph}_2\text{SO}_2 + \text{H}_2\text{SO}_4$ , and  $\text{PhSO}_3\text{H} + \text{C}_6\text{H}_6 = \text{Ph}_2\text{SO}_2 + \text{H}_2\text{O}$ . As the sulphone does not appear until the concentration of sulphuric acid has fallen below 10%, its production by the direct action of benzene on sulphuric acid appears to be excluded. F. G. W.

**Special Examples of Grignard's Reaction.** H. GOUDET and H. PAILLARD (*Helv. Chim. Acta*, 1924, **7**, 638—640).— $\beta$ -Phthalimidoethyl bromide ( $\omega$ -bromoethylphthalimide) interacts with magnesium phenyl bromide to form a compound which when treated with water yields 3-hydroxy-3-phenyl-2- $\beta$ -bromoethyliso-indolinone, colourless needles, m. p. 179.5—180.5°. This product will not react further with a Grignard reagent (cf. Sachs and Ludwig, A., 1904, i, 266), nor will the intermediate magnesium



complex interact with magnesium. The magnesium complex obtained by treating  $\beta$ -bromoethylamine with magnesium ethyl bromide will not react with magnesium.

Monochloroacetone is not affected by magnesium but methyl  $\alpha$ -chloroethyl ketone undergoes reaction, provided the magnesium is previously amalgamated and some ethyl bromide is used to start the reaction. With cyclohexanone as medium a poor yield of 1- $\beta$ -acetyl-ethylcyclohexan-1-ol, m. p. 123—124°, is obtained. W. A. S.

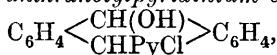
### ***o*-Chlorodinitrotoluenes. V. 2-Chloro-3:6-dinitrotoluene.**

G. T. MORGAN and T. GLOVER (*J. Chem. Soc.*, 1924, 125, 1597—1601).—The completion of the set of six 2-chlorodinitrotoluenes demanded by theory is realised in the synthesis of 2-chloro-3:6-dinitrotoluene. By the action of toluene-*p*-sulphonyl chloride on 6-chloro-*o*-toluidine, 6-chlorotoluene-*p*-sulphonyl-*o*-toluidide was obtained, prisms, m. p. 119°, giving when nitrated 6-chloro-5-nitrotoluene-*p*-sulphonyl-*o*-toluidide, m. p. 157°. Hydrolysis of this gave 6-chloro-5-nitro-*o*-toluidine (m. p. 162°), which was oxidised by Caro's acid in the cold. 2-Chloro-3:6-dinitrotoluene forms long, colourless needles, m. p. 61.5—63°. 6-Chloro-2:5-tolylenediamine, m. p. 89—90°, was obtained by reducing an alcoholic solution of 6-chloro-5-nitro-*o*-toluidine by means of zinc dust and ammonium chloride. Nitration of 6-chloroaceto-*o*-toluidide gave chiefly 6-chloro-3-nitroaceto-*o*-toluidide, identified by hydrolysis to 6-chloro-3-nitro-*o*-toluidine.

W. E. E.

**Studies in Chemical Reactivity. II. The Anthracene  $\rightleftharpoons$  Dianthracene Reaction, Photochemical and Thermal.** H. A. TAYLOR and W. C. MCC. LEWIS.—(See ii, 580.)

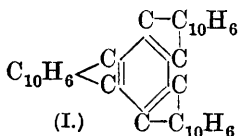
**Anthracene Derivative.** BADISCHE ANILIN- UND SODA-FABRIK and H. HOPFF (D.R.-P. 381180; from *Chem. Zentr.*, 1924, i, 1446).—The following compounds, obtained from the chlorination of anthracene in the presence of pyridine, are mentioned: 9:10-dihydroanthracenedipyridinium chloride,  $C_6H_4 \begin{smallmatrix} <CHPyCl \\ <CHPyCl \end{smallmatrix} C_6H_4$ , crystals, m. p. 180°; anthranolylpyridinium chloride,



a brown substance.

G. W. R.

**Decacyclene. I. Reduction of Decacyclene.** K. DZIEWOŃSKI and J. SUSZKO (*Bull. Acad. Polon. Sci. Lett.*, 1923, [A], 17—24; from *Chem. Zentr.*, 1924, i, 1377—1378).—By reduction of decacyclene (trinaphthylenebenzene, annexed formula) with hydriodic acid and red phosphorus the following compounds are obtained: hexahydrodecacyclene,  $C_{36}H_{24}$ , a brown, amorphous mass, m. p. 355—365°; octahydrodecacyclene,  $C_{36}H_{26}$ , an amorphous, reddish-brown mass, m. p. 300—310°; dodecahydrodecacyclene,  $C_{36}H_{30}$ , dark red, microcrystalline, m. p. 255°; hexa-



decahydrodecacyclene,  $C_{33}H_{34}$ , orange-yellow, microcrystalline, m. p.

150—160°; *octadecahydrodecacyclene*,  $C_{36}H_{36}$ , yellow, microcrystalline, m. p. 125—128°; *hexaeikosihydrodecacyclene*,  $C_{36}H_{44}$ , light yellow oil, b. p. 330—340°/10—12 mm. Structural formulæ, showing hydrogenation by stages of the naphthylene residues, are given for each of the reduction products. G. W. R.

**cycloHexylamines.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 382714; from *Chem. Zentr.*, 1924, i, 1592).—*cycloHexylamines* are prepared by heating *cyclohexanol* with primary or secondary amines or their substitution products and zinc chloride. *cycloHexylaniline* is an oil, b. p. 130°/4 mm.; *N-cyclohexyl-m-toluidine*, b. p. 155—160°/13 mm.; *N-cyclohexylethyl-o-toluidine*, an oil, b. p. 175°/22 mm. G. W. R.

**Reactions of Thiocarbonyl Chloride. I. Reaction with Aromatic Primary Amino Compounds.** G. M. DYSON and H. J. GEORGE (*J. Chem. Soc.*, 1924, 125, 1702—1708).—When an aromatic amine is substituted in the nucleus by a halogen, nitro, or hydroxyl group, the Hofmann method of preparing symmetrically disubstituted thiocarbamides is unsatisfactory. A general method of preparing this type of compound is described, based on the action of thiocarbonyl chloride on aniline, by which phenylthiocarbimide is obtained. The presence of a single halogen atom, hydroxyl, alkoxyl, or carbethoxyl group does not lessen the activity of the amine; the presence of a nitro group increases its activity. Thiocarbimides are obtained when equal weights of thiocarbonyl chloride and amine are used and thiocarbamides when the amine is in excess. The following new compounds are described:—*3:4-dimethylphenylthiocarbimide*, pale yellow oil, b. p. 263—264°; *3:4-dimethylphenylthiocarbamide*, by the action of boiling aqueous alcoholic ammonia on the preceding compound, m. p. 141·5—142·5°; *s-di-3:4-dimethylphenylthiocarbamide*, m. p. 178·5—179°; *2:4-dimethylphenylthiocarbimide*, m. p. 28—29°; *2:4-dimethylphenylthiocarbamide*, m. p. 181·5°; *s-di-2:4-dimethylphenylthiocarbamide*, m. p. 149—150°; *2:5-dimethylphenylthiocarbimide*, a pale, straw-coloured oil, b. p. 262—263°; *2:5-dimethylphenylthiocarbamide*, m. p. 134·5—135·5°; *s-di-2:5-dimethylphenylthiocarbamide*, m. p. 148—148·5°; *ψ-cumidylthiocarbimide*, m. p. 22—23°; *ψ-cumidylthiocarbamide*, m. p. 167·5—168°; *s-di-ψ-cumidylthiocarbamide*, m. p. 145—146·5°; *5-bromo-o-tolylthiocarbimide*, m. p. 48—49°; *5-bromo-o-tolylthiocarbamide*, m. p. 186°; *s-di-5-bromo-o-tolylthiocarbamide*, m. p. 159°; *p-nitrophenylthiocarbimide*, m. p. 189—190°; *5-nitro-o-tolylthiocarbimide*, m. p. 55—56°; *5-nitro-o-tolylthiocarbamide*, m. p. 188·5°; *s-di-5-nitro-o-tolylthiocarbamide*, m. p. 130—131°; *nitromesitylthiocarbimide*, pale yellow, hair-like crystals, m. p. 74—75°; *s-di-(nitromesityl)thiocarbamide*, m. p. 244°; *nitromesitylthiocarbamide*, m. p. 199°; *m-hydroxyphenylthiocarbamide*, m. p. 287° (decomp.); *p-anisylthiocarbamide*, m. p. 210—211°; *p-phenetylthiocarbimide*, m. p. 75—76°; *p-phenetylthiocarbamide*, m. p. 175—176°; *s-di-p-phenetylthiocarbamide*, m. p. 171°; *o-carbethoxyphenylthiocarbimide*, yellow oil, b. p. 288—290° (slight

decomp.); *o*-carbethoxyphenylthiocarbamide, m. p. 306—308°; *s*-di-*o*-carbethoxyphenylthiocarbamide, decomp. before melting.

W. E. E.

**Halogen-substituted Arylthiocarbimides.** F. D. CHATTAWAY, R. K. HARDY, and H. G. WATTS (*J. Chem. Soc.*, 1924, 125, 1552—1555).—In Hofmann's method of preparing thiocarbimides, the yield of the intermediate carbamide and also that of the final product depend on the nature of the substituents in the aromatic nucleus. Whereas aniline and *o*- and *p*-toluidine react readily with carbon disulphide, their monohalogen derivatives are much less active and their dihalogen derivatives almost inert. When a thiocarbamide, obtained by the addition of phenylthiocarbimide to a halogen-substituted arylamine, is hydrolysed by acid, the more basic unsubstituted residue is removed and a halogen-substituted arylthiocarbimide is produced.

*p*-Chlorophenylthiocarbimide, crystals, m. p. 44·5°, warmed with concentrated aqueous ammonia, gives the corresponding carbamide, m. p. 178°. 2:4-Dichlorophenylthiocarbimide, m. p. 39°, b. p. 208°/17·5 mm. 2:4-Dichlorophenylthiocarbamide, m. p. 158°. Methyl dichlorophenylthiocarbamate, m. p. 48·5°; corresponding ethyl and *n*-propyl esters, m. p. 79° and 72°, respectively. 2:4-Dibromophenylthiocarbimide, m. p. 59·5°; corresponding carbamide, m. p. 170°. Ethyl 2:4-dibromophenylthiocarbamate, m. p. 62°; corresponding *n*-propyl ester, m. p. 68°. *n*-Butyl phenylthiocarbamate, m. p. 55°; *n*-butyl *p*-tolylthiocarbamate, m. p. 65°. *p*-Chlorophenyl-*p*-tolylthiocarbamide, m. p. 173°; *p*-chlorophenyl-*o*-tolylthiocarbamide, m. p. 119·5°; *p*-bromophenyl-*p*-tolylthiocarbamide, m. p. 182°; 2:4-dichlorodiphenylthiocarbamide, m. p. 157°; 2:4-dibromodiphenylthiocarbamide, m. p. 165°; 2:4-dichlorophenyl-*p*-tolylthiocarbamide, m. p. 145°.

W. E. E.

**Some Binary Systems composed of Acetic Acid and the Homologues of Aniline.** E. A. O'CONNOR (*J. Chem. Soc.*, 1924, 125, 1422—1427; cf. T., 1921, 119, 401).—The solid additive compounds formed on mixing certain amines with glacial acetic acid have been isolated and the composition of the liquid phases in equilibrium with these solids determined for various temperatures. *o*-Toluidine forms a compound,  $C_7H_7 \cdot NH_2 \cdot C_2H_4O_2$ , m. p. 24·8°, deposited over a large range of composition. *m*-Toluidine forms a compound,  $C_7H_7 \cdot NH_2 \cdot 2C_2H_4O_2$ , existing as a stable  $\alpha$ -form, m. p. 10·0°, and a metastable or  $\beta$ -form, m. p. 7·3°. The  $\beta$ -form was metastable to the  $\alpha$ -form throughout the range investigated, but no definite conditions for their separation were discovered. The invariant points  $\alpha$ - and  $\beta$ - $C_7H_7 \cdot NH_2 \cdot 2C_2H_4O_2$ - $C_7H_7 \cdot NH_2$ -liquid lie at -37·7° and 13% and -39·0° and 16·0% acetic acid, respectively. *p*-Toluidine forms  $C_7H_7 \cdot NH_2 \cdot 2C_2H_4O_2$ , m. p. 48·0°; mesidine forms  $C_9H_{11} \cdot NH_2 \cdot C_2H_4O_2$ , m. p. 18·9°. Dimethylaniline forms no compound with acetic acid as a solid phase; the heat evolution is extremely small, whilst the complexes of the tertiary amine and acid lack the viscosity at low temperatures characteristic of the primary amines. Combination obviously takes

place in the case of monomethylaniline but no solid phase could be induced to separate. The ratio 1 amine : 1 acid appears to hold where the primary amine possesses a methyl group in the ortho-position; where this is not the case the ratio is 1 amine : 2 acid. The type  $2C_6H_5 \cdot NH_2, C_2H_4O$  seems to be peculiar to aniline.

A. C.

**Derivatives of Naphthylaminesulphonic Acids and Amino-naphtholsulphonic Acids.** CHEM. FABR. VORM. WEILER-TER MEER and H. SUIDA (D.R.-P. 380578; Austr. Pat. 93324; from *Chem. Zentr.*, 1924, i, 1593—1594).—The patent describes the preparation of colouring matters containing sulphur by the action of sulphur monochloride on salts of naphthylaminesulphonic acids and aminonaphtholsulphonic acids.

G. W. R.

**Monoiodo Derivatives of o-Nitrophenol. I.** S. KEIMATSU (*J. Pharm. Soc. Japan*, 1924, No. 507, 319—326).—Hübner's  $\alpha$ - and  $\beta$ -iodonitrophenols (*Ber.*, 1874, 7, 462) are stated to be the 5- and 6-iodo-2-nitrophenols (cf. Beilstein, II, 700). By heating 3-nitro-4-hydroxyphenylarsinic acid (4 g.) with potassium iodide (8 g.) in water (56 c.c.), 5*N*-sulphuric acid (16 c.c.), and alcohol (10 c.c.) during 3 hours, 4-iodo-2-nitrophenol, m. p. 80—81°, is obtained (cf. Roberts, T., 1923, 123, 2707). When the nitration product, m. p. 214—218°, of *o*-hydroxyphenylarsinic acid (probably a mixture of at least two nitro compounds) is treated with potassium iodide and sulphuric acid as above, a mixture of 6-iodo-2-nitrophenol (obtained by Brenans by the nitration of *o*-iodophenol), and 2-iodo-4-nitrophenol is obtained. It is concluded that Hübner's  $\alpha$ - and  $\beta$ -compounds are the 3- and 4-iodo derivatives.

K. K.

**Derivatives of 2 : 6-Dinitrophenol.** E. FROMM and R. EBERT (*J. pr. Chem.*, 1924, [ii], 108, 75—87).—2 : 6-Dinitrophenyl benzoate forms flat needles, m. p. 112°. Bromination of 2 : 6-dinitrophenol in alcohol gives 4-bromo-2 : 6-dinitrophenol, m. p. 78°; benzoate, m. p. 154°; 4-bromo-2 : 6-dinitroanisole has m. p. 88°. By the action of benzoyl chloride on 2 : 6-diaminophenol hydrochloride is formed 6-benzamido-2-phenylbenzoxazole, m. p. 222°, and some 2 : 6-dibenzamidophenol, m. p. 181°; benzoate, m. p. 220°. 2 : 6-Diacetamidophenol has m. p. 165°, and its acetate, m. p. 224°; tetra-acetyl-2 : 6-diaminophenyl acetate, m. p. 167°. 6-Acetamido-2-methylbenzoxazole, obtained by heating 2 : 6-diacetamidophenyl acetate at 230—235°, has m. p. 148°.

2 : 6-Diaminophenyl p-toluenesulphonate has m. p. 141°; dibenzoyl derivative, m. p. 191°; 2 : 6-di-p-toluenesulphonamidophenol, m. p. 190°.

2 : 6-Diaminoanisole dihydrochloride was obtained by reduction of 2 : 6-dinitroanisole; the following derivatives of the base were obtained: dibenzoyl, m. p. 157°; diacetyl, m. p. 222°; di-p-toluenesulphonyl, m. p. 185°. 2 : 6-Diaminophenetole dihydrochloride was prepared; 2 : 6-diacetamidophenetole has m. p. 240°.

2 : 6-Diamino-p-cresol dihydrochloride is described; 2 : 6-diacetamido-p-cresol has m. p. 225—227°; acetate, m. p. 228°.

Oxidation of 2 : 6-diacetamidophenol with ferric chloride gives 3 : 5 : 3' : 5'-*tetra-acetamidodiphenoquinone*, a dark blue, crystalline precipitate, which is reduced by hyposulphite to 3 : 5 : 3' : 5'-*tetra-acet-amido-4 : 4'-dihydroxydiphenyl*. With formaldehyde, 2 : 6-diaminophenol forms a compound,  $C_8H_{10}O_2N_2 \cdot 2HCl$ .

2 : 3 : 6-*Tribenzamidoanisole*, m. p. 225—226°, is obtained by coupling diazobenzene-*p*-sulphonic acid with 2 : 6-diaminoanisole, reducing the azo dye, and benzoylating the resulting triaminoanisole. The last forms with benzil a *quinoxaline* derivative, giving a *hydrochloride*,  $C_{21}H_{18}ON_3Cl$ , bright red needles. E. H. R.

**Chromammmines. I. Salts of Nitro and other Dyes.** H. J. S. KING (*J. Chem. Soc.*, 1924, 125, 1329—1337).—Dyes containing chelate groups, as those of the quinoneoxime, alizarin, and azosalicylic acid series, readily displace ammonia from the chromammmin complex. The chloropentammmino- and hexammminochromic salts of the nitro dyes picric acid, aurantia, naphthol-yellow N and S, resemble those obtained from the cobaltammmines (T., 1922, 121, 1723); on boiling they liberate 3 ammonia molecules in about 20 minutes, with precipitation of chromic hydroxide and formation of the ammonium salt of the dye, a reaction which differentiates them from compounds containing chelate groups. It was not found possible to prepare normal hexammminochromic alizarinate, the mono-salt being obtained. Hexammminochromic picramate contains no chelate grouping, possibly indicating that picramic acid has a *p*-quinonoid structure. The alkaline solution obtained from aquopentammminocobaltic chloride and moist silver oxide reacts with naphthol-yellow S as if containing hydroxopentammminocobaltic hydroxide. A. COUSEN.

**Derivatives of *para*-Substituted Phenylcarbamides.** C. F. BOEHRINGER U. SÖHNE G.M.B.H., L. ACH, and A. ROTHMANN (D.R.-P. 377816 and 377817; from *Chem. Zentr.*, 1924, i, 964; cf. A., 1923, i, 948).—as-*p*-*Hydroxyphenylmethylcarbamide*,  $N(C_6H_4OH)Me \cdot CO \cdot NH_2$ , forms needles, m. p. 175°; as-*p*- $\beta$ -*hydroxyethoxyphenylmethylcarbamide*,  $N(C_6H_4 \cdot O \cdot C_2H_4OH)Me \cdot CO \cdot NH_2$ , forms needles, m. p. 140—141°. G. W. R.

**Electrochemical Oxidation of the three Tolyl Methyl Ethers.** F. FICHTER and H. RIS (*Helv. Chim. Acta*, 1924, 7, 803—813; cf. this vol., i, 282, 629).—Anodic oxidation of *p*-tolyl methyl ether gives methyl alcohol, anisaldehyde, anisic acid, 2-*hydroxy-2'-methoxy-5 : 5'-dimethyldiphenyl*, an oil, b. p. 205°/12 mm., and 2 : 2'-*dimethoxy-5 : 5'-dimethyldiphenyl*, m. p. 71°, b. p. 188°/12 mm. (also prepared by methylating the corresponding diphenol), together with unidentified products of high b. p. The constitution of Fichter and Ackermann's 2 : 2'-*dihydroxy-5 : 5'-dimethyldiphenyl* (A., 1919, i, 586) was verified by preparing it from *o*-tolidinedisulphonic acid; it yields a *dibenzoyl* derivative, m. p. 136°. Anisaldehyde is converted by anodic oxidation, using a platinum anode, into anisic acid. The oxidation of *p*-tolyl methyl ether in the nucleus, not in the side-chain to anisic acid, is favoured

by high current density, and by using a weak acid and a platinum anode. *m*-Tolyl methyl ether suffers no attack in the side-chain, but is converted into toluquinol (by cathodic reduction of the quinone formed by oxidation), toluquinone, and 4-hydroxy-4'-methoxy-2:2'-dimethyldiphenyl, b. p. 230—235°/12 mm. *o*-Tolyl methyl ether yields methyl alcohol, toluquinol, and a viscous oil, b. p. 190—280°/12 mm., the relative amount of which increases when a higher current density or a platinum anode is used; this appears to be chiefly 4-hydroxy-4'-methoxy-3:3'-dimethyldiphenyl, and gives the corresponding diphenol on demethylation. Toluquinol is oxidised, in cold acetic acid solution containing sulphuric acid, to ditolyl-diquinone; its dimethyl ether to 2:2':5:5'-tetramethoxy-4:4'-dimethyldiphenyl, and a quinone (cf. Nietzki and Bernard, A., 1898, i, 529).  
W. A. S.

***o*-Hydroxydiphenyl.** K. VON AUWERS and G. WITTIG (*J. pr. Chem.*, 1924, [ii], **108**, 99—112).—The reactions of *o*-hydroxydiphenyl are in general similar to those of *o*-cresol. Bromination in acetic acid gives an oily mixture of monobromo derivatives, 3:5-dibromo-2-hydroxydiphenyl, m. p. 56—57°, and 3:5:4'-tribromo-2-hydroxydiphenyl, m. p. 151—152° (methyl ether, m. p. 98—98·5°, benzoate, m. p. 132—133°). By 2*N*-sodium hydroxide the tribromo derivative is converted into a red, amorphous substance.

*o*-Hydroxydiphenyl reacts slowly with formaldehyde in the cold to form 2-hydroxy-3:5-dihydroxymethyldiphenyl, m. p. 124·5°, which with hydrogen bromide in acetic acid forms 2-hydroxy-3:5-dibromomethyldiphenyl, m. p. 100·5—101°. By the Friedel-Crafts reaction, *o*-diphenyl methyl ether gives 5-acetyl-*o*-diphenyl methyl ether, m. p. 91·5—92°; semicarbazone, m. p. 209—210°. By heating *o*-hydroxydiphenyl acetate at 130° with aluminium chloride, a mixture of 2-hydroxy-5-acetyldiphenyl (m. p. 172—173°; semicarbazone, m. p. 213°) and 2-hydroxy-3-acetyldiphenyl (m. p. 60—61°; semicarbazone, m. p. 214—215°; oxime, m. p. 165—166°) is obtained. 2-Hydroxy-5-ethyldiphenyl is a pale yellow oil, b. p. 171—172°/18 mm.; phenylurethane, m. p. 114—115°.

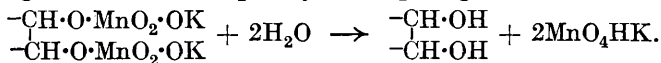
*o*-Diphenyl allyl ether, b. p. 166—167°/12·5 mm.,  $d_4^{20.9}$  1·0601,  $n_D^{20.9}$  1·58910, changes at 250—300° into 2-hydroxy-3-allyldiphenyl, b. p. 176—178°/13 mm.,  $d_4^{28.7}$  1·0735,  $n_D^{28.7}$  1·59411; phenylurethane, m. p. 124·5—125·5°. The allyl derivative changes when heated with methyl-alcoholic potassium hydroxide into 2-hydroxy-3-propenyldiphenyl, b. p. 185—187°/13 mm.,  $d_4^{6.3}$  1·0897,  $n_D^{6.3}$  1·61994; phenylurethane, m. p. 166—167·5°; methyl ether, b. p. 173—174°/12 mm. Reduction of the propenyl compound with sodium and alcohol gives 2-hydroxy-3-propyldiphenyl, b. p. 169—172°/13 mm.,  $d_4^{16}$  1·0512,  $n_D^{16}$  1·57462; phenylurethane, m. p. 126·5—127·5°. Oxidation of the methyl ether of the propenyl compound with permanganate gives 2-methoxydiphenyl-3-carboxylic acid, m. p. 119—120°.

*o*-Hydroxydiphenyl propionate, b. p. 168—169°/12 mm., is converted by aluminium chloride into 2-hydroxy-5-propionyldiphenyl, m. p. 148°. 2-Hydroxy-5-propyldiphenyl has b. p. 178—179°/12 mm.; phenylurethane, m. p. 132—132·5°.

5-Benzeneazo-2-hydroxydiphenyl has m. p. 95—96° and 3:5-bis-benzeneazo-2-hydroxydiphenyl, m. p. 157°. E. H. R.

**Univalent Oxygen. III. 9-Chloro-10-phenanthroxyl. S.** GOLDSCHMIDT and C. STEIGERWALD (*Annalen*, 1924, **438**, 202—216; cf. A., 1922, i, 1148, 1149).—9-Chloro-10-hydroxyphenanthrene (Schmidt and Lump, A., 1909, i, 34) is oxidised in chloroform solution to 9-chloro-10-phenanthryl peroxide, a colourless substance, m. p. 124—125° (decomp.). In solution, this compound undergoes dissociation into the free radical, 9-chloro-10-phenanthroxyl, the dissociation being influenced by the presence of traces of hydrogen chloride and therefore proceeding best when pyridine is present; 69% of the substance may then be present as the free radical. When the original oxidation of the chlorophenanthrol is carried out quickly, as by using potassium ferriocyanide in aqueous solution, and the product is immediately extracted with chloroform, the free radical is present to the extent of 10% (determined by titration with hydrazobenzene; cf. Goldschmidt and Wolffhardt, this vol., i, 886). The two substances may be separated by fractionally precipitating the chloroform solution with petrol, the peroxide being first thrown down, and the phenanthroxyl separating later as an amorphous blue deposit. 9-Chloro-10-phenanthroxyl resembles its congeners (*loc. cit.*); it unites with bromine to form a yellow compound in which the bromine must be attached to the oxygen atom. W. A. S.

**Mechanism of the Action of Potassium Permanganate on Unsaturated Compounds.** S. NAMETKIN (*J. pr. Chem.*, 1924, [ii], **108**, 46—51).—By the action of potassium permanganate on unsaturated compounds, glycols are formed, but it has never been decided whether these are produced by hydration of primarily formed oxides. It is shown, by reference to cyclohexanediol and some of its homologues, that this cannot be the case, since hydration of the oxide gives a *cis*-glycol whereas oxidation of the cyclohexene with permanganate gives the *trans*-glycol. It is probable that 2 mols. of permanganate participate in the oxidation, forming at the double bond a complex which by hydration gives a glycol and a manganate, the latter quickly decomposing:



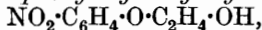
In this way either a *cis*- or *trans*-glycol could be formed, but only the *trans*-isomeride is found. E. H. R.

**Molecular Transpositions. Preparation and Dehydration of  $\alpha\gamma$ -Triphenyl- $\beta\beta$ -dimethylpropan- $\alpha$ -ol.** (MME.) P. RAMART (*Compt. rend.*, 1924, **179**, 276—279).—By the action of magnesium phenyl bromide on benzyldimethylacetophenone,  $\alpha\gamma$ -triphenyl- $\beta\beta$ -dimethylpropan- $\alpha$ -ol, m. p. 100—101°, distilling without decomposition at 280°/25 mm., is obtained. By the action of thionyl chloride on this,  $\alpha$ -chloro- $\alpha\gamma$ -triphenyl- $\beta\beta$ -dimethylpropane is obtained. Dehydration of the alcohol by means of a mixture of

acetic anhydride and acetyl chloride yields a mixture of two isomeric hydrocarbons,  $C_{23}H_{22}$ , difficult to separate, m. p.  $110^{\circ}$  and  $89.9^{\circ}$  respectively. The latter is converted into the former on treatment with a solution of hydrogen bromide in acetic acid. Dehydration by the action of heat ( $300\text{--}350^{\circ}$  at 25 mm.) in the presence of infusorial earth yields isobutylbenzene, b. p.  $171^{\circ}$ , benzophenone, and the hydrocarbon, m. p.  $110^{\circ}$ . J. W. B.

**Application of the Grignard Reaction to some Acetylenic Compounds. II.** F. J. WILSON and W. MCN. HYSLOP (*J. Chem. Soc.*, 1924, **125**, 1556—1558; cf. *ibid.*, 1923, **123**, 2612).—On heating with sulphuric acid,  $\alpha\theta$ -diphenyl- $\gamma\zeta$ -dimethyl- $\Delta^{\alpha\gamma}$ -octadiene- $\gamma\zeta$ -diol ( $\alpha$  modification) is converted into 2:5-diphenylacetylenyl-2:5-dimethyltetrahydrofuran, b. p.  $206\text{--}207^{\circ}/0.5$  mm. Except for some charring,  $\alpha\zeta$ -diphenyl- $\gamma\delta$ -dimethyl- $\Delta^{\alpha\epsilon}$ -hexadiene- $\gamma\delta$ -diol was not affected by this treatment. With sodium hydroxide solution both glycols gave, as the only recognisable product, phenylacetylene. Attempts were made to obtain acetylenic ketols. Diacetyl and magnesium phenylacetylenyl bromide gave  $\alpha$ -phenyl- $\gamma$ -methyl- $\Delta^{\alpha}$ -pentinene- $\gamma$ -ol- $\delta$ -one, b. p.  $120^{\circ}/0.5$  mm. (semicarbazone, m. p.  $171\text{--}172^{\circ}$ ), together with the glycol previously described. When acetonylacetone was subjected to this reaction, only the glycol was obtained. Two tetra-acetylenic glycols have been prepared:  $\alpha\alpha\beta\beta$ -tetraphenylacetylenylethylene glycol (m. p.  $147^{\circ}$ ) from ethyl oxalate and magnesium phenylacetylenyl bromide, and  $\alpha\alpha\delta\delta$ -tetraphenylacetylenyl- $\alpha\delta$ -butylene glycol (m. p.  $134\text{--}136^{\circ}$ ) from ethyl succinate and the same Grignard reagent. W. E. E.

**Glycol Ethers of certain Aromatic Nitrohydroxy Compounds.** O. MATTER (D.R.-P. 379881; from *Chem. Zentr.*, 1924, i, 1103—1104).—*p*-Nitrophenyl hydroxyethyl ether,



from *p*-chloronitrobenzene and ethylene glycol, has m. p.  $96\text{--}97^{\circ}$ . *o*-Nitrophenyl hydroxyethyl ether, m. p.  $37\text{--}38^{\circ}$ , and 4-nitronaphthyl hydroxyethyl ether, m. p.  $131\text{--}132^{\circ}$ , were also prepared.

G. W. R.

**Thiophenols. VIII. 5-Chloro-2-methylthioltriphenylcarbinols.** K. BRAND and W. GROEBE (*J. pr. Chem.*, 1924, [ii], **108**, 1—18; cf. this vol., i, 852).—By reduction of 4-chloro-2-nitrophenyl methyl sulphide in methyl-alcoholic solution with iron and concentrated hydrochloric acid in presence of copper chloride, 4-chloro-2-aminophenyl methyl sulphide is obtained, m. p.  $29^{\circ}$ , b. p.  $273\text{--}274^{\circ}$ ,  $d_{25}^{25}$  1.2754,  $n_D^{25}$  1.63118; hydrochloride, m. p.  $198\text{--}199^{\circ}$ ; nitrate, unstable, m. p.  $148\text{--}158^{\circ}$ ; sulphate, m. p.  $138\text{--}140^{\circ}$  (decomp.); formyl derivative, m. p.  $79\text{--}80^{\circ}$ ; acetyl derivative, m. p.  $95\text{--}96^{\circ}$ ; benzoyl derivative, m. p.  $105\text{--}106^{\circ}$ . Through the diazonium compound (sulphate), the amino compound was converted into: 4-chloro-2-bromophenyl methyl sulphide, m. p.  $32\text{--}33^{\circ}$ ; b. p.  $140\text{--}150^{\circ}/15$  mm.;  $d_{25}^{25}$  1.6315;  $n_D^{16}$  1.64223; 2:4-dichlorophenyl methyl sulphide, b. p.  $135\text{--}140^{\circ}/15$  mm.;  $d_{25}^{25}$  1.3633;  $n_D^{26}$  1.61678; 4-chloro-2-iodophenyl methyl sulphide, m. p.  $26\text{--}27^{\circ}$ ,



b. p. 175—185°/15 mm.;  $d^{25}_D$  1.881;  $n^{25}_D$  1.6857. When the last was heated with copper bronze at 260—280° it gave 5:5'-dichloro-2:2'-dimethylthioltriphenyl, m. p. 160°. 4-Chloro-2-cyanophenyl methyl sulphide, m. p. 104—105°, is hydrolysed by boiling alcoholic potassium hydroxide to 5-chloro-2-methylthiolbenzoic acid, m. p. 184—185°; methyl ester, m. p. 65—66°. 4-Chloro-2-hydroxyphenyl methyl sulphide was only obtained in poor yield from the above diazonium sulphate; its benzoyl derivative has m. p. 72°.

The magnesium compound of 4-chloro-2-bromophenyl methyl sulphide reacts with benzophenone in presence of a trace of iodine to form 5-chloro-2-methylthioltriphenylcarbinol, m. p. 111—112°, slightly volatile in steam; the corresponding chloride begins to decompose at 114°, m. p. 128°; in concentrated acids the colour is yellowish-green. 5-Chloro-2-methylthioltriphenylmethane has m. p. 97—98°; with methyl sulphate it forms a sulphonium methosulphate, m. p. 186—187°.

Ethyl benzoate reacts with magnesium 5-chloro-2-methylthiolphenyl bromide to form 5:5'-dichloro-2:2'-dimethylthioltriphenylcarbinol, m. p. 134—135°; the unstable chloride has m. p. 115—126°. 5:5'-Dichloro-2:2'-dimethylthioltriphenylmethane has m. p. 120—121°.

From 4-chloro-2-bromophenyl methyl sulphide and methyl 5-chloro-2-methylthiolbenzoate by the Grignard reaction was obtained 5:5':5''-trichloro-2:2':2''-trimethylthioltriphenylcarbinol, prisms, m. p. 171—172°, from alcohol and rhombs, m. p. 181—182° from benzene. In a mixture of acetic and sulphuric acids it gives a yellowish-green colour, changing to yellow and then disappearing; the chloride reddens at 160°, and has m. p. 170° (decomp.), and the corresponding triphenylmethane has m. p. 125—126°. p-Chlorophenyl methyl sulphide has b. p. 170°. E. H. R.

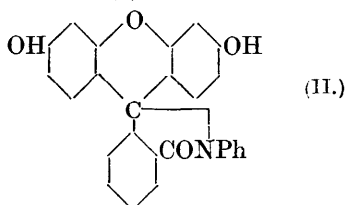
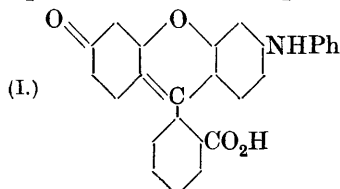
**Thiophenols. IX. o-Ethylthioltriphenylcarbinols.** K. BRAND and H. STEIN (*J. pr. Chem.*, 1924, [ii], 108, 19—28).—o-Nitrophenyl ethyl sulphide, obtained by reduction of oo'-dinitrophenyl disulphide (Brand, A., 1909, i, 855) followed by ethylation of the o-nitrophenylmercaptan, has b. p. 172°/10 mm.,  $d^{18}_D$  1.262,  $n^{18}_D$  1.62126. It is reduced by iron and hydrochloric acid (cf. preceding abstract) to o-aminophenyl ethyl sulphide, b. p. 144°/15 mm.,  $d^{18}_D$  1.087,  $n^{18}_D$  1.60324. By Sandmeyer's method the last was converted into o-bromophenyl ethyl sulphide, b. p. 148°/15 mm.,  $d^{18}_D$  1.4224,  $n^{18}_D$  1.60904; o-iodophenyl ethyl sulphide, b. p. 181°/40 mm.,  $d^{18}_D$  1.677,  $n^{18}_D$  1.65687; and o-cyanophenyl ethyl sulphide, b. p. 170°/15 mm.,  $d^{18}_D$  1.110,  $n^{18}_D$  1.58570.

Magnesium o-ethylthiolphenyl bromide condenses with benzophenone to give o-ethylthioltriphenylcarbinol, m. p. 94°; the corresponding chloride has m. p. 117° and o-ethylthioltriphenylmethane, m. p. 52°.

oo'-Diethylthioltriphenylcarbinol, m. p. 124°, is obtained by the interaction of the above magnesium compound and ethyl benzoate. The corresponding chloride could not be obtained, but reduction of the carbinol by the method of Kauffmann and Pannwitz (A., 1912, i, 351) gave oo'-diethylthioltriphenylmethane, m. p. 98°.

*Ethyl o-ethylthiolbenzoate* has m. p.  $28^{\circ}$ , b. p.  $152^{\circ}/10$  mm.,  $d_{20}^{30}$  1.118,  $n_D^{30}$  1.56309. It reacts with the above magnesium compound to give oo'o''-triethylthioltriphenylcarbinol, m. p.  $96^{\circ}$ ; the corresponding *chloride* has m. p.  $134^{\circ}$ . The colour reactions of the carbinols described are similar to those of the corresponding *o*-methylthiol derivatives (cf. preceding abstract). E. H. R.

**Condensation of Fluorescein and Aniline Homologues in Presence of Hydrochloric Acid.** T. MAKI (*J. Chem. Ind., Japan*, 1924, 27, 1—15).—When fluorescein (1 mol.) is heated with aniline, *o*- or *p*-toluidine (7 mols.), and hydrochloric acid (1 mol.) at  $210^{\circ}$ , a mixture of colourless and coloured anilides or toluidides is produced as follows: *fluoresceinanilide*,  $C_{26}H_{17}O_4N$ , colourless, m. p.  $310$ — $311^{\circ}$ , and purple, m. p.  $311$ — $312^{\circ}$ ; *fluorescein-o-toluidide*,  $C_{27}H_{19}O_4N$ , colourless, m. p.  $323$ — $324^{\circ}$ , and red, m. p.  $317$ — $318^{\circ}$ ; and *fluorescein-p-toluidide*,  $C_{27}H_{19}O_4N$ , colourless, m. p.  $322$ — $323^{\circ}$  (uncor.), and violet, m. p.  $333$ — $334^{\circ}$  (uncor.). The colourless anilide gives a *diacetyl* derivative, m. p.  $252$ — $253^{\circ}$ , and the purple one a *monoacetyl* derivative, m. p.  $159$ — $160^{\circ}$ . The absorption curve and the position of the point of maximum absorption of the purple anilide indicate a quinonoid structure (I) for this isomeride.



The wave-lengths of the points of maximum absorption of the purple anilide and its homologues are as follows: purple anilide, 5550, red *o*-toluidide, 5330, violet *p*-toluidide, 5570. It is considered that the lactone form of fluorescein is converted into the purple anilide and that the colourless anilide is derived from the quinonoid form of fluorescein. Formula II is suggested for the colourless anilide. K. K.

**Preparation of Nitriles from Acid Amides.** FARBWEEKE VORM. MEISTER, LUCIUS, UND BRÜNING, E. SCHIRM, and F. HENLE (D.R.-P. 380323; from *Chem. Zentr.*, 1924, i, 1272).—Nitriles are prepared by the action of sulphochlorides of the benzene or naphthalene series on acid amides in the presence of alkali halides or of tertiary bases. Acetonitrile and benzonitrile are prepared from the corresponding amides. G. W. R.

***o*-Aminobenzenecarboxylic Acids.** KALLE U. CO., AKT.-GES. and M. SCHMIDT (D.R.-P. 375616; from *Chem. Zentr.*, 1924, i, 966).—*o*-Aminocarboxylic acids are prepared by oxidation of isatin and its derivatives, particularly with hydrogen peroxide in alkaline solution. 5-Bromo-2-amino-*m*-toluic acid has m. p.  $229^{\circ}$ .

G. W. R.  
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**N-Substituted Derivatives of Aminobenzoic Acid.** C. F. BOEHRINGER U. SOEHNE G.M.B.H. (Austr. Pat. 94307; Swiss Pat. 101513; from *Chem. Zentr.*, 1924, i, 1595).—The following new compounds are mentioned: N-2-phenylquinoline-4-carboxylanthr-anilic acid,  $C_9H_5N(Ph) \cdot CO \cdot NH \cdot C_6H_4 \cdot CO_2H$ , m. p. 226—227°; 2-(2'-carboxyphenylamino)quinoline-4-carboxylic acid,  $CO_2H \cdot C_9H_5N \cdot NH \cdot C_6H_4 \cdot CO_2H$ , m. p. 301° (decomp.), dimethyl ester, m. p. 164°; N-2-phenyl-6-methyl-quinoline-4-carboxylanthr-anilic acid, m. p. 212°, methyl ester, m. p. 155—156°; condensation compound from 2-phenylquinoline-4-carboxylic chloride and 4-chloroanthranilic acid; 2-(2'-carboxy-4'-hydroxyphenylamino)quinoline-4-carboxylic acid, m. p. about 280°; condensation compound from 2-phenylquinoline-4-carboxylic chloride and *p*-aminobenzoic acid, m. p. 282°; the corresponding compound with *m*-aminobenzoic acid, m. p. 287°; 2-(3'-carboxy-phenylamino)quinoline-4-carboxylic acid and 2-(4'-carboxyphenyl-amino)quinoline-4-carboxylic acid, m. p. above 305°. G. W. R.

**Formula of Anthranil.** E. BAMBERGER (*Helv. Chim. Acta*, 1924, 7, 814—815).—Objections are raised (cf. A., 1903, i, 432, etc.) to the "nitron" formula suggested by Staudinger and Miescher (A., 1919, i, 584). W. A. S.

**Catalytic Racemisation of the Diastereoisomeric *l*-Menthyl Phenylbromoacetates.** A. MCKENZIE and I. A. SMITH (*J. Chem. Soc.*, 1924, 125, 1582—1593; cf. *ibid.*, 1923, 123, 1962).—The production of *l*-menthyl  $\alpha$ -phenylbromoacetate in the esterification of *l*-phenylbromoacetic acid by *l*-menthol in the presence of hydrogen chloride shows that *l*-phenylbromoacetic acid is catalytically racemised by hydrogen chloride; *l*-menthol + *l*-phenylbromoacetic acid  $\rightarrow$  *l*-menthyl *l*-phenylbromoacetate + *l*-menthyl *d*-phenylbromoacetate. Crystallisation of the mixture gives the *d*-isomeride. When heated with alcoholic hydrogen chloride, the *d*-ester racemises to a mixture of *d*- and *l*-esters, in which the *l*-ester slightly predominates. When esterified in the presence of sulphuric acid, the *d*-acid gives *d*-ester. One or two drops of alcoholic alkali produce catalytic racemisation, the rate of which is greater in the case of *d*-ester than in the case of *l*-ester. Moreover, notably in the case of *l*-menthyl *d*-phenylchloroacetate, the proportions of the two optical isomerides at the end of the racemisation were not equal. The cause of this can be ascribed to the directive influence of the asymmetrical *l*-menthyl group. The following compounds are described:—*l*-Menthyl *d*-phenylbromoacetate, m. p. 78—79°,  $[\alpha]_D^{18} + 9.4^\circ$ ,  $[\alpha]_{5461}^{18} + 13.2^\circ$  in ethyl alcohol. *l*-Menthyl *l*-phenylbromoacetate, m. p. 40—41°,  $[\alpha]_D^{15} - 146.1^\circ$ ,  $[\alpha]_{5461}^{15} - 172.8^\circ$  in ethyl alcohol;  $[\alpha]_D^{17} - 139.8^\circ$ ,  $[\alpha]_{5461}^{17} - 166.9^\circ$  in benzene. *l*-Phenylbromoacetic acid has  $[\alpha]_D^{14} - 147.7^\circ$  in benzene. W. E. E.

**Constitution of Curcumone from Curcuma [Turmeric] Oil.** H. RUPE and F. WIEDERKEHR (*Helv. Chim. Acta*, 1924, 7, 654—669; cf. A., 1911, i, 293).—When curcuma oil is treated with ozone an acid is obtained which is now shown to be identical with (not, as

was at first supposed, different from) curcumatic acid,  $C_{11}H_{14}O_2$ . The latter has m. p. 42—43°, b. p. 163—164°/10 mm.,  $[\alpha]_D^{20} + 46.53^\circ$  or  $+47.58^\circ$  according to the method of preparation. Its *ethyl* ester has b. p. 133—134°/10 mm.; the *calcium* and *silver* salts of the acid are described.

*p*-Tolyl methyl ketone reacts with ethyl bromoacetate and zinc to give a mixture of esters (b. p. 150—153°/9 mm.) which, when hydrolysed by alcoholic potassium hydroxide yields chiefly *p*-tolyl- $\Delta^a$ -butenoic acid, needles, m. p. 135°, together with a little  $\beta$ -hydroxy- $\beta$ -*p*-tolylbutyric acid. *Ethyl p*-tolyl- $\Delta^a$ -butenoate has b. p. 145—156°/10 mm. When *p*-tolyl- $\Delta^a$ -butenoic acid is reduced with hydrogen and a nickel catalyst,  $\beta$ -*p*-tolylbutyric acid,  $C_{11}H_{14}O_2$ , m. p. 91°, b. p. 165°/10 mm., is formed; its *chloride* has b. p. 125°/9 mm.; the *p*-toluidide, m. p. 112—113°, the *ethyl* ester, b. p. 133—135°/10 mm., and the *calcium* salt are described. This synthetic acid has the same b. p. as curcumatic acid; the esters also resemble one another. Only in m. p. and optical activity do the two acids differ. They give similar products when oxidised with cold dilute potassium permanganate solution: curcumatic acid yields *p*-tolyl methyl ketone and an optically active dibasic acid,  $C_{11}H_{12}O_4$ , m. p. 227—229°,  $[\alpha]_D^{20} + 35.34^\circ$ , whilst the synthetic acid yields *p*-tolyl methyl ketone and an optically inactive acid of the same composition and m. p. (226°), presumably  $\beta$ -*p*-carboxyphenylbutyric acid. A mixture of the two acids has m. p. 225—227°. Curcumatic acid is thus proved to be *d*- $\beta$ -*p*-tolylbutyric acid.

$\beta$ -*p*-Tolylbutyryl chloride and zinc methyl yield  $\beta$ -*p*-tolylpropyl methyl ketone,  $Me \cdot C_6H_4 \cdot CHMe \cdot CH_2 \cdot CO \cdot Me$ , b. p. 130.5°/11 mm.,  $d_4^{20}$  0.9598; *oxime*, b. p. 165—166°/13 mm., *semicarbazone*, m. p. 145—146°, *azine*, b. p. 245—246°/11 mm., *benzylidene* derivative, m. p. 88°. Curcumone has b. p. 130°/11 mm.,  $d_4^{20}$  0.9618; it yields an optically active *oxime*, b. p. 165—166°/13 mm., a *semicarbazone*, m. p. 121°, an optically active *azine*, b. p. 245—246°/11 mm., and a *benzylidene* derivative, m. p. 106°. Curcumone is therefore *d*- $\beta$ -*p*-tolylpropyl methyl ketone.

Before the true nature of the acid obtained by ozonising curcuma oil was discovered attempts were made to reproduce it synthetically. When *p*-tolylacetonitrile is treated in ethereal solution with sodamide followed by methyl iodide, it affords the nitrile of *p*-methylhydratropic acid (b. p. 123°/12.5 mm.; cf. Errera, A., 1892, 605) which, on hydrolysis, yields *p*-methylhydratropic acid, m. p. 34°, b. p. 161—161.5°/12.5 mm., *chloride*, b. p. 122—123°/13.5 mm., *amide*, m. p. 195°, *p*-toluidide, m. p. 102—103°. The latter is accompanied by a little *p*-tolylaceto-*p*-toluidide, m. p. 163°, and after purification serves as a convenient source of pure samples of the parent acid. *Ethyl p*-methylhydratropate has b. p. 123.5°/11 mm. Similarly, by using ethyl iodide in the first reaction,  $\alpha$ -*p*-tolylbutyric acid, m. p. 67—68°, b. p. 160—161°/11 mm., is prepared, *via* its *nitrile*, b. p. 135°/14 mm. The *chloride* has b. p. 118—120°/12 mm., the *amide* m. p. 105°, the *p*-toluidide m. p. 118°; the *methyl* ester (b. p. 123°/10 mm.), the *ethyl* ester (b. p. 130°/11.5 mm.), and the *magnesium* salt also are described.

W. A. S.

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**Acid Constituents of the Gum of the Aleppo Pine. I.  $\alpha$ - and  $\beta$ -Alepic Acids.** G. DUPONT (*Bull. Soc. chim.*, 1924, [iv], 35, 879—889).—The gum is separated by compression into solid and liquid constituents. By dissolving the dry solid in the minimum amount of cold ethyl alcohol and fractionally precipitating with water, samples are obtained which on rapid recrystallisation from cold acetone give a mixture of crystals of two isomeric acids,  $C_{20}H_{30}O_2$ , termed  $\alpha$ - and  $\beta$ -alepic acids. The crystalline forms of the two acids are distinct.  $\alpha$ -Alepic acid forms orthorhombic prisms, m. p.  $148^\circ$ ,  $[\alpha]_D -66^\circ$ ;  $\beta$ -alepic acid forms clinorhombic prisms, m. p.  $157$ — $159^\circ$ ,  $[\alpha]_D -66.8^\circ$ . Both acids are easily isomerised to  $\alpha$ -abietic acid, especially in alcoholic solution in presence of a trace of hydrochloric acid. The rotatory power of the  $\alpha$ -acid falls to  $[\alpha]_D -12.4^\circ$  and then rises to  $[\alpha]_D -84.4^\circ$ , whereas the minimum value shown by the  $\beta$ -acid under these conditions is  $[\alpha]_D -55.0^\circ$ , rising finally to  $[\alpha]_D -86.0^\circ$ , the value for  $\alpha$ -abietic acid being  $-104^\circ$ , and m. p.  $173^\circ$ .

The author considers that in the change from  $\alpha$ -alepic acid to  $\alpha$ -abietic acid, an intermediate alepabietic acid is first formed, whereas the  $\beta$ -acid changes directly into  $\alpha$ -abietic acid.  $\alpha$ -Abietic acid was isolated from the last of the fractional precipitations by water from the alcoholic solution of the pressed gum, which contains about 75% of  $\alpha$ - and 25% of  $\beta$ -alepic acid. A. E. C.

**Acids contained in the Gum of the Aleppo Pine. II.** G. DUPONT and L. DESALBRES (*Bull. Soc. chim.*, 1924, [iv], 35, 890—892).—The authors have isolated alepabietic acid (cf. preceding abstract) and shown that  $\beta$ -alepic acid is merely an isomorphous mixture of alepabietic acid and abietic acid. Aleppo pine gum contains  $\alpha$ -alepic acid and a certain amount of alepabietic acid and abietic acid. The isomorphism of the two latter acids is proved by crystallographic measurements. A. E. C.

**The Phenylalanine Series. V. Hydrogenation of Tyrosine.** E. WASER and E. BRAUCHLI (*Helv. Chim. Acta*, 1924, 7, 740—758; cf. A., 1923, i, 337, 338).—The physical constants and other properties of hexahydrotyrosine already recorded (*loc. cit.*) are incorrect. When tyrosine is catalytically reduced with platinum black, hexahydrophenylalanine is always produced to some extent. Thus, when the hydrogenation is carried out in acid solution, about 75% of the material suffers this change; in neutral suspension, 40—44%; in alkaline suspension very little, *viz.*, only about 16%. Only a little alkali is needed (0.04 equivalent of potassium hydroxide); if one equivalent be present, practically no action takes place. Phenol behaves in a similar way (cf. Willstätter and Hatt, A., 1912, i, 845). Pure hexahydrotyrosine was separated as the ethyl ester. The regenerated 1-hexahydrotyrosine has m. p. (in a sealed tube, quickly heated)  $285^\circ$  (decomp.),  $[\alpha]_D^{20} +14.65^\circ$  (in acid solution); its hydrochloride has m. p.  $238^\circ$  (decomp.). The ethyl ester (which cannot be obtained by hydrogenating tyrosine ester, only hexahydrophenylalanine ester being formed) has m. p. 99—100°, b. p.  $184.5^\circ/11$  mm.,  $[\alpha]_D^{20} +15.19^\circ$ ; hydrochloride, m. p.  $261^\circ$  (decomp.). N-p-Nitro-

*benzoylhexahydrotyrosine* has m. p. 225—226°. 3 : 6-*Di-p-hydroxy-hexahydrobenzyl-2 : 5-diketopiperazine*, which remains behind when the ester is distilled, has m. p. 332° (decomp.). Hexahydrotyrosine yields a *phenylcarbimido* compound, m. p. 112° (1H<sub>2</sub>O) or 141° (decomp. 145° (anhydrous)); when a solution containing this compound and sulphuric acid is evaporated, the *phenylhydantoin* derivative, m. p. 206.5°, is obtained. *l*-Hexahydrophenylalanine, separated from the above, has m. p. 324° (decomp.) or 282° (decomp.), and  $[\alpha]_D^{20} + 13.30^\circ$ ; its hydrochloride has m. p. 246°; the chloroplatinate, benzoyl, and other derivatives have already been described (*loc. cit.*) as hexahydrotyrosine chloroplatinate, etc. The *ethyl* ester, obtained as described, either directly or by hydrogenating tyrosine ethyl ester, has b. p. 149—150°/11 mm.,  $[\alpha]_D^{20} + 11.45^\circ$ , and forms a *hydrochloride*, m. p. 195—196°. When *d*-phenylalanine is hydrogenated the *l*-isomeride ( $[\alpha]_D^{20} + 13.32^\circ$ ) is produced, and the racemic form, also with m. p. 246°, is obtained from *dl*-phenylalanine. When tyramine and *p*-methoxyphenylalanine are catalytically reduced the chief product, in both cases, is *cyclohexyl-ethylamine*.

*Addendum.* A New Characteristic Colour Reaction for  $\alpha$ -Amino-acids.—When 1 mg. or more of an  $\alpha$ -amino-acid (23 compounds gave positive results) is dissolved in 3—4 c.c. of 10% sodium carbonate solution, the solution heated and a few crystals of *p*-nitrobenzoyl chloride are added, a transient but very intense dark red or violet coloration is produced. The reaction is specific for nitrobenzoyl chloride and, as stated, for  $\alpha$ -amino-acids, with the exception of glycine and cystine.

W. A. S.

**$\alpha$ -Naphthol-4-carboxyarylamides.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 100363, 100364, 100365; from *Chem. Zentr.*, 1924, i, 2011; cf. this vol., i, 173).—The following compounds are described:  $\alpha$ -naphthol-4-carboxy-*o*-toluidide, m. p. 238°;  $\alpha$ -naphthol-4-carboxy-*p*-toluidide, m. p. 215°;  $\alpha$ -naphthol-4-carboxy-*N*-methylanilide, m. p. 232°.

G. W. R.

**Ketobutyric Acids.** FARBWERKE VORM. MEISTER, LUCIUS, U. BRÜNING and F. MAYER (D.R.-P. 376635; from *Chem. Zentr.*, 1924, i, 966—967).—Ketobutyric acids are obtained by the condensation of succinic anhydride with hydrocarbons and their derivatives. Condensation compounds (ketobutyric acids) of succinic anhydride with the following compounds are mentioned: with  $\alpha$ -naphthyl methyl ether, m. p. 174°; with fluorene, m. p. 109°; with anthracene, m. p. 160°; with diphenylene oxide, m. p. 185°; with acenaphthene, m. p. about 202—203°; with dihydroanthracene, m. p. 156.5—157.5°.

G. W. R.

**Aromatic Dimethylamines.** KALLE UND CO., AKT.-GES. (D.R.-P. 375463; from *Chem. Zentr.*, 1924, i, 966).—Phenyliminodiacetic acid or its derivatives are treated with ferrous sulphate, ferric sulphate, or ferric oxide in acid solution. The following compounds are mentioned: *o*-tolyliminodiacetic acid; dimethyl-

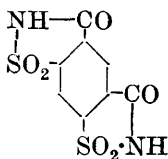
*o*-toluidine; *p*-ethoxyphenyliminodiacetic acid, m. p. 120°; dimethyl-*p*-phenetidine.  
G. W. R.

**Melting Point of Acetylsalicylic Acid.** M. E. PUTNAM (*Ind. Eng. Chem.*, 1924, **16**, 778).—The melting point of pure acetylsalicylic acid, considered as the temperature of formation of the first liquid globule in a sample contained in a melting-point tube inserted in a bath at 130°, the temperature of which is rising at exactly 3° per minute, is 133.5°.  
F. G. W.

**s-N-Aminophthalimide.** M. A. MIHĂILESCU and L. FLORESCU (*Bull. Acad. Sci. Roumaine*, 1923, **8**, 303—320; cf. A., 1912, i, 311).—The action of a concentrated aqueous solution of hydrazine sulphate and sodium acetate on a boiling solution of phthalic anhydride in glacial acetic acid yields a product isomeric with those previously obtained by Rottemburg (A., 1894, i, 285) and Försterling (A., 1895, i, 354) to which the constitution  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} N \cdot NH_2$  is attributed. *s*-N-Aminophthalimide melts above 340° without subliming. It is sparingly soluble in hot water, hydrolysing slightly to *N*-aminophthalamic acid. The potassium salt,  $C_8H_7O_5N_2K$ , is identical with that obtained by Försterling from phthalylhydrazide,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$ , to which accordingly the structure  $C_6H_4(CO_2K)CO \cdot NH \cdot NH_2$  is now assigned. Only monometallic salts could be obtained and these are precipitated from solution by alcohol, but not by carbon dioxide. They are converted by acids into the original *N*-aminophthalimide. *Diacetyl-N-aminophthalimide*, m. p. 132°, by crystallisation from alcohol or boiling water is converted into the *monoacetyl* derivative,  $C_{10}H_8O_3N_2$ , m. p. 170°. The *monobenzoyl* derivative, m. p. 220—222°, sublimes at 200°. No condensation product could be obtained with acetone or with aliphatic aldehydes or with benzaldehyde. *N*-Aminophthalimide and cinnamaldehyde yield *cinnamylidene-N-aminophthalimide*,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} N \cdot N : CH : CH : CHPh$ , m. p. 224°. *p*-Methoxycinnamylidene-*N*-aminophthalimide has m. p. 188—190°. R. B.

**Disaccharins.** A. F. HOLLEMAN and H. J. CHOUFOER (*Proc. K. Akad. Wetensch., Amsterdam*, 1924, **27**, 353—360).—The compound of m. p. 129° described by Wischin (A., 1891, 73) as 1:3-xylene-2:4-disulphochloride on account of its conversion, by heating with phosphorus pentachloride, into 2:4-dichloro-*m*-xylene, has been shown to be the dichloride of the 4:6-disulphonic acid by synthesis from 6-nitro-*m*-xylene by the following steps:  $C_6H_3Me_2NO_2(1:3:6) \rightarrow C_6H_2Me_2(SO_3H) \cdot NO_2(1:3:4:6) \rightarrow C_6H_2Me_2(SO_3H) \cdot NH_2 \rightarrow C_6H_2Me_2(SO_3H) \cdot SH \rightarrow C_6H_2Me_2(SO_3H)_2(1:3:4:6)$ ; cf. Pfannenstill (Dissertation, Lund, 1894), and Pollak and Lustig (this vol., i, 30). Some change of orientation must therefore have occurred in Wischin's experiment. This disulphochloride is also the chief product of the action of chlorosulphonic acid on *m*-xylene. It yields a *disulphonamide*, m. p.

249°, which is oxidised by permanganate to the *disaccharin*, isophthalicdisulphinide (annexed formula), m. p. 268—270°, of acid and bitter taste.



The other possible disaccharin derived from *m*-xylene has not yet been prepared, but the oily disulphochloride of a disulphonic acid isolated as a by-product in the sulphonation of *m*-xylene-2-sulphonic acid (Pfannenstill, *loc. cit.*) probably has the required structure,  $C_6H_2Me_2(SO_3H)_2(1:3:2:4)$ . It yields a *disulphonamide*, m. p. 220°.

Direct sulphonation of *p*-xylene yields the 2:6-disulphonic acid, and its disulphonamide does not yield a di-imide on oxidation. *p*-Xylene-2:5-disulphonic acid was synthesised from the *p*-xylylene-sulphonic acid,  $C_6H_2Me_2(NH_2)(SO_3H)(1:4:2:5)$ , by replacing the amino group by a sulphonic group. The *disulphochloride*, m. p. 162°, is identical with a by-product observed by Pfannenstill in the action of chlorosulphonic acid on *p*-xylene. It yields a *disulphonamide*, m. p. 310°, oxidised by permanganate to *terephthalic-2:5-disulphinide*, m. p. 320°, of bitter taste.

A liquid *o*-xylenedisulphochloride was prepared through the stages:  $C_6H_2Me_2(NH_2)(1:2:6) \rightarrow C_6H_2Me_2(SO_3H) \cdot NH_2(1:2:3:6) \rightarrow C_6H_2Me_2(SO_3H) \cdot SH \rightarrow C_6H_2Me_2(SO_3H)_2$ , but the orientation of these compounds has not been finally established. The chloride yields a *disulphonamide*, m. p. 251°, converted by permanganate into a *phthalicdisulphinide*, m. p. 275—280°, of bitter taste.

G. M. B.

**Ester of Cholic Acid.** GEHE U. CO., AKT.-GES., and H. REUME (D.R.-P. 375370 and 381350; from *Chem. Zentr.*, 1924, i, 969).—*Benzyl cholate* is a greyish-white powder, softening at about 69°.

G. W. R.

**Additive Compounds of Cholic Acid.** C. H. BOEHRINGER SOHN, CHEMISCHE FABRIK (D.R.-P. 376470; from *Chem. Zentr.*, 1924, i, 968—969).—The preparation of *additive* compounds of cholic acid with the following aliphatic esters is described: ethyl lactate; amyl acetate; ethyl carbamate; ethyl chloromalonate; bornyl valerate; ethyl butyrate.

G. W. R.

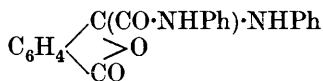
**Derivatives of *p*-Aminophenol.** KALLE U. CO., AKT.-GES., and E. SPRÖNGERTS (D.R.-P. 383190; from *Chem. Zentr.*, 1924, i, 1592).—The following new compounds are mentioned: *p*-ethoxyphenyliminodiacetic acid, from *p*-phenetidine and chloroacetic acid, m. p. 118° (decomp.); *p*-hydroxyphenyliminodiacetic acid, from *p*-aminophenol and chloroacetic acid, m. p. 165° (decomp.).

G. W. R.

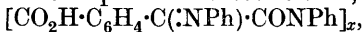
**Constitution of Phthalonic Acid. Its Compounds with Aniline.** A. CORNILLON (*Compt. rend.*, 1924, 179, 274—276; cf. this vol., i, 288, 515).—Evidence for the structure of phthalon-2-anilic acid and phthalondianilide, prepared by Kuroda and Perkin (T., 1923, 123, 2094), is deduced. The dianilide is stable



towards acids and dissolves in concentrated solutions of alkalis and therefore possesses the lactonic structure,



It does not react with semicarbazide, but reacts readily as a secondary amine to yield a *phenylurethane*, m. p. 203·5°. The structure is confirmed by its synthesis from aniline and the anilide of  $\alpha$ -chlorophthalonic acid. The anilic acid reacts with excess of aniline in benzene solution to yield only the dianilide (the aniline  $\alpha$ -anilino- $\alpha$ -hydroxyhomophthalanilate described by Kuroda and Perkin, *loc. cit.*, not being obtained) and therefore behaves as if it possessed the lactonic structure. In alcohol solution, however, a small quantity of an amorphous acid which has the same empirical formula as the dianilide and yields colloidal solutions is obtained. This is the *phenylimine* of phthalon-2-anilic acid,



and can only be derived from the ketonic form of the anilic acid. The action of thionyl chloride on the anilic acid yields the anilide of  $\alpha$ -chlorophthalonic acid as the main product but in addition a small quantity of the *N-phenylphthalonimide*, m. p. 217°, is produced by dehydration of the ketonic form. The anilic acid thus reacts mainly in its lactonic form but contains a small quantity of the ketonic modification.

J. W. B.

**$\alpha$ - and  $\beta$ -Disalicylides.** R. ANSCHÜTZ and K. RIEPENKRÖGER (*Annalen*, 1924, **439**, 1—8; cf. A., 1920, i, 48).—Salicyloyl chloride heated at 20 mm. begins to lose hydrogen chloride at 110°, decomposition being complete at 180°, and the chloroform solution of the product deposits polysalicylide, whilst the mother-liquor contains the tetrasalicylide. *o*-Diplosal chloride (*o*-salicyloylsalicyloyl chloride) similarly yields a mixture of the poly- and tetra-salicylides. The  $\alpha$ -disalicylide is also obtained when diethylaniline is added to an ice-cold solution of salicyloyl chloride in benzene. The product obtained by the action of  $\alpha$ -disalicylide on aniline or *p*-toluidine is shown to be the *N*-salicyloyl derivative of the base by the conversion of *o*-diplosalanilide into *O*-acetyl-*o*-diplosalanilide, m. p. 140—141°, which is also obtained by the action of aniline in dry ether on *O*-acetyl-*o*-diplosal chloride, m. p. 104—105°. *o*-Diplosal-amide on heating is converted into disalicyloylimide. By excess of ammonia the amide is converted into the ammonium salt of the imide, and by acetyl chloride, in the presence of pyridine, into *O*-acetyl-*o*-diplosalamide,  $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CONH}_2$ , m. p. 158—159°. *Diacetyldisalicyloylimide*,  $(\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO})_2\text{NH}$ , has m. p. 114—116°. The  $\beta$ -disalicylide treated with an equimolecular quantity of ammonia in chloroform solution, slowly forms only the yellow ammonium salt of the disalicyloylimide, and reacts with aniline only at 155—165°, forming salicoylanilide.

J. W. B.

**$\alpha$ -Dicresotides.** R. ANSCHÜTZ (*Annalen*, 1924, **439**, 8—19).—By the distillation of the three *O*-acetylcresotic acids under reduced

pressure, *o*-, *m*-, and *p*- $\alpha$ -dicresotides corresponding with the disalicylides (cf. preceding abstract) are obtained. No corresponding  $\beta$ -dicresotides were isolated. They are also obtained in good yields by the distillation of the phenyl ester of the respective cresotic acid under 100 mm. Subsequent distillation under 12 mm. yields the dicresotide. By the action of diethylaniline in benzene solution on the *o*-, *m*-, and *p*-cresotoylcresotoyl chlorides (dimethyldiplosal chlorides), hydrogen chloride is split off and the corresponding  $\alpha$ -dicresotide produced. Distillation of the  $\alpha$ -dicresotide under ordinary pressure yields the corresponding dimethylxanthone. The dicresotides give a series of derivatives corresponding with those of the disalicylides.

[With F. POST and E. CORTY.]—Fractional crystallisation, from chloroform, of the product of distillation of acetyl-*o*-cresotic acid yields also the tetra-*o*-cresotide ( $\alpha$ -homosalicylide, A., 1893, i, 166) and by heating under 18 mm. this is practically completely converted into  $\alpha$ -dicresotide. *Methyl o-cresotoyl-o-cresotate* has m. p. 56°. *Di-o-cresotoylimide*,  $[\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}]_2\text{NH}$ , m. p. 170°, with excess of ammonia yields the ammonium salt, from which the corresponding silver, mercury, copper, calcium, strontium, and barium salts are obtained. It forms an anilide, and a *p*-toluidide, m. p. 184°.

[With K. RIEMER and E. CORTY.]— $\alpha$ -Di-*m*-cresotide is identical with that obtained by Einhorn and Mettler (A., 1903, i, 30). *Phenyl acetyl-m-cresotate* has m. p. 71—72°; *m-cresotoylamide*, m. p. 182.5°; *m-cresotoyl-m-cresotic acid*, m. p. 162°, *chloride*, m. p. 122°, *methyl ester*, m. p. 115°, *amide*, which on heating yields the *imide*, m. p. 211—212°, forming an ammonium salt from which the corresponding silver, mercury, copper, calcium, strontium, and barium salts are obtained; *anilide*, m. p. 189°, *p-toluidide*, m. p. 202°.

[With R. INDERHEES and A. LÜSSEM.]— $\alpha$ -Di-*p*-cresotide has m. p. 197—199°. The tetra-*p*-cresotide obtained, by extraction with hot chloroform, from the product of the distillation of acetic acid, acetic anhydride, and *p*-cresotic acid is converted practically completely into the  $\alpha$ -di-*p*-cresotide by distillation under 12 mm.; *p-cresotoyl-p-cresotic acid*, m. p. 128—129°; *chloride*, m. p. 93—95°; *methyl ester*, m. p. 104—105°; *ethyl ester*, m. p. 97—98°; *acetyl derivative*, m. p. 133—134°; *anilide*, m. p. 159—160°, *p-toluidide*, m. p. 176—177°. The amide on heating yields the *imide*, m. p. 173—174°, of which ammonium, silver, mercury, copper, calcium, strontium, and barium salts are described. *Diacetyldi-p-cresotoylimide* has m. p. 140—141°. J. W. B.

**Menthyl  $\alpha\gamma$ -Diacetyl- $\beta$ -methylglutarate.** H. RUPE and F. BECHERER (*Helv. Chim. Acta*, 1924, 7, 670—681).—The following results were obtained in an abortive effort to prepare an alcohol possessing high optical activity. Menthyl acetoacetate (A., 1913, i, 884) and acetaldehyde undergo the Knoevenagel condensation and yield two isomeric forms of *menthyl  $\alpha\gamma$ -diacetyl- $\beta$ -methylglutarate*. The chief product has m. p. 200° and  $[\alpha]_{\text{D}}^{20} -49.01^\circ$ , and affords a *semicarbazone*, m. p. 196—197°; the subsidiary product, not

isolated in every case, has m. p.  $152^{\circ}$  and  $[\alpha]_D^{20} -26.48^{\circ}$ , its *semicarbazone* melting at  $165-166^{\circ}$ . The second form is converted into the first by recrystallisation from benzene, the product having, however,  $[\alpha]_D^{20} -68.01^{\circ}$ . When ethyl  $\alpha\gamma$ -diacetyl- $\beta$ -methylglutarate is heated with one molecular proportion of menthol at  $150-160^{\circ}$ , *menthyl ethyl  $\alpha\gamma$ -diacetyl- $\beta$ -methylglutarate*, m. p.  $154-155^{\circ}$ ,  $[\alpha]_D^{20} -28.99^{\circ}$ , is obtained (*semicarbazone*, m. p.  $169-170^{\circ}$ ); this, heated with more menthol, affords the second form, m. p.  $152-153^{\circ}$ , of the ester described above. The ester of m. p.  $200^{\circ}$  is converted by treatment in ethereal solution with a little hydrogen chloride into *menthyl 5-keto-1:3-dimethyl- $\Delta^6$ -cyclohexene-2:4-dicarboxylate*, m. p.  $185-186^{\circ}$ ,  $[\alpha]_D^{20} -27.90^{\circ}$ , *semicarbazone*, m. p.  $179-180^{\circ}$ , whilst the ester of m. p.  $152^{\circ}$ , similarly treated, yields a stereoisomeric form of this cyclic compound, m. p.  $137-138^{\circ}$ ,  $[\alpha]_D^{20} -56.27^{\circ}$ , *semicarbazone*, m. p.  $104-105^{\circ}$ . The isomerism of the above compounds is discussed, it being pointed out that all three carbon atoms in the glutaric acid "spinal column" are asymmetric. Reduction of the menthyl ethyl  $\alpha\gamma$ -diacetyl- $\beta$ -methylglutarate by Bouveault and Blanc's method failed to give a primary alcohol and hydrolysis of the dimenthyl ester did not take place normally. W. A. S.

**Attempts to Synthesise Benzophenone-2:3':4'-tricarboxylic Acid.** H. DE DIESBACH and P. BULLIARD (*Helv. Chim. Acta*, 1924, 7, 618-627).—Benzophenone-2:3':4'-tricarboxylic acid, Limpricht's "phthaloylphthalic acid," can easily be produced from *o*-xylene, but pure supplies of the latter are not readily obtainable. The preparation of the compound by other methods has therefore been investigated. 3'-Amino-4'-methylbenzophenone-2-carboxylic acid (Limpricht, A., 1898, i, 322) is converted by the Sandmeyer reaction into 3'-cyano-4'-methylbenzophenone-2-carboxylic acid, m. p.  $194^{\circ}$ , of which the *methyl* ester, m. p.  $87.5^{\circ}$ , and the *copper* salt are described. This nitrile is not hydrolysed by sulphuric acid without condensation to anthraquinone derivatives also taking place, but boiling 30% potassium hydroxide converts it into the expected 4'-methylbenzophenone-2:3'-dicarboxylic acid, m. p.  $216^{\circ}$ ; *dimethyl* ester, m. p.  $94^{\circ}$ . Treatment of the nitrile with nitric acid, *d* 1.15 at  $200^{\circ}$  for 8 hours, brings about simultaneous oxidation and hydrolysis, "phthaloylphthalic acid" being obtained. The product has m. p.  $199.5^{\circ}$ , higher than any previously recorded.

The conversion of 2:3'-dichloro- or -dibromo-4'-methylbenzophenone into the corresponding 2:3'-dicarboxylic acid by treatment with cuprous cyanide and pyridine (cf. de Diesbach, A., 1923, i, 804, etc.) was examined as an alternative. The results of the unsuccessful experiments illustrate the conditions under which the replacement of halogen by the cyano group takes place. *o*-Bromobenzophenone, when simply boiled with pyridine and cuprous cyanide for two days, affords *o*-benzoylbenzonitrile, m. p.  $83.5^{\circ}$ , b. p.  $215-225^{\circ}/20$  mm., yielding anthraquinone when treated with sulphuric acid and *o*-benzoylbenzoic acid when submitted to the action of nitric acid, *d* 1.15, at  $150^{\circ}$ . 3-Chloro-4-methylbenzophenone (Heller, A., 1913, i, 631) is not attacked by cuprous cyanide

and pyridine even at 200°. When a mixture of benzoyl chloride and *o*-bromotoluene is treated with aluminium chloride a product is obtained which is stated by Mayer and Freund (A., 1922, i, 865) to be a mixture of 3- and 2-bromo-4-methylbenzophenones. Actually the substance, an oil of b. p. 195—210°/24 mm., interacts with cuprous cyanide and pyridine at 150° to yield an oil from which a small quantity of 3-cyano-4-methylbenzophenone, m. p. 106·5°, convertible into 4-benzoylphthalic acid, is obtained, yet if the crude nitrile be simultaneously oxidised and hydrolysed, and the impure dicarboxylic acid obtained purified by fractional crystallisation of its copper salt, the product is benzophenone-2 : 4-dicarboxylic acid. Thus migration of the bromine atom during the reaction with aluminium chloride, as described by Mayer and Freund, has taken place. When *o*-chlorobenzoyl chloride and *o*-chlorotoluene are treated with aluminium chloride in suspension in carbon disulphide, 2 : 3'-dichloro-4'-methylbenzophenone, m. p. 43·5°, b. p. 220—221°/24 mm., is obtained; the corresponding 3'-chloro-2-bromo-4'-methylbenzophenone, prisms, m. p. 50°, b. p. 229—231°/25 mm., is produced from *o*-bromobenzoyl chloride. When the first of these is treated with cuprous cyanide in pyridine at 200°, or the second at the b. p. of pyridine, 3'-chloro-2-cyano-4'-methylbenzophenone, m. p. 118·5°, is produced, yielding 3-chloro-4-methylbenzophenone-2'-carboxylic acid on hydrolysis. If the reaction with cuprous cyanide in pyridine be carried out at higher temperatures, complex products, still containing chlorine, are obtained; the chlorine atom therefore is not labile. *o*-Bromobenzoyl chloride and *o*-bromotoluene give a mixture of 2 : 3'- and 2 : 2'-dibromo-4'-methylbenzophenones, an oil, b. p. 240—243°/24 mm., solidifying eventually and then melting at 51°. When it is treated for two days with cuprous chloride and pyridine at 150° a mixture is obtained from which, if the pyridine be removed by distillation, a small amount of a dinitrile, m. p. 110°, can be separated; if however, the pyridine be removed by treating the mixture with hydrochloric acid, another product, possibly an amide, m. p. above 250°, is obtained. Both yield "phthaloylphthalic" acid when treated with dilute nitric acid at 200°. A further attempt to prepare phthaloylphthalic acid was based on the replacement, as above, of the chlorine atom in 3'-chloro-4'-methylbenzophenone-2-carboxylic acid, obtained from phthalic anhydride and *o*-chlorotoluene. Actually the chlorine atom remained in its place, but the carboxyl radical was detached, the product of the action of the cuprous cyanide and pyridine at 200° being 3-chloro-4-methylbenzophenone: substitution by the "phthaloyl" radical takes place therefore in the *para*-position to the methyl group, not to the chlorine atom as stated by Heller (*loc. cit.*).

W. A. S.

**Products of Decomposition of Benzaldoxime Peroxide.** E. PARISI (*Gazzetta*, 1924, 54, 485—490; cf. A., 1923, i, 579; this vol., i, 52).—When kept between filter-paper, benzaldoxime peroxide undergoes gradual decomposition, yielding  $\alpha$ -benzaldoxime, benzaldehyde, benzoic acid, benzonitrile, dibenzoylazoxime, and the

*N*-benzoyl derivative of benzhydroxamic acid. A cold 10% solution of potassium hydroxide in alcohol also decomposes the peroxide, with formation of nitrogen, ammonia, nitrous acid,  $\beta$ -benzaloxime, benzoic acid, hydroxamic acid, and dibenzenzylazoxime.

T. H. P.

**Colour and Molecular Geometry. II. Explanation of the Results of Chattaway and Clemo.** J. MOIR (*J. Chem. Soc.*, 1924, 125, 1548—1551; cf. *ibid.*, 1923, 123, 3041).—Alternate single and double bonds do not *per se* imply the possession by the substance of a "high" colour and the experimental results of Chattaway and Clemo are considered to be better accounted for by the orbit theory than by Hewitt's theory. In *p*-nitrobenzaldehyde phenylhydrazone, the orbit of the revolving electron surrounds the chain  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{N}$ . When  $\text{CH}_2$  is substituted for the secondary amino group, the orbit contracts to include only the chain  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N}$ . Hence the wave-length of the characteristic absorption band is decreased and the substance exhibits a lower colour. In *p*-nitrophenylhydrazine and benzyldiene-*p*-nitrobenzylamine, the orbit is assumed to surround the chains  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N}$  and  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N}$ , respectively. Hence the absorption bands of these substances should be, as in fact they are, in nearly the same position. With benzaldehyde-*p*-nitrophenylhydrazone the interfocal distance of the orbit is supposed to be the same as in *p*-nitrophenylhydrazine, but since the orbit now embraces the bulky benzyldiene group, the periodic time of the electron is greater and hence the colour of the substance is higher. In general, the wave-length absorbed increases with the magnitude of the "loading." Results of the spectroscopic examination of some of the substances in the presence and absence of potassium hydroxide are given.

W. E. E.

**Isomerism of the Oximes. XIX. Substituted Cinnamaldoximes.** O. L. BRADY and H. J. GRAYSON (*J. Chem. Soc.*, 1924, 125, 1418—1421; cf. *ibid.*, 1922, 121, 2098).—*o*-Methoxycinnamantialdoxime, prepared by the action of hydroxylamine hydrochloride on the aldehyde suspended in sodium hydroxide solution, has m. p. 82°. The *acetyl* derivative also has m. p. 82°. It dissolves slowly in warm 2*N*-sodium hydroxide giving the sodium salt of the original oxime, thus establishing the *anti*-configuration of the latter. Thus *o*-methoxy- resembles the nitro-cinnamaldehydes, rather than the cinnamaldehydes. *o*-Methoxycinnamsynaldoxime, m. p. 135.5°, is obtained in the absence of alkali; *hydrochloride*, m. p. 142° (decomp.). The *acetyl* derivative, m. p. 77°, is formed instead of the usual nitrile by the action of acetic anhydride at 30°. *Benzoyl-o*-methoxycinnamantialdoxime, m. p. 128°, is obtained from both the *syn*- and *anti*-oximes; it yielded only the *antialdoxime* on hydrolysis (cf. T., 1922, 121, 2098). The 2:4-dinitrophenyl ether of *o*-methoxycinnamsynaldoxime, m. p. 202° (decomp.), is obtained from the *anti*-oxime. *m*-Nitrocinnamsynaldoxime, m. p. 163°, was obtained when the *hydrochloride*, m. p. 175° (decomp.)

(formed on saturating a solution of the *anti*-oxime in hot benzene with hydrogen chloride), was treated with sodium hydroxide. Admixture with the *anti*-isomeride (m. p. 157°) caused a depression of the m. p.; its *acetyl* derivative, m. p. 98—100°, yielded *m*-nitrocinnamionitrile with alcoholic potassium hydroxide; this fixes its entity, as the *anti*-oxime under similar conditions gives an *acetyl* compound (m. p. 136°) from which the *anti*-oxime is regenerated. *o*-Nitrocinnamsynaldoxime, m. p. 138°, was obtained through its *hydrochloride*, m. p. 144° (decomp.), similarly to the *m*-nitro-compound. A purer compound, m. p. 140°, was obtained by Dunstan and Thole's method (P., 1911, 27, 233). Its conversion into *o*-nitrocinnamionitrile proved its *syn*-configuration. *p*-Nitrocinnamsynaldoxime was not obtained in the pure state; its *hydrochloride*, m. p. 173° (decomp.), gave an oxime of m. p. 140° which depressed the m. p. (179°) of the *anti*-isomeride. A. C.

**Preparation of Piperonal from *iso*Safrole and  $\alpha$ -Homopiperonal from Safrole by Ozone.** S. NAGAI (*J. Fac. Eng. Tokyo*, 1923, 13, 185—192).—*iso*Safrole ozonide is readily prepared by passing ozonised air into a solution of *isosafrole* in perfectly dried solvents, e.g., a mixture of chloroform, carbon tetrachloride or tetrachloroethane, and light petroleum. The ozonide decomposes spontaneously at the ordinary temperature, more readily on heating gently or in presence of water, with the production of considerable amounts of resinous matter. The best yield of piperonal is obtained when the ozonide is decomposed in the presence of reducing agents; thus, by employing a saturated aqueous solution of sodium hydrogen sulphite a yield of 85% of theory was produced.

Safrole ozonide is obtained in a similar manner, but owing to its lesser solubility mixed solvents are not required. The best method of decomposition of the ozonide consists in the gradual addition of zinc dust and water to its solution in glacial acetic acid, when yields of 60—65% of  $\alpha$ -homopiperonal result. The aldehyde has b. p. 131—133°/8 mm.,  $d_4^{15}$  1.2654,  $n_D^{15}$  1.5547; *oxime*, m. p. 109°, *semicarbazone*, m. p. 175—176°, and *phenylhydrazone*, m. p. 176°. C. J. S.

**Photochemical Reactions in Solutions of the Alkali Halides in Acetophenone.** J. L. R. MORGAN, O. M. LAMMERT, and R. H. CRIST (*J. Amer. Chem. Soc.*, 1924, 46, 1170—1178).—Pure acetophenone is decomposed by the light from a quartz-mercury lamp, apparently with the production of benzoic acid. A yellow colour appears, possibly due to the formation of condensation products, and the specific electrical resistance decreases. In the dark this again increases, but the yellow colour continues to deepen. The presence of water accelerates the reaction. A solution of sodium iodide in acetophenone increases in resistance in the light, iodine is liberated, and a fine, white deposit, which appears to be sodium benzoate, is formed. There are breaks in the curves showing variation of resistance with time, thus indicating that concurrent or overlapping reactions are taking place in the solution. A scheme

of combined thermal and photochemical reactions has therefore been put forward as a possible explanation of the changes observed.

The effective wave-lengths for the reactions in glass vessels are 300  $\mu\mu$  and 400  $\mu\mu$ . The effects are more pronounced and differ somewhat in character in quartz vessels, indicating that the shorter wave-lengths are more effective for at least some of the reactions.

M. S. B.

**Beckmann's Rearrangement. XII. Catalytic Action of Reduced Copper on Acetophenoneoxime.** S. YAMAGUCHI (*Mem. Coll. Sci. Kyoto*, 1924, 7, 281—285).—Acetophenoneoxime, when passed with hydrogen over reduced copper at 200°, yielded benzoic acid, ammonium benzoate,  $\alpha$ -phenylethylamine,  $\alpha\alpha$ -diphenylethylamine, benzonitrile, acetophenone, and unchanged oxime.

F. G. M.

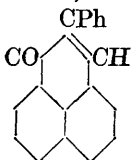
**Mono- and Di-chloro-1-ketotetrahydronaphthalene.** TETRALIN G.M.B.H. and W. RIEBENSAHM (D.R.-P. 377587; from *Chem. Zentr.*, 1924, i, 956).—By chlorination of 1-ketotetrahydronaphthalene are obtained *dichloro-1-ketotetrahydronaphthalene*, m. p. 75—76°, and *monochloro-1-ketotetrahydronaphthalene*, m. p. 45°. G. W. R.

**Changes in State of Aggregation and Polymorphism. IV. Formation of Metastable Benzophenone.** K. SCHAUM and K. ROSENBERGER (*Z. anorg. Chem.*, 1924, 136, 329—336).—The addition of hydrogen chloride to either the rhombic  $\alpha$  or the monoclinic, metastable,  $\beta$  form of benzophenone results in an equilibrium being established between the two modifications, which, at low temperatures, corresponds with the formation of the eutectic mixture. The hydrogen chloride acts as a catalyst in this change probably by forming an unstable additive product with the benzophenone since, on passing the gas into the molten compound, the latter develops a bright grass-green colour. This view is strengthened by the fact that compounds, such as metallic chlorides, which are known to give additive products with benzophenone also accelerate the change from the stable  $\alpha$  to the metastable  $\beta$  form. Benzophenone forms eutectic mixtures with 70 and 30 mol. % of diphenylamine (m. p. 29.5° and 25° respectively), with 39 mol. % of benzhydrol (m. p. 23°), with 24 mol. % of triphenylmethane (m. p. 33°), with 10 mol. % of 4 : 4'-dichlorobenzophenone (m. p. 43°), and with 26 mol. % of ditolyl ketone (m. p. 34°). Of a number of substituted benzophenones tested only *p*-ditolyl ketone exhibited polymorphism.

A. R. P.

**Vat Dyes.** KALLE U. Co. (D.R.-P. 384982; from *Chem. Zentr.*, 1924, i, 1111).—*Potassium 1-aldehydonaphthalene-8-carboxylate* condenses with phenylacetonitrile to give 1- $\beta$ -cyanostyrylnaphthalene-8-carboxylic acid, m. p. 162—165°, which is converted by sulphuric acid into 2-phenylperinaphthindone (annexed formula), m. p. 142°. The last is converted by fusion with potassium hydroxide into a blue vat dye.

G. W. R.

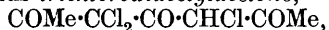


**Aryl 4-Hydroxynaphthyl Ketones.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 100366, 100367, 100368, 100369, 100370, and 100371; from *Chem. Zentr.*, 1924, i, 2204—2205; cf. this vol., i, 174—175).—The following new compounds are mentioned: *o*-chlorophenyl 4-hydroxynaphthyl ketone, m. p. 216°; *p*-chlorophenyl 4-hydroxynaphthyl ketone, m. p. 210°; 2:4-dichlorophenyl 4-hydroxynaphthyl ketone, m. p. 222°. G. W. R.

**An Aryl Hydroxynaphthyl Ketone.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 101402; from *Chem. Zentr.*, 1924, i, 2205; cf. preceding abstract).—2-Benzoyl-1-naphthol-4-sulphonic acid is obtained by the action of benzotrichloride on sodium 1-naphthol-4-sulphonate. G. W. R.

**Residual Affinity and Co-ordination. XVIII. Interaction of Zirconium Salts and  $\beta$ -Diketones.** G. T. MORGAN and A. R. BOWEN (*J. Chem. Soc.*, 1924, 125, 1252—1261).—The method developed by Biltz and Clinch (A., 1904, i, 715) to form zirconium acetylacetone in aqueous solution proved impracticable when tried with homologues of acetylacetone, whilst the higher aliphatic diketones and sodium benzoylacetone (which produced zirconyl bisbenzoylacetone) also gave unsuccessful results. In place of this, a general reaction was obtained between anhydrous zirconium tetrachloride and the  $\beta$ -diketones in dry chloroform or benzene, whereby three chlorine atoms were replaced. *Zirconium trisdibenzoylmethane chloride*, so obtained, is very stable in the dry state and gives crystalline double salts such as the *ferrichloride*, *chloroaurate*, and *chloroplatinate*. *Zirconium trisbenzoylacetone chloride* is less stable, whilst the *trisacetylacetone chloride* is the most readily hydrolysable member of the series. A. COUSEN.

**Action of Selenium Tetrachloride on Di- and Tri-ketones. Selenium Phenylacetyl- and  $\beta$ -Phenylpropionyl-acetones.** G. T. MORGAN and C. R. PORTER (*J. Chem. Soc.*, 1924, 125, 1269—1277).—The copper derivative of  $\omega$ -phenylacetylacetone reacts readily with selenium tetrachloride producing mainly the dimeric *selenium  $\omega$ -phenylacetylacetone* and *3-chloro- $\omega$ -phenylacetylacetone*.  $\beta$ -Phenylpropionylacetone similarly reacts to give *selenium  $\beta$ -phenylpropionylacetone*. These compounds, reduced with hydriodic acid, give *diselenium bis- $\omega$ -phenylacetylacetone* and *bis- $\beta$ -phenylpropionylacetone*, respectively, anhydrous hydrocyanic acid also reacting to give *cyanoselenium  $\omega$ -phenylacetylacetone* and the  $\beta$ -phenylacetylacetone. The products are all enolic, the reduction compounds being orange-coloured oils which are also obtained as by-products of the original condensations. Selenium tetrachloride reacts with the barium salt of diacetylacetone chiefly as a dehydrating and chlorinating agent, the chief derivative being 3:5-dichloro-2:6-dimethylpyrone, white needles, m. p. 148—150°, whilst much free selenium is also obtained. This pyrone with barium hydroxide affords an enolic substance, probably 3-chloro-5-acetyl-4-hydroxy-2-methylfuran, m. p. 83—84°. Chlorination of barium diacetylacetone yields *trichlorodiacetylacetone*,

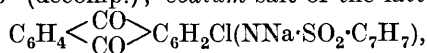


m. p. 105—106°.

A. COUSEN.



**1-Chloro-2-acylamidoanthraquinones.** E. KOPETSCHNI (D.R.-P. 376471; from *Chem. Zentr.*, 1924, i, 967).— $\beta$ -Acylamidoanthraquinones are chlorinated by means of sulphuryl chloride in an indifferent solvent. 1-Chloro-2-acetamidoanthraquinone has m. p. 241°; 1-chloro-2-p-toluenesulphamidoanthraquinone, green needles, m. p. 204—205° (decomp.); sodium salt of the latter,



red crystals.

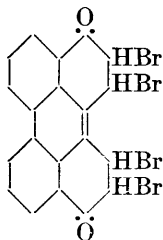
G. W. R.

**Sodium Alizarate and Alumina.** F. S. WILLIAMSON (*J. Phys. Chem.*, 1924, 28, 891—892).—Experiments are described from which the author infers that no definite aluminium alizarate is formed when aluminium hydroxide and sodium alizarate are mixed, contrary to the supposition of Liechti (*J. Soc. Chem. Ind.*, 1886, 5, 523).

**Action of Thionyl Chloride on Hydroxyanthraquinones. I. Thionylalizarin.** A. GREEN (*J. Chem. Soc.*, 1924, 125, 1450—1451).—Thionylalizarin,  $\text{C}_{14}\text{H}_6\text{O}_2 < \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} > \text{SO}$ , prepared by the action of boiling thionyl chloride on dry alizarin, forms yellow crystals, m. p. 171—172°; the colour changes to orange-yellow after a few hours in a sealed tube, but the m. p. and sulphur content remain unchanged. The substance is stable in dry air, but converted into alizarin by moisture. The colours of its solutions in aqueous sodium hydroxide and concentrated sulphuric acid are the same as those of alizarin. Alizarin monoacetate, m. p. 201—202°, is formed on boiling thionylalizarin with glacial acetic acid, and the diacetate, m. p. 185°, on using acetic anhydride.

A. C.

**Perylene and its Derivatives. IV.** A. ZINKE and H. SCHÖPFER [with G. MÜLLER, R. SABATHY, M. SCHNEIDER, and W. SPITZY] (*Monatsh.*, 1924, 44, 365—370).—Careful bromination of perylenequinone in the cold yields, besides dibromoperylenequinone (A., 1920, i, 541), 1 : 2 : 11 : 12-tetrabromotetrahydroperylenequinone (annexed formula), bright yellow needles, rapidly darkening, which readily loses hydrogen bromide, giving dibromoperylenequinone. On chlorination in nitrobenzene on the water-bath, perylenequinone similarly yields 1 : 2 : 11 : 12-tetrachlorotetrahydroperylenequinone, which is more stable than the tetrabromo compound, but at about 265°, or by crystallisation from aniline or heating with pyridine, is converted into dichloroperylenequinone, which dyes cotton pure yellow. Nitration of perylenequinone with concentrated nitric acid in boiling acetic acid solution gives, besides the mononitro



derivative previously described (Zinke and Unterkreuter, *loc. cit.*), a dinitroperylenequinone,  $\text{C}_{20}\text{H}_8\text{O}_2(\text{NO}_2)_2$ , which dyes cotton dull violet. On reduction with alkaline sodium hyposulphite, the mononitro compound yields aminoperylenequinone,  $\text{C}_{20}\text{H}_9\text{O}_2 \cdot \text{NH}_2$ ,

and the dinitro compound gives diaminoperylenequinone,  $C_{20}H_{12}O_2N_2$ ; *diacetyl* derivative; *dibenzoyl* derivative, needles.

R. B.

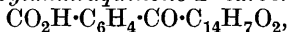
**Perylene and its Derivatives.** V. A. ZINKE and A. PONGRATZ (*Monatsh.*, 1924, **44**, 379—382).—Perylenequinone stands between  $\alpha$ -naphthaquinone and anthraquinone in its quinonoid properties, and is much more stable than *pp'*-diphenoquinone, from which it is genetically derived (cf. Willstätter and Kalb, A., 1905, i, 361). It gives no reaction with aqueous hydriodic acid in nitrobenzene solution or with guaiacum resin or hæmatoxylin in alcoholic solution. With phenylhydrazine and hydroxylamine at higher temperatures, it yields no hydrazone or oxime, but apparently undergoes reduction. It does not react with sulphurous acid, but is reduced by stannous chloride in acetic acid solution. A solution of perylenequinone in acetic acid, on the addition of potassium iodide, gives after some minutes a reaction for free iodine; *p*-benzoquinone gives an immediate reaction,  $\alpha$ -naphthaquinone after a few seconds, and anthraquinone an uncertain reaction after 30 to 35 mins. The solution of perylenequinone gradually deposits brownish-violet needles of *perylenequinhydrone*,  $C_{40}H_{20}O_4$ . *Perylenequinol*,  $C_{20}H_{12}O_2$  (cf. Zinke and Unterkreuter, A., 1920, i, 541), obtained by reduction of perylenequinone with potassium iodide and red phosphorus in acetic acid solution, or with zinc dust and acetic acid, shows an intense yellowish-green fluorescence in solution and readily oxidises in air to a quinhydrone.

R. B.

**Aminoperylenequinones.** H. PEREIRA (Brit. Pat. 199721).—Mononitro-, dinitro-, and *bromodinitro*-perylenequinones afford, on reduction with hot alkaline sodium hyposulphite, *monoamino*-, *diamino*-, and *bromodiamino*-perylenequinones, respectively, all of which form dark needles and dye cotton in brown to violet shades (cf. A., 1920, i, 542, and Brit. Pat. 199720).

F. G. W.

**Attempt to Synthesise Dinaphthanthracenediquinone [Dinaphthanthradiquinone].** H. DE DIESBACH and L. CHARDONNENS (*Helv. Chim. Acta*, 1924, **7**, 609—613).—When “phthaloyl-phthalic anhydride” (the anhydride of benzophenone-2 : 3' : 4'-tricarboxylic acid; Limprieth, A., 1900, i, 599) and benzene are treated with aluminium chloride, 1 : 5-*dibenzoylbenzene*-2 : 2'-*dicarboxylic acid*, m. p. 177—180°, is produced. This undergoes further condensation when treated with strong sulphuric acid on the water-bath, yielding 2-*benzoylanthraquinone*-2'-*carboxylic acid*,



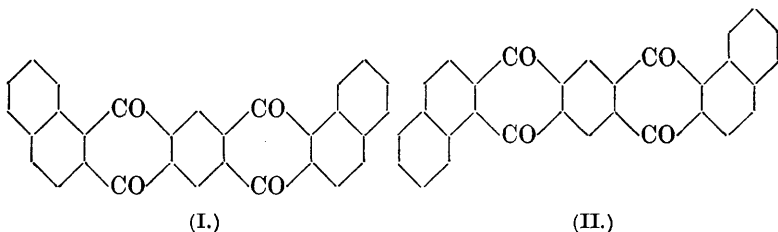
yellow prisms giving a bottle-green “vat” with sodium hydro-sulphite, soluble in benzene, m. p. 218° after sintering at 198°, together with a little 2-*benzoylanthraquinone*-3-*carboxylic acid*, insoluble in benzene and giving a reddish-brown “vat” (cf. Fairbourne, T., 1921, **419**, 1580). The former was also prepared by condensing phthalic anhydride with 9 : 10-dihydroanthracene, much anthroylbenzoic acid or similar compounds being formed as by-products (cf. Schaarschmidt, A., 1916, i, 381); further condensation

to dinaphthanthradiquinone was not satisfactorily brought about. 1-*p*-Methylbenzoyl-5-benzoylbenzene-2 : 2'-dicarboxylic acid undergoes a similar condensation, not wholly decomposition, as stated by Limpricht (*loc. cit.*), when heated with strong sulphuric acid, yielding 2 : 6-benzoylmethylanthraquinone-2'-carboxylic acid, m. p. 213°. (Cf. this vol., i, 1074.) W. A. S.

**Dibenzoylxylenes and Dinaphthanthradiquinones. II.** H. DE DIESBACH and L. CHARDONNENS (*Helv. Chim. Acta*, 1924, 7, 614—618; cf. A., 1923, i, 804).—When  $\alpha$ -cumidic acid is treated with sulphuric acid and potassium nitrate at 50° it yields solely a mononitro derivative, 2-nitro-*m*-xylene-4 : 6-dicarboxylic acid, m. p. 294°, the *dimethyl* ester of which has m. p. 143·5—144·5°. Reduction of the nitro-acid affords the corresponding *amino-acid*, m. p. 305—306°, the *dimethyl* ester of which has m. p. 95·5—97°. By the action of phosphorus pentachloride followed by aluminium chloride, on a solution of the nitrocumidic acid in benzene 2-nitro-4 : 6-dibenzoyl-*m*-xylene is obtained, m. p. 126—127°. This compound is oxidised by the action of nitric acid, *d* 1·15, at 200°, affording 2-nitro-4 : 6-dibenzoylisophthalic acid, m. p. 235—238°, which, by treatment with sulphuric acid at 200°, is converted into 6-nitro-5 : 7 : 12 : 14-dinaphthanthradiquinone, subliming without melting at 285—290°. W. A. S.

**Some Derivatives of Dinaphthanthradiquinone and the Synthesis of Dinaphthalinoanthradiquinone.** H. DE DIESBACH and V. SCHMIDT (*Helv. Chim. Acta*, 1924, 7, 644—653; cf. A., 1923, i, 804; Philippi, A., 1923, i, 576; 1913, i, 627).—Pyromellitic anhydride and toluene react (Philippi, *loc. cit.*) in presence of aluminium chloride to give a mixture of much 4 : 6-di-*p*-toluoylisophthalic acid, the *methyl* ester of which has m. p. 194—195°, and a little 2 : 5-di-*p*-toluoylterephthalic acid, *methyl* ester, m. p. 203°, less soluble in alcohol than its isomeride. Philippi's conclusions (*loc. cit.*) as to the possibility of further condensation taking place are now shown to be unfounded : when the crude mixture of the above acids, or the first alone, is treated with 90% sulphuric acid at 180°, a poor yield of 2 : 10-*dimethyl*-5 : 7 : 12 : 14-dinaphthanthradiquinone is obtained, not melting below 350°, which, like its congeners described previously and below, yields a brown "hypo-sulphite vat" which turns blue on exposure to air. The isomeric 2 : 9-*dimethyl*-5 : 7 : 12 : 14-dinaphthanthradiquinone was also obtained. Similarly, pyromellitic anhydride and *o*-chlorotoluene yield (82% of theory) 4 : 6-di-3'-chloro-*p*-toluoylisophthalic acid, m. p. 302°, which affords a *methyl* ester, m. p. 234—235°, and 2 : 5-di-3'-chloro-*p*-toluoylterephthalic acid, m. p. 315°, *methyl* ester, m. p. 241°. When the crude mixture of acids is heated with 90% sulphuric acid at 180°, 40% of the theoretical yield of the corresponding dinaphthanthradiquinones is obtained. The two substances are separated by fractional extraction with nitrobenzene. Neither interacts with toluidine in presence of sodium acetate and a copper salt; the chlorine atoms therefore are not adjacent to

the carbonyl groups. 3 : 9-Dichloro-2 : 10-dimethyl-5 : 7 : 12 : 14-dinaphthanthradiquinone decomposes at 320°, whilst 3 : 10-dichloro-2 : 9-dimethyl-5 : 7 : 12 : 14-dinaphthanthradiquinone remains unmelted at 350°. From *p*-chlorotoluene, in like manner, 4 : 6-di-3'-chloro-*o*-toluoylisophthalic acid, m. p. 313°, giving a methyl ester, m. p. 164—165°, was obtained, together with 2 : 5-di-3'-chloro-*o*-toluoyltetraphthalic acid, m. p. 325°, methyl ester, m. p. 182°. The first of these, or the crude mixture, as it contains only a very small proportion of the second acid, yields 4 : 8-dichloro-1 : 11-dimethyl-5 : 7 : 12 : 14-dinaphthanthradiquinone, m. p. 270° (decomp.). When aluminium chloride is added to a solution of pyromellitic anhydride, naphthalene, and benzene at 30°, and the mixture heated during 10 hours at 30—60°, two acids are obtained which may be separated from one another by fractional crystallisation from water, acetic acid, and alcohol, used in succession. 4 : 6-Di- $\alpha$ -naphthoylisophthalic acid has m. p. (when anhydrous) 302°; its methyl ester has m. p. 205°. 2 : 5-Di- $\alpha$ -naphthoyltetraphthalic acid has m. p. 316°. For effecting the further condensation to the anthradiquinone derivatives, sulphuric acid cannot be used, because sulphonation takes place (some products of the action are described); but the reaction can be brought about by heating the acid with phosphorus pentoxide at 300—310°. If the crude mixture of acids be used, a product is obtained which may be separated into its two components by fractional extraction with acetic acid and crystallisation from nitrobenzene; or the two isomerides may be prepared each from its appropriate acid. In this way 1 : 2 : 10 : 11-dibenzo-5 : 7 : 12 : 14-dinaphthanthradiquinone (syn-biangular-2 : 3 : 6 : 7-dinaphthalino-1 : 4 : 5 : 8-anthradiquinone, Stelzner's nomenclature), brick-red needles, decomposing without melting at 320° (I), and the corresponding 1 : 2 : 8 : 9-compound (anti-biangular-2 : 3 : 6 : 7-dinaphthalino-1 : 4 : 5 : 8-anthradiquinone), somewhat paler needles,



unaltered even at 360° (II), are obtained. Both substances yield a violet "vat" with sodium hyposulphite, the colour changing to green and eventually to orange, on exposure to air.

When tetrahydronaphthalene is used instead of naphthalene, the condensation takes place smoothly and appears to result in the production of only one of the possible isomerides, *viz.*, 4 : 6-di- $\beta$ -ar-tetrahydronaphthoylisophthalic acid, m. p. 289—290°. Attempts to convert this compound into an anthradiquinone failed, oxidation taking place at high temperatures.

W. A. S.

**Action of Tetrachloro- and Tetrabromo-phthalic Acids on Turpentine. New Method of Preparing Camphols and *d*- and *l*-Camphor.** A. HALLER (*Compt. rend.*, 1924, 178, 1933—1937; cf. Bouchardat and Lafont, A., 1892, 199; Bouchardat and Tardy, A., 1895, i, 673).—Bornyl and fenchyl esters may be prepared by the action of acids on terpenes provided that the acid used is soluble in the terpene. Tetrahalogenophthalic acids fulfil this condition and react with pinenes yielding bornyl, *isobornyl*, and fenchyl esters from which mixtures of these alcohols may be obtained on hydrolysis. Both the yield and the relative proportion of esters obtained depend on the temperature and also on the duration of the reaction, and details of experiments carried out with turpentine from *Pinus maritima* and *P. halepensis* and tetrachloro- and tetrabromo-phthalic acids under different conditions are given.

H. J. E.

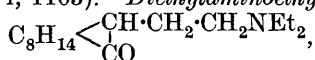
**The Camphor and Camphenilone Series. Reply to L. Ruzicka.** S. NAMETKIN (*Annalen*, 1924, 438, 202).—Explanatory (cf. this vol., i, 64).

W. A. S.

**The Camphenilane Series.** S. NAMETKIN (*Annalen*, 1924, 438, 185—201).—A review of earlier work (cf. A., 1915, i, 699) with particular reference to the results of Komppa and Roschier (A., 1922, i, 1167). The compound described as  $\beta$ -nitrocamphenilane (Nametkin and Chuchrikova, A., 1915, i, 701) is now termed  $\alpha$ -nitrocamphenilane, whilst the 6-nitro- is now the 2-nitro derivative. The *apofenchocamphoric acid* previously described (m. p. 144.5—145°) is now shown to be *cis-apofenchocamphoric acid*. Various salts are briefly described. The solubility of the acid in water is 0.72 g. per 100 c.c. at 19°. With acetyl chloride in the cold, it yields the *anhydride*, m. p. 136—137°. The acid affords a *monoanilide*, m. p. 155—157°, and a *dianilide*, m. p. 148—150°. *trans-apoFenchocamphoric acid*, m. p. 147—148°, is obtained when the *cis*-variety is heated with hydrochloric and acetic acids at 180—200°. This acid is more soluble in water than the *cis* isomeride (0.81 g. per 100 c.c. at 17°). It yields a *monoanilide*, m. p. 138—142°, and a *dianilide*, m. p. 215—216°.

W. A. S.

**Dialkylaminoalkylcamphors.** FARBERWERKE VORM. MEISTER, LUCIUS, U. BRÜNING, and M. BOCKMÜHL (D.R.-P. 376348; from *Chem. Zentr.*, 1924, i, 1103).—*Diethylaminoethylcamphor*,



is an oil; the *hydrochloride* has m. p. 145°. *Dimethylaminoethylcamphor* is a yellow oil, b. p. 135—150°/10 mm.; *hydrochloride*, m. p. 231°.

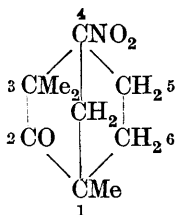
G. W. R.

**Origin of Fenchol in Bouchardat and Lafont's Reaction.** M. DÉLÉPINE (*Compt. rend.*, 1924, 178, 2087—2089; cf. Bouchardat and Lafont, A., 1892, 199).—The action of benzoic and trichloroacetic acids on *d*-pinene and on *l*-pinene, respectively, results in formation of both fenchol and borneol derivatives in all four cases.

H. J. E.

**Nitrofenchones and some of their Reactions.** S. NAMETKIN (*J. pr. Chem.*, 1924, [ii], 108, 29—45).—By the action of nitric acid on fenchone, a *sec.*- and *tert.*-nitrofenchone were obtained by Kononov (A., 1904, i, 257). These products have been further investigated.

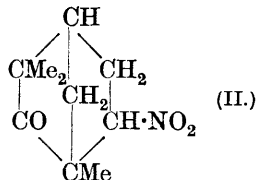
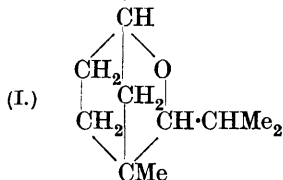
[With (Miss) W. CHOCHRJAKOV.]—The *tert.*-nitrofenchone has the annexed formula, instead of that given by Kononov (*loc. cit.*).



The reduction product with tin and hydrochloric acid is not a hydroxyfenchone, but a *diketone*,  $C_{10}H_{16}O_2$ , a colourless oil with a pleasant odour, b. p. 126.5—127°/11 mm.,  $d_4^{20}$  1.0028,  $n_D^{20}$  1.4641 [ $\alpha$ ]<sub>D</sub> -46.59° in alcohol. It forms a *disemicarbazone*,  $C_{10}H_{16}(N \cdot NH \cdot CO \cdot NH_2)_2$ , decomp. 220°, and a *dioxime*, m. p. 123—124°. The diketone is reduced by sodium and alcohol to a *glycol*,  $C_{10}H_{18}(OH)_2$ , b. p. 151—152°/11 mm., [ $\alpha$ ]<sub>D</sub>

+44.54° in alcohol, giving a *diacetate*, b. p. 152—153°/12 mm.,  $d_4^{20}$  1.0189,  $n_D^{20}$  1.4530. The dry glycol is converted by warm sulphuric acid into the *oxide*,  $C_{10}H_{18}O$ , b. p. 171—172°/749 mm.,  $d_4^{20}$  0.8985,  $n_D^{20}$  1.4478; its formation is accompanied by that of other products. The formation of the diketone from the *tert.*-nitrofenchone involves the scission of one ring. The readiness with which the glycol forms an anhydride renders extremely probable the formula  $CO-CH_2 > CMe \cdot CO \cdot CHMe_2$  for the diketone, scission having occurred between carbon atoms 3 and 4 of the fenchone ring. The oxide then has the formula I.

[With (Miss) K. LÜBOVZOV.]—The *sec.*-nitrofenchone, m. p. 88°, [ $\alpha$ ]<sub>D</sub> -42.88° in benzene, is a true nitro compound. With bromine in alkaline solution, it forms *bromonitrofenchone*,  $C_{10}H_{14}O \cdot BrNO_2$ , m. p. 53°. The only product of the acid reduction of *sec.*-nitrofenchone is a *ketonic acid*,  $C_9H_{15}O \cdot CO_2H$ , which begins to melt at 73°, forms a cloudy liquid at 76° and clears at 79—80°;



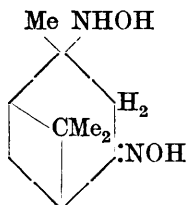
it forms a *semicarbazone*, decomp. 188°. This acid possibly has the structure  $CHMe \cdot CH_2 > CH \cdot CH_2 \cdot CO_2H$ , and is related to *isocamphoric acid* which, with  $\alpha\alpha$ -dimethyltricarballic acid, is formed during the nitration of fenchone. *sec.*-Nitrofenchone probably has formula II.

By the action of nitric acid on camphenilone, two products are obtained, a liquid and crystals, m. p. 90—92°, apparently isomeric *nitro* derivatives. As a by-product, *isocamphoric acid* was identified, and its formation supports the accepted formula for camphenilone.

E. H. R.

**Preparation of Monoalkylpulegones.** A. HALLER and (MME.) P. RAMART (*Compt. rend.*, 1924, **179**, 120—122).—Pulegone in ethereal solution is treated first with an equimolecular quantity of powdered sodamide and then with the theoretical quantity of the requisite alkyl iodide, the alkylpulegone being finally isolated by distillation. The yields are low, owing chiefly to intermolecular condensation of the pulegone under the influence of the sodamide. The following compounds are described. *Methylpulegone*, b. p.  $114^{\circ}/19$  mm.,  $d_4^{25}$  0.9256,  $[\alpha]_D^{15}$   $-26.24^{\circ}$ , *semicarbazone*, liquid; *ethylpulegone*, b. p.  $117-121^{\circ}/20$  mm.,  $d_4^{15}$  0.9315,  $[\alpha]_D^{15}$   $-25.12^{\circ}$ , *semicarbazone*, m. p.  $216^{\circ}$ ; *n-propylpulegone*, b. p.  $127-131^{\circ}/20$  mm.,  $d_4^{15}$  0.9476,  $[\alpha]_D^{15}$   $-22.10^{\circ}$ , *semicarbazone*, m. p.  $170^{\circ}$ ; *isobutylpulegone*, b. p.  $128-132^{\circ}/20$  mm.,  $d_4^{15}$  0.9225,  $[\alpha]_D^{15}$   $-18.28^{\circ}$ , *semicarbazone*, liquid; *allylpulegone*, b. p.  $129-133^{\circ}/20$  mm.,  $d_4^{15}$  0.9399,  $[\alpha]_D^{15}$   $-27.86^{\circ}$ , odour resembling that of vetiver and ionone, *semicarbazone*, m. p.  $196^{\circ}$ . F. G. M.

**Chemistry of the Terpene Group. I. Formation and Transformations of Verbenone and Verbenol from Turpentine.** H. WIENHAUS and P. SCHUMM (*Annalen*, 1924, **439**, 20—48).—The auto-oxidation of Grecian turpentine in air, very slow under ordinary conditions, but much more rapid in sunlight and in the presence of an appropriate catalyst, yields verbenol and verbenone. A resin acid,  $C_{20}H_{30}O_2$ , known to be formed by the oxidation of turpentine, was isolated. In the oxidation of pinene by means of colloidal osmium and oxygen (cf. Willstätter and Sonnenfeld, A., 1913, i, 1200)  $\alpha$ -pinene takes up 1 mol. of oxygen and, from the acid, viscous liquid produced, *d*-verbenone is isolated; oxime, m. p.  $119-120^{\circ}$  (cf. Blumann and Zeitschel, A., 1913, i, 495, give m. p.  $115^{\circ}$ ), *semicarbazone*, m. p.  $208^{\circ}$  (decomp.). Excess of

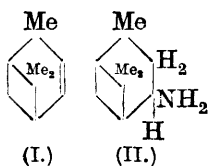


hydroxylamine yields the *hydroxylamino-oxime* (annexed formula), decomp.  $165^{\circ}$  ( $170^{\circ}$  with rapid heating). Catalytic reduction of verbenoneoxime using palladium and hydrogen gives only a resinous product when 1 mol. of hydrogen is used, but with 3 mols. the product is verbanylamine, which is obtained by similar reduction of verbanoneoxime. By the action of 15% hydrogen peroxide in methyl-alcoholic sodium hydroxide solution, *d*-verbenone yields an *oxide*, b. p.  $115^{\circ}/16$  mm., m. p.  $6.5^{\circ}$ ,  $d_4^{20}$  1.0561,  $n_D^{20}$  1.48312, *semicarbazone*, m. p.  $220^{\circ}$  (decomp.). The formation of this oxide is a typical reaction for  $\alpha\beta$ -unsaturated ketones and together with the formation of the hydroxylamine-oxime proves that the double bond in the ring is conjugated with the keto group. The presence of a  $CH_2$  group adjacent to the carbonyl group follows from the easy formation of an oximino derivative. Oxidation of verbenone and its oxime with ozone yields pinonic acid. Catalytic reduction (with palladium and hydrogen) of verbenone yields *d*-verbanone, which on reduction with sodium yields verbanol, b. p.  $100^{\circ}/13$  mm., m. p.  $58^{\circ}$ , and a *pinacone*, m. p.  $211-212^{\circ}$ , b. p.  $250-254^{\circ}/22$  mm. Verbanone yields a *hydrazone*, m. p.  $27^{\circ}$ , b. p.  $146^{\circ}/22$  mm.,  $d_4^{27}$  0.986,  $n_D^{27}$  1.51743,

which at 140—160° yields pinane; *semicarbazone*, decomp. 230°; oxime, m. p. 88° (Blumann and Zeitschel, *loc. cit.*, give 77—78°), *hydrochloride*, m. p. 131°. Dilute sulphuric acid, (1:5, 1:2) regenerates the ketone from its oxime, but concentrated acid (1:1) yields a little *nitrile*, b. p. 230—236°, which is also obtained from the oxime by treatment with phosphorus pentoxide. Reduction of the nitrile with either sodium and alcohol, aluminium amalgam and moist ether, or platinum black and hydrogen, yields *verbanylamine*, b. p. 113—114°/20 mm., 211°/750 mm.,  $d_4^{20}$  0.9184,  $n_D^{20}$  1.48125; *hydrochloride*, decomp. 245—250°; *nitrate*, decomp. 200°; *oxalate*, m. p. 131°. Concentrated mineral acids resinify verbanone, but by the action of 12% hydrochloric acid or 20% sulphuric acid it is converted into  $\Delta^1$ -*o*-menthen-3-one, which on reduction by means of palladium black yields *o*-menthan-3-one. Reduction of verbanone by means of amalgamated zinc and 12% hydrochloric acid yields *o*-menthane, b. p. 169—170°/752 mm.,  $d_4^{20}$  0.8297,  $n_D^{20}$  1.45649,  $[\alpha]_D +14.9^\circ$ , identical with that synthesised from *o*-tolylidimethylcarbinol (cf. Sabatier and Murat, A., 1913, i, 255). Fission of the six membered ring, leaving the four-membered ring intact, is accomplished by the action of sodamide and *iso*amyl nitrite on verbanone, which yields an *oximino* derivative, m. p. 140°. This on treatment with acetic anhydride yields the isomeric *imide* of the pinocamphoric acid obtained by Wallach and Engelbrecht (A., 1906, i, 684), m. p. 96°. Hydrolysis by means of dilute sodium hydroxide of either the oximino derivative or the imide yields the corresponding *amide*, m. p. 120°, which, unlike the amide of camphoric acid, is stable towards dilute alkalis. By means of the Grignard reaction verbanone yields the tertiary alcohol, *methylverbanol*, m. p. 187°, which yields a stable chromate sensitive to light. On distillation at ordinary pressure, or by heating with anhydrous oxalic acid the tertiary alcohol yields *homopinene*, b. p. 184—188°/748 mm.,  $d_4^{20}$  0.8538,  $n_D^{20}$  1.47144, which shows considerable exaltation of molecular refraction. Like camphor, verbanone yields a white *additive* product on treatment with sodamide and carbon dioxide in anhydrous ether, which on acidification regenerates carbon dioxide and verbanone and is therefore an ester of the acid  $C_8H_{14} \begin{smallmatrix} <CH \\ CO \cdot CO_2H \end{smallmatrix}$ .

The isolation of pure verbenol from the fraction, b. p. 130—150°/17 mm., of the product of auto-oxidation of Grecian turpentine is much more difficult. Catalytic reduction (palladium and hydrogen) of the crude verbenol yields crude verbanol, of which a fraction, b. p. 102°/20 mm.,  $d_{20}$  0.940,  $n_D^{20}$  1.47618, forms a phthalate, m. p. 127°, and on oxidation by means of chromic acid and acetic acid yields pure verbanone.

*Methyl verbanylxanthate*, b. p. 100—110°/23 mm., on distillation yields a *hydrocarbon*, b. p. 156—159°/748 mm.,



$d_4^{20}$  0.8604,  $n_D^{20}$  1.46672,  $[\alpha]_D -6.22^\circ$ , which is not  $\alpha$ -pinene, since it yields a viscous red oil and not pinene hydrochloride on treatment with hydrochloric acid, and is probably  $\delta$ -pinene (I), the preparation of which by the exhaustive methylation of verbanylamine (II) is in pro-



gress. Crude verbanol is probably a mixture of stereoisomeric alcohols. J. W. B.

**Turpentine.** G. DUPONT (*Ann. Chim.*, 1924, [x], **1**, 184—274).—An amplification and extension of previous work (cf. Dupont, A., 1922, i, 357; Vèzes and Dupont, A., 1922, i, 1042; Dupont, A., 1922, i, 1043; Dupont and Desalbres, A., 1923, i, 812; Dupont and Brus, A., 1923, i, 934; Dupont and Desalbres, A., 1923, i, 1215). Indian turpentine is characterised by its large proportion of  $\Delta^3$ -carene and of longifolene, a sesquiterpene, whilst the percentages of pinene (24.8) and nopinene (9.7) are relatively small. The purest specimens of pinene obtained by the author from Aleppo turpentine had  $d^{15}_D$  0.8620,  $n^{20}_D$  1.4650, and  $[\alpha]_D +48.08^\circ$ , the velocity of crystallisation at  $-75^\circ$  being 34 mm./min.; whilst the corresponding figures for pinene from Bordeaux turpentine were 0.8620, 1.4649,  $-46.65^\circ$ , and 16.3 mm./min. The values for nopinene are 0.8740, 1.4872, and 196.5 mm./min. A study of the chemical properties of pinene and nopinene leads to the generalisation that if these two substances, by fixation of two atoms or groups, yield the same derivative, one of the entering groups must be a hydrogen atom. The following constants are given for  $\Delta^3$ -carene: b. p.  $170^\circ$ ,  $70^\circ/10$  mm.,  $d^{15}_D$  0.8668,  $n^{20}_D$  1.4675 (cf. Simonsen, T., 1920, **117**, 570). Hydrochloric acid acts on this substance, yielding a mixture of sylvestrene and dipentene hydrochlorides; potassium permanganate oxidises it to carene glycol, thence to *trans*-caronic acid. H. J. E.

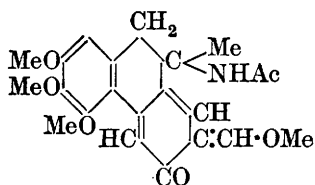
**Transformations of Pinene by Acids.** M. DELÉPINE (*Compt. rend.*, 1924, **179**, 175—178).—A discussion on the probable reactions occurring when pinene under the influence of acids—in particular of hydrochloric acid—is converted into esters of borneol, *isoborneol*, and fenchol, and also into camphene and limonene. F. G. M.

**Essential Oils.** SCHIMMEL U. CO. (*Report Schimmel u. Co.*, 1923, 1—240; from *Chem. Zentr.*, 1924, i, 2213—2215).—The following data are given for essential oils: essential oil from *Abies pindrow*,  $d^{15}_D$  0.8655;  $\alpha_D -10^\circ 41'$ ;  $n^{20}_D$  1.47220; saponification number, *S.N.*, 0; esterification number, *E.N.*, 8.4; Brazilian rosewood oil,  $d^{15}_D$  0.9120;  $\alpha_D +6^\circ 20'$ ;  $n^{20}_D$  1.47975; *S.N.*, 0; *E.N.*, 0; acetyl number, 131.6; American *Artemisia* oil,  $d^{15}_D$  0.9575;  $\alpha_D -0^\circ 26'$ ;  $n^{20}_D$  1.47750; *S.N.*, 0.6; *E.N.*, 11.2; essential oil from *Nepeta cataria*, var. *citriodora*, Beck,  $d^{15}_D$  0.8915;  $\alpha_D -1^\circ 34'$ ;  $n^{20}_D$  1.47485; *S.N.*, 5.6; *E.N.*, 8.4. G. W. R.

**Constituents of Resins.** X. PINORESINOL and the Natural Resin of Pine. A. ZINKE, A. ERBEN, and F. JELE (*Monatsh.*, 1924, **44**, 371—377).—The crystalline dibenzoate of pinoresinol,  $C_{33}H_{28}O_8$ , m. p.  $159^\circ$ , is more serviceable for the purification of the  $\alpha$ -resin than Bamberger's process of crystallising the potassium salt. On hydrolysis with 10% alcoholic potassium hydroxide the pinoresinol is obtained, m. p.  $120$ — $121^\circ$ . Oxidation of dibenzoyl-pinoresinol with chromic acid in acetic acid gives two new products, A and B, benzoic acid also being isolated. The yellow substance (A),

$C_{32}H_{24}O_{10}$ , m. p.  $219^\circ$ , is evidently formed from the original resin by simultaneous loss of a methyl and formation of a carboxyl group. It gives an intense red solution in sodium hydroxide, and when it is heated benzoic acid is formed and a small quantity of oil distils, possessing a eugenol-like odour. The substance *B*, m. p.  $148^\circ$ , has the composition,  $C_{20}H_{18}O_5$ , and is also soluble in sodium hydroxide. It yields a bromo derivative,  $C_{20}H_{17}O_5Br$ , m. p.  $155^\circ$ . Pinoresinol gives a *di-p-bromobenzoate*, m. p.  $231-232^\circ$ , which on oxidation similarly yields two products, yellow plates, m. p.  $245^\circ$ , of the composition  $C_{32}H_{22}O_{10}Br_2$ , corresponding with product *A*, and reddish crystals, m. p.  $169-171^\circ$ , which contain halogen and are insoluble in sodium hydroxide. The structure of pinoresinol is discussed and a partial solution of the problem suggested. R. B.

**Constitution of Colchicine.** A. WINDAUS (*Annalen*, 1924, 439, 59-75).—The constitution of colchicine is deduced from its various decomposition products to be best represented by the

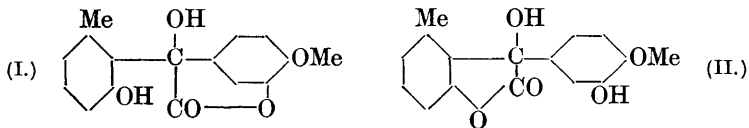


annexed formula. Treated with concentrated hydrochloric acid, 1 mol. of acetic acid is split off yielding trimethylcolchicine, which on heating with hydrogen iodide loses 3 mols. of methyl iodide and hence contains three methoxyl groups.

With benzenesulphonyl chloride this acid yields a dibenzenesulphonyl derivative, existing in two isomeric forms, which on careful hydrolysis give the same *N*-benzenesulphonyl-trimethylcolchicine. This behaviour is explained by the presence of a hydroxymethylene group. When warmed for a short time with dilute hydrochloric acid, colchicine loses 1 mol. of methyl alcohol, yielding colchicine, which, treated with a strongly alkaline solution of potassium iodide, yields a phenol, iodo-*N*-acetylcolchicinol,  $C_{22}H_{22}O_5NI$ , by the replacement of a  $-CHO$  group by iodine, a reaction typical of aromatic hydroxymethylene or hydroxy-aldehyde compounds. The presence of a methylene group is shown by the oxidation of colchicine with chromic anhydride to the ketone oxycolchicine; semicarbazide, m. p.  $220-223^\circ$ . Oxidation of colchicine, colchicine, trimethylcolchicine, acid, or iodo-*N*-acetylcolchicinol with potassium permanganate yields 3 : 4 : 5-trimethoxy-*o*-phthalic acid, whilst complete oxidation yields oxalic and succinic acids. Oxidation with hot potassium permanganate of the methyl ether of iodo-*N*-acetylcolchicinol splits two of the six-membered rings, giving 5(?)-iodo-4-methoxy-*o*-phthalic acid. Reduction of the methyl ether with zinc dust gives *N*-acetylcolchicinol methyl ether, which on energetic oxidation with chromic anhydride yields 4-methoxy-*o*-phthalimide, and hence the nitrogen atom is attached to the carbon atom next to the junction with the third ring. The methyl ether therefore contains three different six-membered rings, and since there are fifteen carbon atoms directly combined, it must be a derivative of methylanthracene or methylphenanthrene. *N*-Acetylcolchicinol methyl ether, on treatment with methyl-alcoholic

hydrochloric acid, yields colchinel methyl ether, which with 1 mol. of methyl iodide yields the *hydriodide* of *N-methylcolchinel methyl ether*, m. p. 244—245° (decomp.) (*picrate*, m. p. 200°), which with more methyl iodide yields the *hydriodide* of the *tertiary base*, m. p. 236° (decomp.) (*picrate*, m. p. 195—196°), and a *quaternary ammonium salt*, m. p. 231—232° (*picrate*, m. p. 193°), from which by means of silver oxide the *quaternary ammonium hydroxide* is obtained. This on heating in high vacuum yields trimethylamine, water, and 2:3:4:7-tetramethoxy-9-methylphenanthrene, m. p. 111°, which with hydrogen iodide yields the corresponding tetrahydric phenol, converted on distillation with zinc dust into 9-methylphenanthrene, m. p. 88—89°, identified by comparison with a specimen obtained by a rational synthesis. Colchicine is the methyl ether of colchicine, which is the *N*-acetyl derivative of trimethylcolchicine acid. Confirmation of these formulæ is obtained by catalytic reduction of colchicine and colchicine. Each takes up 8 atoms of hydrogen, yielding *octahydrocolchicine*, m. p. 125—126°, and *octahydrocolchicine*, m. p. 198—200°; *acetyl* derivative, m. p. 160—161°. Oxycolchicine similarly yields *octahydro-oxycolchicine*, m. p. 267—268°. J. W. B.

**Phyllodulcin, a Sweet Principle of the Leaves of *Hydrangea Thunbergii*.** S. H. MANIWA (*J. Pharm. Soc. Japan*, 1924, No. 507, 348—398; cf. *ibid.*, 1915, No. 406, 1399).—By extracting the leaves of the plant with alcohol three isomerides are obtained: *d*-phyllodulcin, m. p. 120°,  $[\alpha]_D^{20} +67^\circ$  to  $69^\circ$ ; *d*-isophyllodulcin, m. p. 131°,  $[\alpha]_D^{20} +20^\circ$ ; and *dl*-isophyllodulcin, m. p. 131—132°. They contain one methoxy group, two hydroxy groups, and a lactone ring. By fusion with potassium hydroxide, phyllodulcin gives 3:4-dihydroxybenzoic acid and 3-hydroxy-*o*-toluic acid,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{H}$ . The constitutions of phyllodulcin and isophyllodulcin have been suggested by Asahina and Ueno (*ibid.*, 1916, No. 408, 146) to be (I) or (II):



The author has synthesised 3-hydroxy-*o*-toluic acid from aceto-*o*-toluidide and identified it with one of the decomposition products of phyllodulcin. Aceto-*o*-toluidide is nitrated to 3-nitro-*o*-toluidine, which is converted successively into a nitrile and an acid amide. By nitrous acid the amide is changed into 3-nitro-*o*-toluic acid, which is reduced, diazotised, and converted into 3-hydroxy-*o*-toluic acid, m. p. 168°. 3-Methoxy-*o*-toluic acid has m. p. 137—138° and the *ethoxy* compound, m. p. 126—127° (cf. Asahina and Kondo, *ibid.*, 1922, No. 482, 264). By heating *d*-phyllodulcin with potassium hydroxide, methyl iodide, and methyl alcohol in a sealed tube, *d*-phyllodulcin dimethyl ether, m. p. 87°, is produced. Its lactone ring is opened by heating with alcoholic potassium hydroxide, but is closed again by making the solution acidic. After opening

the lactone ring of the dimethyl ether, it is oxidised with potassium permanganate in the presence of magnesium sulphate, 3-methoxy-*o*-toluic acid being produced. *d*-Phyllodulcin diethyl ether has m. p. 96—97°. By the same method, *dl*-isophyllodulcin dimethyl ether, m. p. 117°, and diethyl ether, m. p. 119—120°, give 3:4-dimethoxybenzoic acid and 3-ethoxy-4-methoxybenzoic acid, m. p. 166—167°, respectively. The last is prepared from 5-nitroguaiacol ethyl ether through the amino and cyano compounds. From these results, the constitutions of phyllodulcin and its isomeride are determined to be (I) and (II) respectively. The preparation of isovanillic acid from anethole was attempted. 3-Nitroanisic acid, obtained from anethole by oxidising with nitric acid, is reduced to the amino compound with tin and hydrochloric acid. The hydrolysis of the diazo compound is accomplished with a concentrated sulphuric acid solution of cupric sulphate (D.R.-P. 167211), crystals, m. p. 213—214°, being produced, identical with 3:5-dihydroxy-4-methoxybenzoic acid (methyl ester, m. p. 95°) prepared from anisaldehyde.

K. K.

**Saponins. I. The Sapogenin of the White Soapwort (*Gypsophila sapogenin*).** P. KARRER, W. FIORONI, R. WIDMER, and H. LIER (*Helv. Chim. Acta*, 1924, 7, 781—789; cf. Rosenthaler and Ström, A., 1912, i, 640).—The aqueous extract from *Radix saponaria levantica* was concentrated, heated with alcohol and sulphuric acid at 150°, and the sapogenin, termed by the authors *albsapogenin*, extracted with ether. Rosenthaler's formula,  $C_{24}H_{34}O_5$  (*loc. cit.*), is rejected in favour of  $C_{28}H_{44}O_4$ . It yields a methyl ester, m. p. 192°, having begun to decompose at about 140°; an oxime, m. p. 264—265° (decomp.); a semicarbazone, m. p. 272° (cf. Rosenthaler, *loc. cit.*); and an acetyl derivative, sintering at 178° and melting at 192—194°. *Albsapogenin* may thus be formulated  $C_{27}H_{42}O(OH) \cdot CO_2H$ . When it is reduced by hydrogen and platinum black it yields (the ketonic group having been reduced) the dihydroxycarboxylic acid, *albsapogenol*, m. p. 321—322°; the *diacetyl* derivative sinters at 150°, m. p. 169°. *Albsapogenin* is oxidised by a cold mixture of chromic and acetic acids to *albsapogenic acid*,  $C_{26}H_{41}O \cdot CO_2H$ , m. p. 256°. When *albsapogenin* is heated with 80% sulphuric acid at 100—120° only 1 mol. of carbon monoxide is evolved, proving that it is an  $\alpha$ -ketocarboxylic acid. When it is boiled with hydrochloric and acetic acids, or with sulphuric and acetic acids (although here another action takes place), but not with acetic acid alone, it is converted into *albsapin*, which is not an acid, but possibly a lactone.

W. A. S.

**Decomposition of Chlorophyllic Extracts.** A. MAILHE (*Compt. rend.*, 1924, 178, 1988—1990).—The alcoholic extract of plants after evaporation of the solvent ("chlorophyllic extract") was submitted to the action of anhydrous zinc chloride and magnesium chloride at various temperatures. Distillation with the latter substance at 300° yields a gas of the composition: carbon dioxide 57%, carbon monoxide 14%, hydrogen 20.5%, ethylenic hydrocarbons 9%. Simultaneously, a slightly acid liquid is obtained

consisting of paraffins and ethylenic hydrocarbons. This was fractionated and from the fractions of higher boiling point, crystals of dinonyl ketone were deposited. The acidity of the distillate is due to partial hydrolysis of the catalyst. H. J. E.

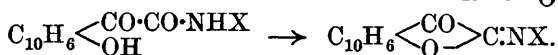
**Hydrolytic Product of Chlorophyll containing Iron.** S. MATYSIAK (D.R.-P. 376287; from *Chem. Zentr.*, 1924, i, 968).—Phæophytin free from magnesium, obtained by the hydrolysis of chlorophyll, is treated with ferric acetate. An amorphous, dark red substance is obtained which shows a biological similarity to hæmoglobin. It contains 2.53% of iron, and chars at 263° after sintering at 250°. G. W. R.

**Bile Pigments. VIII. Mesobiliviolin, Mesobiliviolinogen, and the Condensation of Mesobilirubinogen with Aldehydes. Bisazo Pigment from Mesobilirubin.** H. FISCHER and G. NIEMANN (*Z. physiol. Chem.*, 1924, 137, 293—316).—Mesobilirubin, m. p. 295—315°, is prepared by heating bilirubin with potassium methoxide and hydrazine in a closed tube at 180°. In alkaline solution, it is converted by atmospheric oxidation into mesobiliverdin and with ammoniacal copper solution it gives a crystalline copper salt. Mesobilirubin reacts with diazobenzenesulphonic acid, giving a violet pigment. On coupling it with diazobenzene chloride, a violet pigment,  $C_{45}H_{48}O_6N_8 \cdot 2HCl$ , m. p. 192° (decomp.), is obtained. The methyl ester yields a similar bluish-grey pigment,

$C_{47}H_{52}O_6N_8 \cdot 2HCl$ , m. p. 178° (decomp.). Mesobilirubinogen (A., 1911, i, 1005) gives a double salt,  $C_{33}H_{44}O_6N_4 \cdot 2FeCl_3$ , when treated with ferric chloride and hydrochloric acid. *Mesobiliviolin*,  $C_{33}H_{40}O_8N_4$ , m. p. 215° (decomp.), is obtained by heating a suspension of this double salt in 4% hydrochloric acid on a water-bath; it separates in violet globules. With alcoholic zinc acetate, it shows a fluorescence characteristic of urobilin. On hydrogenation in alcoholic solution in presence of platinum, it yields *mesobiliviolinogen*,  $C_{33}H_{48}O_5N_4$ , fine prisms, m. p. 228—230°. In its properties it resembles mesobilirubinogen, giving an intense aldehyde reaction, but with zinc acetate it shows urobilin fluorescence only after some time. Mesobilirubinogen condenses with benzaldehyde in presence of hydrochloric acid giving a yellow monobasic acid (benzylidenebilirubic acid),  $C_{24}H_{28}O_3N_2$ , m. p. 240°. Its methyl ester,  $C_{25}H_{30}O_3N_2$ , m. p. 212—213°, is similar to, although not identical with, xanthobilirubin ester. On oxidation with concentrated nitric or chromic acid, the monobasic acid yields methylethylmaleinimide and benzoic acid, respectively. With *p*-nitrobenzaldehyde, mesobilirubinogen yields a similar condensation product (*p*-nitrobenzylidenebilirubic acid),  $C_{24}H_{27}O_5N_3$ , m. p. 253°. D. R. N.

**Action of Oxalyl Chloride on Naphthols.** M. GIUA and V. DE FRANCISCIS (*Gazzetta*, 1924, 54, 509—516).—4 : 5-Benzocoumaran-2 : 3-dione (cf. A., 1917, i, 204) may be obtained in good yield by heating on the water-bath a carbon disulphide solution of  $\beta$ -naphthol (1 mol.) and oxalyl chloride (1 mol.), and, when the evolution of hydrogen chloride tends to moderate, adding a small

quantity of aluminium chloride. When this compound, suspended in alcohol, is treated with an organic base (1 mol.), the reddish-yellow diketone passes slowly into solution, giving a colourless or pale yellow liquid and sometimes a white precipitate, which is probably the substituted amide of the naphtholglyoxylic acid, formed by opening of the lactonic ring. When the action of the base and of heat is continued, the ring becomes closed again, with elimination of a molecule of water or alcohol and condensation of the amino group and a ketonic group :  $C_{10}H_6 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CO} + NH_2X \rightarrow$

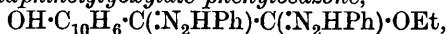


4 : 5-Benzocoumaran-2 : 3-dioneanil,  $C_{10}H_6 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C:NPh}$ , obtained by the action of aniline on the diketone, forms yellow needles, m. p. 126—127° (slight decomp.), and gives an intense, deep red coloration with concentrated sulphuric acid. The *o*-methylanil,  $C_{19}H_{13}O_2N$ , prepared by means of *o*-toluidine, has m. p. 166—167°.

4 : 5-Benzocoumarophenazine,  $C_{10}H_6 \begin{smallmatrix} \text{C:N} \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{C:N} \end{smallmatrix} \text{C}_6H_4$ , prepared by the action of *o*-phenylenediamine on 4 : 5-benzocoumaran-2 : 3-dione, forms orange-yellow needles, m. p. 286—287°.

4 : 5-Benzocoumaran-2 : 3-dione forms a *picrate*,  $C_{18}H_9O_{10}N_3$ , m. p. 109°; a *monosemicarbazone*,  $C_{13}H_9O_3N_3$ , m. p. 240—241°; and a *monophenylhydrazone*,  $C_{18}H_{12}O_2N_2$ , m. p. 226—227°.

*Ethyl 2 : 1-naphtholglyoxylate phenylosazone*,



obtained by the action of phenylhydrazine (2 mols.) on 4 : 5-benzocoumaran-2 : 3-dione, forms white needles (+ $C_6H_6$ ), m. p. (rapid heating) 165—166° (slight decomp.).

6 : 7-Benzocoumaran-2 : 3-dione, obtained in small yield from  $\alpha$ -naphthylloxalyl chloride, has m. p. 146—147° (decomp.). When treated with *o*-phenylenediamine, it yields 6 : 7-benzocoumarophenazine, garnet-red needles, m. p. 232—233°. T. H. P.

### Colouring Matter of the Blue Pansy [“Emperor William”].

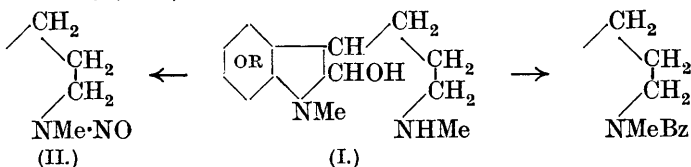
G. S. CURREY (*Proc. Roy. Soc.*, 1924, **B**, 96, 374—382).—The petals of the blue pansy, “Emperor William,” are shown to contain violanin (6.3%, as potassium salt, of dried petals). The pigment (crystalline chloride) was deep ruby-red, as stated by Everest (A., 1918, i, 420). Rutin (9.68%) was also isolated, but as the presence of myricetin or cyanidin was not detected, no further evidence is obtained that an anthocyan pigment is formed within a flower by reduction of the corresponding flavonol pigment (cf. Everest and Hall, A., 1921, i, 485). A. J. H.

### Degradation of Hydrogenated Derivatives of Eserine.

M. and M. POLONOVSKI (*Compt. rend.*, 1924, 179, 178—181; cf. A., 1923, i, 700, 831, 939, 940).—Hydroetheserolene, prepared by the reduction of etheserolene either with zinc and hydrochloric acid or with colloidal palladium or platinum in neutral or acid solution, has now been purified by conversion into the *hydrochloride*,

$C_{15}H_{19}ON, HCl$ , m. p.  $177^\circ$ . The regenerated pure base has  $[\alpha]_D +3^\circ$  in 95% alcohol, and  $+35^\circ$  in light petroleum, but undergoes inversion in acids, having  $[\alpha]_D -31^\circ$  in dilute hydrochloric acid. *Hydroeseretholmethine methiodide*, m. p.  $140^\circ$  (zinc chloride *additive* compound, m. p.  $263^\circ$ ), when warmed in concentrated solution with sodium hydroxide undergoes two simultaneous changes, losing methyl iodide to give hydroeseretholmethine, and losing trimethylamine hydriodide to give hydroetheserolene (*chlorozincate*, m. p.  $248^\circ$ ). It is concluded that reduction of etheserolene to hydroetheserolene does not involve the saturation of an ethylenic linking present in the former, and two possible constitutional formulæ for each of the two bases are suggested. F. G. M.

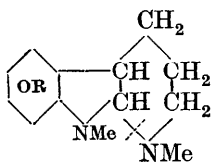
**Nitroso and Benzoyl Derivatives of Eserine.** M. and M. POLONOVSKI (*Compt. rend.*, 1924, **179**, 334—336; cf. A., 1923, i, 831).—Eserine and eserethole can react as secondary bases in the formation of nitroso and benzoyl derivatives. By the addition of a concentrated solution of sodium nitrite to eserine dissolved in a slight excess of acetic acid, *nitrosoeserine* (II) is obtained as a yellow, neutral oil. Similarly, eserethole yields *nitrosoeserethole*, a viscous, neutral, optically inactive oil, soluble in dilute acids, but which forms no crystalline salts except the *picrate*, m. p.  $133$ — $134^\circ$ . By the Schotten-Baumann reaction on eserethole suspended in dilute sodium hydroxide, *benzoyleserethole* is obtained as a viscous mass which is pulverisable in the presence of ether and petroleum, ( $[\alpha]_D -51^\circ$ ). The formation of these derivatives can only be explained on the open-chain formula for eserine ("eserinol," I) (cf. this vol., i, 980) in accordance with the scheme:



When an eserine salt is decomposed in aqueous solution by sodium hydrogen carbonate, an eserine *hydrate*,  $C_{15}H_{21}O_2N_3 \cdot H_2O$ , m. p.  $82^\circ$ , is obtained. This compound, however, is not regarded as having the eserinol structure. J. W. B.

**Hydrogen Derivatives of Eserine.** M. and M. POLONOVSKI (*Compt. rend.*, 1924, **178**, 2078—2081).—A correction to previous work (A., 1923, i, 831). The formula previously suggested for eserine (quoted with an obvious misprint) with an ethylenic linking in the pyrrole nucleus is untenable, principally because the quaternary salts can combine with but 1 mol. of hydrogen, giving a completely saturated open-chain methine base, although other evidence also is adduced. The new formula suggested is appended. Reduction

in acid solution is then explicable only on the assumption that the ring is opened, at the point indicated by the dotted line, as in the



case of the reduction of the quaternary salts. This view is supported by a reaction with methyl iodide towards which hydroserethole behaves as a secondary open-chain base. L. J. H.

**Quebrachamine.** (Miss) E. FIELD (*J. Chem. Soc.*, 1924, 125, 1444—1450).—This alkaloid, now being prepared commercially from quebracho bark (presumably as a by-product in the manufacture of aspidospermine), has been investigated in the hope of discovering some relationship between it and quebrachine and aspidospermine (from the same bark). Cow (*J. Pharm. Exp. Ther.*, 1913—1914, 5, 341) has found their physiological actions to be similar and to differ only in intensity. Quebrachamine,  $C_{19}H_{26}N_2$ , has m. p.  $147^\circ$  (cf. Hesse, A., 1882, 742),  $[\alpha]_D -109.5^\circ$  in acetone, and distils without appreciable decomposition under high vacuum at  $240-250^\circ$ . It is feebly basic and forms a *sulphate*,  $C_{19}H_{26}N_2 \cdot H_2SO_4 \cdot 2H_2O$ , sparingly soluble in cold water; the *oxalate* has m. p.  $217^\circ$ . The base appears to be fully saturated, and does not absorb hydrogen in the presence of colloidal platinum. It is apparently a mono-acidic tertiary base; the *methiodide* has m. p.  $234^\circ$ , the *methosulphate* m. p.  $235^\circ$ . The nature of the second nitrogen atom has not been definitely ascertained; attempts to methylate it resulted in tarry products. Its behaviour towards nitrous acid suggests that it may be in the form of an imino group. On adding a solution of sodium nitrite to quebrachamine in acetic acid, a green oil is precipitated, changing to a yellow, amorphous solid. Attempts to form phenylcarbimido and acetyl derivatives were unsuccessful. The colour reactions of quebrachamine suggest that it contains an indole grouping. Quebrachamine *picrate*, m. p.  $195-196^\circ$ , exhibits chromoisomerism.

These properties are in harmony with the presence of a non-basic imino group and a benzene ring. The existence of the latter is indicated by the formation of picric acid when the alkaloid is heated with 30% nitric acid at  $150^\circ$ . Other oxidising agents react readily, but the products are amorphous mixtures. Bromine reacts with quebrachamine to form an unstable *perbromide*,  $C_{19}H_{24}N_2Br_6$ , m. p.  $160^\circ$  (decomp.), which, on prolonged boiling with water, loses bromine to give a *bromo* compound,  $C_{19}H_{23}ON_2Br_3$ , not melting at  $290^\circ$ . The compound is not changed by sodium hydroxide, and hence is not a hydrobromide. On boiling with sodium in alcoholic solution, quebrachamine is regenerated.

The high hydrogen content of the alkaloid precludes the presence of more than one benzene ring. A striking resemblance between the molecular formulæ of quebrachamine and aspidospermine ( $C_{22}H_{30}O_2N_2$ ) is pointed out. Hydrolysis of the latter (cf. Ewins, T., 1914, 105, 2738) causes the removal of a methoxyl and a *N*-acetyl group and leaves a base, aspidosine,  $C_{19}H_{26}ON_2$ , a phenolic substance, of which the parent substance,  $C_{19}H_{26}N_2$ , has the same empirical formula as quebrachamine. Aspidosine, like quebrachamine, is a monoacidic tertiary base and contains an imino group and a benzene ring. On the other hand, quebrachamine cannot be acetylated, and forms only a monomethiodide, whilst both



nitrogen atoms in deacetylaspidospermine undergo methylation. Further, aspidospermine and its derivatives do not give the reactions of indoles. Attempts to remove the hydroxyl group from aspidosine were unsuccessful. No similar relationship between quebrachamine and quebrachine (yohimbine) is apparent, and reasons are given to show they can not have the same skeleton. A. C.

**Spectrographic Study of Vegetable Alkaloids. Absorption of Ultra-violet Rays by Alkaloids of the *iso*Quinoline and Morphine Groups.** P. STEINER (*Bull. Soc. Chim. biol.*, 1924, 6, 231).—A detailed study of the ultra-violet absorption spectra of the principal *iso*quinoline and morphine alkaloids and of the compounds from which they are derived. The results of earlier work on the absorption spectra of some of these alkaloids is in general confirmed and a large amount of new quantitative data is presented.

Each alkaloid examined has a definitely characteristic ultra-violet absorption spectrum, which is closely related to that of the principal aromatic nucleus in the molecule when that nucleus is comparatively little modified (*e.g.*, the *iso*quinoline nucleus in papaverine). On the other hand, when the principal nucleus is much modified, the spectrum of the alkaloid is quite unlike that of the nucleus (*e.g.*, *iso*quinoline and berberine). When the molecule is made up of two large aromatic nuclei, its spectrum is determined almost entirely by one of them.

The author has specially investigated cotarnine and hydrastinine with a view to decide between the three structural formulæ which have been proposed for these substances. The absorption curves provide strong evidence that cotarnine has the  $\cdot\text{CH}(\text{OH})\cdot\text{NMe}\cdot$  structure in hexane and ether solutions, thus confirming the conclusions of Dobbie, Lauder, and Tinkler (*cf.* T., 1903, 83, 598), and that it has the  $\cdot\text{CH}\cdot\text{NMe}(\text{OH})\cdot$  structure in aqueous and acid solutions; in alcoholic solution it is apparently a mixture of these two types. There is no evidence for the aldehydic formula.

The alkaloids can be identified and determined by means of their absorption spectra, but the method has been worked out only for solutions of the pure substances. C. T. G.

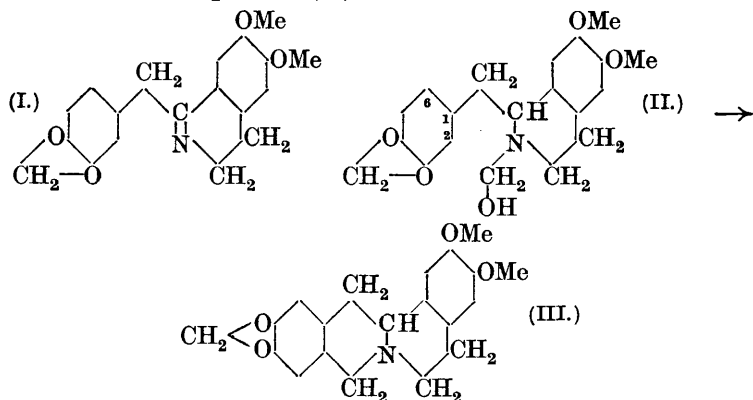
**Preparation of a Mercury Quinine Compound.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Swiss Pat. 100410; from *Chem. Zentr.*, 1924, i, 2206).—A solution obtained by shaking a suspension of mercuric oxide with quinine sulphate solution is added to ethyl alcohol, whereby a precipitate of *mercuriated quinine disulphate* is obtained. G. W. R.

**$\psi$ -*epi*Berberine.** J. S. BUCK and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1924, 125, 1675—1686).—As *epi*berberine has hitherto been obtained only from cryptopine (T., 1918, 113, 492), its synthesis was attempted by a method resembling that for berberine (*cf.* Pictet and Gams, A., 1911, i, 807), and 1-*homopiperonyl*-6:7-*dimethoxytetrahydroisoquinoline* was obtained, but the alkaloid produced from it by the action of formaldehyde and hydrochloric acid was shown to be *tetrahydro- $\psi$ -epiberberine*, instead of *tetrahydroepiberberine*.

For preparation of the starting materials, veratraldehyde from vanillin was condensed with ethyl acetate in presence of sodium to 3:4-dimethoxycinnamic acid, which was reduced by sodium amalgam to 3:4-dimethoxyphenylpropionic acid (cf. Perkin and Robinson, T., 1907, 91, 1079). The acid was converted by dry ammonia at 220—230° into its *amide*, m. p. 121°, which with sodium hypochlorite gave a 70% yield of homoveratrylamine (cf. Decker, A., 1913, i, 272). Condensation of piperonal with hippuric acid gave the azlactone, which was hydrolysed to benzoic acid and piperonylpyruvic acid (Kropp and Decker, A., 1909, i, 248), and oxidation of the latter with hydrogen peroxide (cf. Mauthner, A., 1910, i, 115) yielded homopiperonylic acid.

*Homopiperonylhomoveratrylamine*,

$\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OMe})_2$ , needles, m. p. 130—131°, was prepared (a) by heating homopiperonylic acid with homoveratrylamine at 180—200°, or (b) by addition of homopiperonyl chloride (prepared by use of thionyl chloride) to homoveratrylamine in presence of potassium hydroxide. Digestion with phosphorus oxychloride in boiling toluene gave a phosphate, from which alkali liberated 1-homopiperonyl-6:7-dimethoxy-3:4-dihydroisoquinoline (yield 80%) (I). It is a strong base (colourless *hydrochloride*, m. p. 200°; *picrate*, m. p. 197°); except when pure and dry, it is oxidised by air to a *base*,  $\text{C}_{19}\text{H}_{17}\text{O}_5\text{N}$ , m. p. 152°. Reduction with sulphuric acid and zinc forms 1-homopiperonyl-6:7-dimethoxytetrahydroisoquinoline, irregular plates, m. p. 96° (a strong base, forming colourless *hydrochloride* and *sulphate*). Condensation of this substance with methylal was unsuccessful (cf. Pictet and Gams, *loc. cit.*), but its methyl-alcoholic solution was condensed with formaldehyde in presence of sodium hydrogen carbonate and the product (II) was treated with hot concentrated

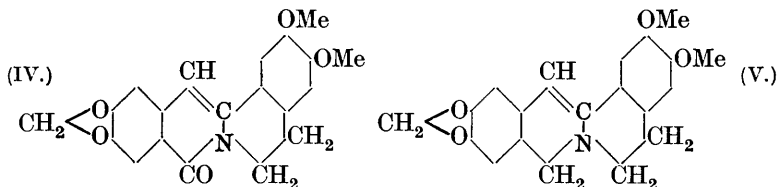


hydrochloric acid. The *hydrochloride* of tetrahydro- $\psi$ -epiberberine was isolated and was decomposed with potassium carbonate, giving the *base*, jagged prismatic needles, m. p. 160—161° (III). It is distinguished from tetrahydroepiberberine by the m. p. and by the mixed m. p. The *picrate* melts at 149—150° (decomp.).

*pp*\*

No trace of tetrahydroepiberberine was formed, showing that ring formation (II  $\rightarrow$  III) takes place solely with the hydrogen atom in position 6, and not with that in position 2.

Tetrahydro- $\psi$ -epiberberine was oxidised by iodine in alcoholic solution, in presence of sodium acetate, and the resulting periodide was decomposed with sulphurous acid, yielding  $\psi$ -epiberberinium iodide,  $C_{20}H_{18}O_4NI$ , yellow, rhombic prisms, m. p. about  $303^\circ$ . Digestion of the iodide with silver chloride gave  $\psi$ -epiberberinium chloride, yellow, existing in 3 modifications:  $C_{20}H_{18}O_2NCl \cdot 4\frac{1}{2}H_2O$ ,  $C_{20}H_{18}O_4NCl \cdot 2\frac{1}{2}H_2O$ , and the dimorphous anhydrous salt. The chloroplatinate and dimorphous picrate, m. p.  $105^\circ$ , were obtained. Decomposition of the chloride with potassium hydroxide is exactly analogous to the decomposition of epiberberinium chloride (T., 1918, **113**, 517). The products are (a) oxy- $\psi$ -epiberberine (IV), almost colourless, m. p.  $206^\circ$ , differing from oxyepiberberine by its m. p., and (b) dihydro- $\psi$ -epiberberine (V), yellow, rhombic prisms, m. p.  $173^\circ$ , distinguished from dihydroepiberberine by their mixed



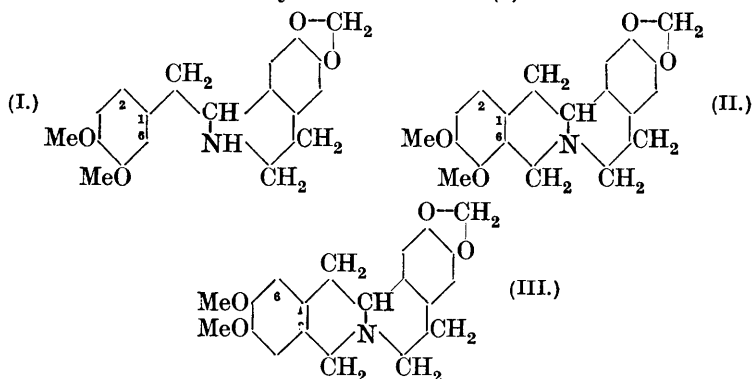
m. p. It forms pale yellow salts; *hydrochloride*, m. p.  $266^\circ$ ; *hydriodide*, m. p. about  $281^\circ$ , with blackening. F. M. H.

**$\psi$ -Berberine.** R. D. HAWORTH, W. H. PERKIN, jun., and J. RANKIN (*J. Chem. Soc.*, 1924, **125**, 1686—1701).—Repetition of a synthesis by Pictet and Gams (A., 1911, i, 807) showed that the product of the action of methylal and hydrochloric acid on 1-veratryl-6:7-methylenedioxytetrahydroisoquinoline is not, as they concluded, tetrahydroberberine, but *tetrahydro- $\psi$ -berberine*. Their synthesis of oxyberberine (A., 1911, i, 483) could not be repeated.

Starting materials were prepared as follows: 3:4-dimethoxyphenylpyruvic acid, yield 50%, obtained by a modification of Kropp and Decker's method (A., 1909, i, 248), gave 3:4-dimethoxyphenylacetic acid (Cain, Simonsen, and Smith, T., 1913, **103**, 1036). A pyridine solution of piperonal and malonic acid in presence of piperidine gave 3:4-methylenedioxy-cinnamic acid (quantitative yield), which furnished 3:4-methylenedioxyphenylpropionic acid (yield 85%) (Perkin and Robinson, T., 1907, **91**, 1079). The *amide* was prepared from the acid chloride and was converted into 3:4-methylenedioxyphenylethylamine (cf. Decker, A., 1913, i, 272).

The yield of homoveratroylhomopiperonylamine was greatly improved; it was obtained (a) by condensation of 3:4-dimethoxyphenylacetyl chloride with 3:4-methylenedioxyphenylethylamine, or (b) by heating this amine with 3:4-dimethoxyphenylacetic acid at  $180^\circ$ . By boiling a toluene solution of homoveratroylhomopiperonylamine with phosphorus oxychloride, the yield (75%) of

1-veratryl-6:7-methylenedioxydihydroisoquinoline is much higher than when phosphoric oxide is used. Pictet and Gams (*loc. cit.*) describe the base as amorphous, m. p. 68—70°, salts indefinite. It is now found to be crystalline, m. p. 88° (*hydrochloride*, m. p. 62°, loses water of crystallisation and then melts at 125°; *hydriodide*, m. p. 239—240°; *picrate*, m. p. 206°). In air, it tends to oxidise to a base,  $C_{19}H_{17}O_5N$ , m. p. 151°. Reduction of the dihydroisoquinoline by means of tin and hydrochloric acid yielded 1-veratryl-6:7-methylenedioxytetrahydroisoquinoline (I), prisms, m. p. 84° (*hydrochloride*, prisms, m. p. 236°, *sulphate*, plates, m. p. 136—137°, *picrate*, yellow needles, m. p. 185—187°); this is analogous to similar tetrahydroisoquinolines, which all melt below 100°, but Pictet and Gams gave as m. p. of the base 208—210° and found the salts difficult to crystallise. When (I) is condensed with



methylal and hydrochloric acid, it would be expected that III would be formed, but Pictet and Gams claim that they obtained tetrahydroberberine (II). This is especially anomalous, since condensation of 1-homopiperonyl-6:7-dimethoxytetrahydroisoquinoline has now been shown to occur normally (cf. Buck and Perkin, this vol., i, 1096). When 1-veratryl-6:7-methylenedioxytetrahydroisoquinoline was treated exactly as in the original synthesis, it gave a base,  $C_{20}H_{21}O_4N$ , small needles, m. p. 177°: but tetrahydroberberine melts at 169° and the mixture at 142—144°. Therefore this must be isomeric with tetrahydroberberine (II) and has been named tetrahydro-ψ-berberine (III) (*hydrochloride* darkens at 222°, m. p. 228—230°; *hydriodide* softens at 178°, m. p. 222°; *sulphate*, m. p. 168°; *picrate*, m. p. 176°; *methiodide*, prismatic needles, m. p. 256° [decomp. 260°]). The yield was small and an amorphous substance was produced containing no tetrahydroberberine. A much better yield (60%) of tetrahydro-ψ-berberine is obtained by condensing a methyl-alcoholic solution of the tetrahydroisoquinoline with formaldehyde and decomposing the formyl derivative with hydrochloric acid (cf. Decker, *loc. cit.*).

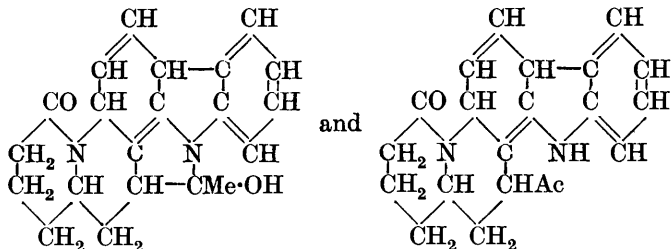
Tetrahydro-ψ-berberine is oxidised by iodine in alcoholic solution to ψ-berberinium iodide, canary-yellow needles, m. p. 274° (decomp.). Silver chloride converts this into ψ-berberinium chloride, obtained



*methiodide* decomposes at 247°.  $\beta$ -*Dihydrodimethylmorphimethine*, obtained by partial reduction of the  $\beta$ -methine, has m. p. 115°.  
G. W. R.

**Preparation of an Additive Product of Codeine.** O. HINSBERG (D.R.-P. 377588; from *Chem. Zentr.*, 1924, i, 968).—Codeine and *p*-acetaminophenol yield an *additive* compound of composition  $C_{18}H_{21}O_3N \cdot OH \cdot C_6H_4 \cdot NHAc$ , m. p. 125°.  
G. W. R.

**Constitutional Formula of Strychnine. III.** E. OLIVERI-MANDALÀ (*Gazzetta*, 1924, 54, 516–528).—In the light of present knowledge concerning the reactions of strychnine and *isostrychnine* (cf. A., 1923, i, 702, 1223), the formulæ which best express the structures of these two bases are respectively,

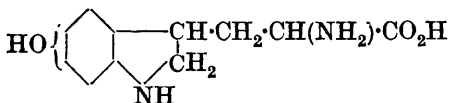


(cf. Perkin and Robinson, T., 1910, 97, 305).

T. H. P.

**Preparation of Acylapocincholoiponitriles.** A. KAUFMANN (D.R.-P. 382911; from *Chem. Zentr.*, 1924, i, 1595–1596).—Acylcincholoiponamides are treated with alkali hypohalogenites. *Benzoylcincholoiponamide* (1-benzoyl-3-ethylpiperidinoacetamide), m. p. 88–89°, is converted by alkaline hypobromite into *benzoylapocincholoiponitrile* (1-benzoyl-3-ethylpiperidine-4-carboxylonitrile). *Benzoylapocincholoiponamide* has m. p. 144°.

**Isolation from Casein of an Amino-acid of the Indole Group with the Composition  $C_{11}H_{14}O_3N_2$ .** E. ABDERHALDEN and H. SICKEL (*Z. physiol. Chem.*, 1924, 138, 108–117).—The amino-acid previously isolated from casein and regarded as a hydroxytryptophan (Abderhalden and Kempe, A., 1907, i, 808) has been found to have the composition  $C_{11}H_{14}O_3N_2 \cdot 2\frac{1}{2}H_2O$ . It has m. p. 146° (slow heating),  $[\alpha]_D^{25} -28.68^\circ$ ,  $-28.10^\circ$  (aqueous solution), and, from its colour reactions, is provisionally considered to be a



hydroxydihydrotryptophan of the annexed structure. When dried at 105° in a vacuum over phosphorus pentoxide it loses its water

of crystallisation and, at the same time, appears to lose further water with the formation of an anhydride. It forms a *dibenzoyl* derivative, decomposing at 136° after sintering at 72°. E. S.

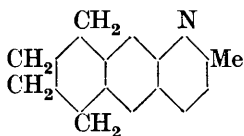
**Chemical Functions of Hypnotics, and of Hydantoin Derivatives in particular.** A. LUMIÈRE and F. PERBIN (*Bull. Soc. chim.*, 1924, [iv], 35, 1022–1026).—The most active hypnotics

known belong to the aliphatic series and contain a quaternary carbon atom linked to alkyl groups. The methyl derivatives are inactive, and the hypnotic effect appears to increase with replacement of methyl by homologous radicals, up to a solubility limit.

Of the dialkylhomophthalimides,  $\text{CO} \begin{smallmatrix} \text{NH} - \text{CO} \\ \text{CR}_2 - \text{C}_6\text{H}_4 \end{smallmatrix}$ , obtained by the action of alkyl iodides on homophthalimide, diethylhomophthalimide, *ethylpropylhomophthalimide*, m. p.  $117^\circ$ , and *diallylhomophthalimide*, m. p.  $140^\circ$ , are hypnotic, whilst *dipropylhomophthalimide*, m. p.  $128^\circ$ , is inactive. Similarly, among the dialkylacetylacetamides, obtained by the action of alkyl halides on the amides in the presence of sodium ethoxide, the following order of hypnotic activity holds: *acetyl-diethylacetamide* > *acetyl-di-propylacetamide*, m. p.  $100^\circ$  > *acetyl-diallylacetamide*, m. p.  $115^\circ$  > *acetyl-ethylisobutylacetamide*, m. p.  $108^\circ$ . In view of the unpleasant effects sometimes produced by hypnotics such as "nirvanol" (phenylethylhydantoin) which contain an aromatic radical, a number of other derivatives of hydantoin have been prepared by warming dialkylcyanoacetamides with sodium hypochlorite. *Ethylisobutylhydantoin*, m. p.  $199^\circ$ , *propylisobutylhydantoin*, m. p.  $173^\circ$ , and especially *dipropylhydantoin*, m. p.  $199^\circ$ , are hypnotic, but not *di-isobutylhydantoin*, m. p.  $220^\circ$ .

R. B.

**Course of the Quinaldine Synthesis with  $\beta$ -Aminotetrahydronaphthalene.** J. LINDNER, M. DJULGEROWA, and A. MAYR (*Monatsh.*, 1924, **44**, 337—347).—Experiments on the course of the quinaldine synthesis with  $\beta$ -aminotetralin (*ar*- $\beta$ -tetrahydronaphthylamine) show that both the linear and the angular compound are produced (cf. Braun and Gruber, A., 1922, i, 762), but the proportions could not be determined owing to the difficulty of separation. High concentrations of hydrochloric acid appeared to favour the synthesis, and from the reaction product after adding alkali, distilling in a vacuum, and removing unchanged  $\beta$ -tetrahydronaphthylamine as *benzoyl-ar*- $\beta$ -tetrahydronaphthylamine, m. p.  $167^\circ$ , the two quinaldines are separated by fractional crystallisation of the picrates from water, or extraction of the hydrobromides with benzene or fractional precipitation of the hydrochlorides or hydrobromides in alcoholic solution with ether. 6:7-Tetramethylene-



quinaldine (annexed formula), m. p.  $45^\circ$ , obtained finally by decomposition of the picrate with ammonia and extraction with benzene, gives a hygroscopic *hydrochloride*,  $\text{C}_{14}\text{H}_{15}\text{N}\cdot\text{HCl}$ , m. p.  $209$ — $212^\circ$ , a *hydrobromide*, m. p.  $212^\circ$ , and a *picrate*, m. p.  $206^\circ$ .

5:6-Tetramethylenequinaldine, m. p.  $57^\circ$ , was obtained similarly. The *hydrochloride*,  $\text{C}_{14}\text{H}_{15}\text{N}\cdot\text{HCl}$ , m. p. about  $240^\circ$ , and *hydrobromide*,  $\text{C}_{14}\text{H}_{15}\text{N}\cdot\text{HBr}$ , m. p.  $220^\circ$ , are non-hygroscopic and are less soluble than the isomeric compounds. The *chromate* is orange, but rapidly turns brown. The *picrate*, m. p.  $190^\circ$ , is less soluble in water than the picrate of the isomeric quinaldine, m. p.  $170^\circ$ . The constitution of the base is established by its dehydrogenation

at 700° to  $\beta$ -naphthoquinaldine, m. p. 81.5—82° (cf. Döbner and Miller, A., 1884, 1373).

In the preparation of  $\beta$ -aminotetrahydronaphthalene by Bamberger and Kitschelt's method (A., 1890, 631) a by-product,  $C_{10}H_{12}N \cdot C_5H_{11}$ , is produced, which is probably an amyl derivative of *ar*- or *ac*-tetrahydronaphthylamine. R. B.

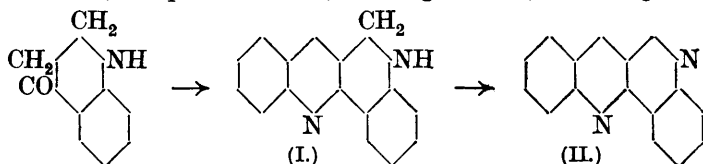
**Synthesis of 4-Tetrahydroquinolone and a new Synthesis of 4-Methoxyquinoline.** G. R. CLEMO and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1924, **125**, 1608—1622).—Condensation, in presence of alkali, of toluene-*p*-sulphonanilide and  $\beta$ -chloropropionic acid yielded *toluene-p-sulphonyl- $\beta$ -anilinopropionic acid*, m. p. 144° (*methyl ester*, m. p. 61—62°). The yield of a *by-product*,  $2C_{16}H_{17}O_4NS.H_2O$  (?), m. p. 213°, can be increased by varying the conditions. Toluene-*p*-sulphonyl- $\beta$ -anilinopropionic acid was converted by phosphoric oxide in boiling xylene into *toluene-p-sulphonyl-4-tetrahydroquinolone*, m. p. 140—141°. Hydrolysis with hydrochloric acid liberated 4-tetrahydroquinolone,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{NH} \cdot \text{CH}_2 \end{smallmatrix}$ , b. p. 195°/20 mm., m. p. 144°.

The action of phosphoryl chloride on toluene-*p*-sulphonyl- $\beta$ -anilinopropionic acid gave *toluene-p-sulphonyl-3-chloro-4-tetrahydroquinolone*, m. p. 124°. Since cold concentrated sulphuric acid eliminates hydrogen chloride, the chlorine atom cannot be situated in the benzene ring, whilst it cannot be attached to nitrogen because the substance does not react with diethylamine, diethylaniline, or potassium iodide. When boiled with concentrated hydrochloric acid, it is converted into 4-tetrahydroquinolone. Whilst toluene-*p*-sulphonyl-4-tetrahydroquinolone is converted by methyl-alcoholic potassium hydroxide into an *isomeric substance*, m. p. 135—150°, the corresponding derivative of 3-chloro-4-tetrahydroquinolone forms 4-methoxyquinoline, b. p. 167°/20 mm., m. p. 39—40°; *methiodide*, m. p. 145° (decomp.); *chloromercurate*, m. p. 201—202° (decomp.) (cf. Meyer, A., 1906, i, 604). Removal of the toluene-sulphonyl group seems to be connected with the presence of the chlorine atom in the  $\beta$ -position adjacent to the carbonyl group; two suggestions as to the mechanism of the reaction are made.

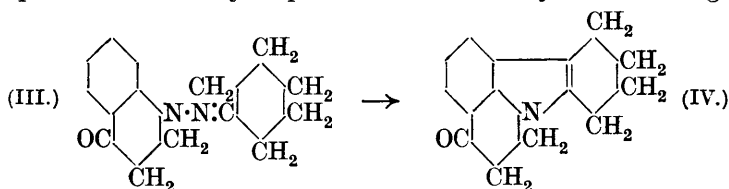
The NH group of tetrahydroquinolone is in evidence since with nitrous acid it gives *nitroso-4-tetrahydroquinolone*, m. p. 98°; it gives a derivative with toluene-*p*-sulphonyl chloride, and with benzoyl chloride gives *benzoyl-4-tetrahydroquinolone*, m. p. 122°. The reactivity of the  $\beta$ -CH<sub>2</sub> group is shown by condensation with benzaldehyde in alcoholic solution, in presence of sodium hydroxide, to 3-benzylidene-4-tetrahydroquinolone, m. p. 214°. The CO group is reactive and with phenylhydrazine there is formed 4-tetrahydroquinolonephenylhydrazone, m. p. 110°. On heating with dilute sulphuric acid, this undergoes the Fischer indole transformation with simultaneous oxidation, yielding 3:4-quinindoline, which melts and sublimes above 320° (*hydrochloride* and *chloroplatinate* described). When isatin and 4-tetrahydroquinolone are condensed and the product is heated under reduced pressure at



210°, carbon dioxide is eliminated, forming *dihydro-2:3-quinolino* (I), m. p. 235—237° (softening at 230°), affording fluores-

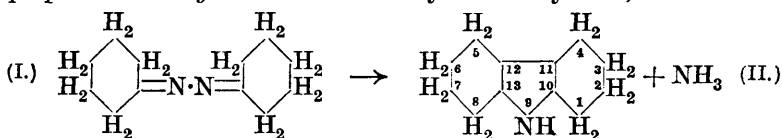


cent solutions. Distillation over lead oxide affords 2:3-*quinolino* (II), m. p. 186—187°. Reduction of nitroso-4-tetrahydroquinolone at 35—40° with zinc dust in presence of *cyclohexanone* gave 1-cyclohexylideneamino-4-tetrahydroquinolone (III), m. p. 112°. Dilute sulphuric acid converts this into *tetrahydrocarbazole-9:8-anhydropropionic acid* (IV), m. p. 135—136°; *phenylhydrazone*, m. p. 191°. 4-Tetrahydroquinolone is reduced by sodium amalgam



to a mixture of 4-*hydroxytetrahydroquinoline*, colourless prisms, m. p. 83—84° (*diacetyl* derivative, m. p. 95—96°), and 4:4'-*dihydroxy-1:2:3:4:1':2':3':4'-octahydro-4:4'-diquinolyl*, decomp. 235°, clear melt at 260°. This pinacol is dehydrated by concentrated sulphuric acid to 1:2:1':2'-*tetrahydro-4:4'-diquinolyl*, m. p. 165° (softening at 155°); *diacetyl* derivative, m. p. 230—231°. On boiling the methyl-alcoholic solution of the pinacol, oxidation occurs to 1:2-*dihydro-4:4'-diquinolyl*, m. p. 210° (softening at 200°); on keeping the solution in contact with air for some days, it yields 4:4'-*diquinolyl*, m. p. 166°. F. M. H.

**1:2:3:4:5:6:7:8-Octahydrocarbazole and its Derivatives.** W. H. PERKIN, jun., and S. G. P. PLANT (*J. Chem. Soc.*, 1924, 125, 1503—1512).—A detailed study of some of the more highly reduced derivatives of carbazole is described (see also T., 1921, 119, 1825; 1923, 123, 676). Catalytic reduction of carbazole by hydrogen in the presence of nickel does not appear to give the desired derivatives (cf. Padoa and Chiaves, A., 1908, i, 104; Von Braun and Ritter, A., 1923, i, 141). *cycloHexylideneazine* (I) was prepared from *cyclohexanone* and hydrazine hydrate, and this on



heating with hydrogen chloride in tetrahydronaphthalene gave a dark red oil. The fraction of b. p. 165—170°/15 mm. solidified

and yielded (28% of the theoretical) 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydrocarbazole* (II), m. p. 102°. The method of synthesis gives the constitution. The *picrate* had m. p. 140°; 9-*acetyloctahydrocarbazole*, m. p. 73°, was easily hydrolysed. Prolonged reduction of the octahydrocarbazole (II) with tin and hydrochloric acid gives 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 13-*decahydrocarbazole* (III), m. p. 75°, in good yield; *picrate*, m. p. 210° (decomp.). This decahydrocarbazole could not be reduced further in the electrolytic cell. Octahydrocarbazole is completely reduced electrolytically to *dodecahydrocarbazole* (IV),  $C_{12}H_{20}NH$ , m. p. 65°; *picrate*, m. p. 187°. It is noteworthy that decahydrocarbazole (III) is not reduced to dodecahydrocarbazole by electrolysis. Octahydrocarbazole (II) probably passes into 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 11-*decahydrocarbazole* and thence to (IV). Octahydrocarbazole is readily alkylated in alcoholic solution. When boiled under reflux with methyl iodide, it gave 9-*methyloctahydrocarbazole* (V), b. p. 139–140°/14 mm. (70% yield); *picrate*, m. p. 147°; *methiodide*, m. p. 194°. Reduction of (V), whether electrolytically or by tin and hydrochloric acid, produced only 9-*methyldecahydrocarbazole*, b. p. 128°/13 mm.; *picrate*, m. p. 162–163°; a definite methiodide was not obtained. 9-*Methyldodecahydrocarbazole*, b. p. 132°/18 mm., was prepared in good yield by the action of methyl iodide on (IV); *picrate*, m. p. 146°.

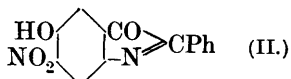
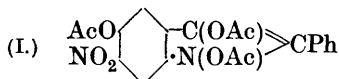
9-*Ethylloctahydrocarbazole*, prepared similarly, is a viscous, colourless oil, b. p. 166–170°/20 mm., which gradually turned yellow and then bright red on exposure to air; *picrate*, m. p. 152°; *methiodide*, m. p. 169°. 9-*Ethyldecahydrocarbazole* can be obtained by both of the methods given for the 9-methyl derivative as a colourless liquid, stable in air, b. p. 148–150°/21 mm.; *picrate*, m. p. 202°; *methiodide*, m. p. 205°. 9-*Ethyldodecahydrocarbazole*, by ethylation of dodecahydrocarbazole, has b. p. 143–145°/22 mm.; *picrate*, m. p. 132–133°; *methiodide*, m. p. 217°.

Several of these *N*-alkyl derivatives of the carbazoles were compared with corresponding compounds obtained by Von Braun and Ritter (*loc. cit.*) by catalytic reduction, and found to differ in important particulars: the 9-methyloctahydrocarbazole of Von Braun and Ritter has m. p. 94° and b. p. 176–178°/16 mm. and gives neither a crystalline *picrate* nor a *methiodide* (see above). The two compounds are isomerides, and it is suggested that the latter is 9-methyl-1 : 2 : 3 : 4 : 8 : 10 : 11 : 13-octahydro- or, more probably, 9-methyl-1 : 2 : 3 : 4 : 7 : 8 : 10 : 13-octahydrocarbazole, whilst that of the present authors has the true pyrrole structure and is 9-methyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrocarbazole. A similar structural difference is suggested for the corresponding isomeric decahydro compounds prepared by the two methods. The electrolytic reduction of tetrahydrocarbazole was found to stop at the hexahydro stage and to give the carbazole (m. p. 99°) in nearly quantitative yield. 9-*Methylhexahydrocarbazole* was obtained by reducing the tetra compound either electrolytically or by tin and hydrochloric acid. It is a colourless liquid, b. p. 144°/15 mm.; *picrate*, m. p. 143–144° (decomp.).

A. C.

**Sodamide as a Dehydrating Agent. Preparation of Indole, Methylinole, and Homologues.** A. VERLEY (*Bull. Soc. chim.*, 1924, [iv], 35, 1039—1040).—Sodamide readily converts aceto-*o*-toluidide into methylinole by heating at 270°, whereas the ordinary dehydrating agents, even thoria at 450°, fail; some *o*-toluidine is formed. The method is applicable to the preparation of homologues of methylinole. Indole can be obtained from formyl-*o*-toluidide, but the reaction must be moderated by dilution with sand or kieselguhr and the addition of a heavy solvent. R. B.

**Hydroxyquinol Derivatives of the Isatogen Series.** P. RUGGLI and W. LEONHARDT (*Helv. Chim. Acta*, 1924, 7, 689—702; cf. A., 1923, i, 833).—6-Nitro-1:3:5-triacetoxy-2-phenylinole, m. p. 194—195° (I), is produced, together with another compound to be described later, when 6-nitro-2-phenylisatogen is treated with acetic anhydride and sulphuric acid, the action resembling that whereby *p*-benzoquinone is converted into 1:2:4-triacetoxybenzene. When the triacetoxy compound is heated with dilute alcoholic hydrochloric acid it affords 6-nitro-5-hydroxy-1:3-diacetoxy-2-phenylinole, m. p. 214—215°, which may be re-acetylated to regenerate its parent, or treated with chloroacetic anhydride to afford 6-nitro-1:3-diacetoxy-5-chloroacetoxy-2-phenylinole, m. p. 156—158° (decomp.). When the diacetoxy compound is treated with diazomethane, it gives 6-nitro-5-methoxy-1:3-diacetoxy-2-phenylinole, m. p. 221—222°. The triacetoxy compound dissolves in cold sulphuric acid to form a dark violet-coloured solution from which, on dilution, 6-nitro-5-hydroxy-3-keto-2-phenylinolenine (II),



cherry-red needles, m. p. 188°, is precipitated. This substance yields an *oxime*, which decomposes at 280°, but when treated with methyl sulphate yields a *methyl* ether, m. p. 172°; this can be acetylated (on the phenolic hydroxyl) to an *acetyl* derivative, m. p. 152°. When 6-nitro-5-methoxy-1:3-diacetoxy-2-phenylinole is treated with concentrated sulphuric acid it yields 6-nitro-5-methoxy-3-keto-2-phenylinolenine, dark red needles, m. p. 157°; the *oxime*, m. p. 263—264°, can be methylated to a *methyl* derivative, m. p. 157°, which may also be obtained by treatment of the above hydroxy-*oxime* with an excess of diazomethane. The methoxy-*oxime* is oxidised by chromic-acetic acid to 3:6-dinitro-5-methoxy-2-phenylinole, m. p. 303—306° (decomp.), whilst 6-nitro-5-methoxy-3-keto-2-phenylinolenine, the parent ketone, is converted by the same reagent into 4-nitro-2-benzoylamido-5-methoxybenzoic acid, m. p. 272°, which is hydrolysed by syrupy phosphoric acid at 130—170°, 4-nitro-2-amino-5-methoxybenzoic acid, violet needles, m. p. 217—218°, being thus obtained. 4-Amino-2-benzoylamido-5-methoxybenzoic acid, colourless scales, decomp. 200°, is obtained by catalytic reduction (nickel) of the nitro acid, and has an *acetyl* derivative, decomp. 275°; when it is diazotised and treated with cuprous oxide 2-benzoylamido-5-methoxybenzoic acid, m. p. 200°, is obtained. This

compound was identified by comparison with a sample prepared as follows. *2-Nitro-5-methoxytoluene*, m. p.  $50^{\circ}$ , is obtained when 6-nitro-*m*-cresol is methylated; it is reduced and forthwith benzoylated yielding *2-benzoylamido-5-methoxytoluene*, colourless needles, m. p.  $200^{\circ}$ , which, when oxidised with hot dilute potassium permanganate solution, yields *2-benzoylamido-5-methoxybenzoic acid*. *2-Benzoylamido-3-methoxybenzoic acid*, obtained via *2-nitro-3-methoxybenzoic acid*, has m. p.  $204.5^{\circ}$ , and *2-benzoylamido-6-methoxybenzoic acid* has m. p.  $120^{\circ}$ . The latter compound was prepared from 6-nitro-*o*-cresol; *2-nitro-6-methoxytoluene* has m. p.  $52^{\circ}$  and when reduced and benzoylated yields *2-benzoylamido-6-methoxytoluene*, m. p.  $177^{\circ}$ .

When 6-nitro-5-methoxy-1 : 3-diacetoxy-2-phenylindole is treated with stannous chloride in acetic acid solution *6-amino-5-methoxy-3-acetoxy-2-phenylindole*, m. p.  $212^{\circ}$ , is obtained, and this is converted by acetic anhydride and sulphuric acid into a *diacetyl* derivative, m. p.  $220^{\circ}$ .

When methyl isatogenate (Pfeiffer, A., 1916, i, 327) is treated with acetic anhydride and a little sulphuric acid a *compound*, m. p.  $193\text{--}195^{\circ}$ , possibly analogous to the one described above, is obtained.  
W. A. S.

#### Action of Oxalyl Chloride on certain Cyclic Organic Bases.

M. GIUA (*Gazzetta*, 1924, **54**, 593—597; cf. Oddo and Sanna, A., 1922, i, 371).—When oxalyl chloride and pyrrole interact below  $0^{\circ}$  and the mass is subsequently heated on a water-bath, black pigments are formed, together with 2-pyrrolyglyoxyl chloride, which yields the acid (cf. Ciamician and Silber, A., 1884, 1044, 1193) in presence of water. From indole an almost theoretical yield of 2-indoleglyoxyl chloride is obtained in absolute ethereal solution, the corresponding acid being obtained by treatment with water; 2-methyl-3-indoleglyoxyl chloride and a magenta colouring matter are obtained similarly from 2-methylindole.

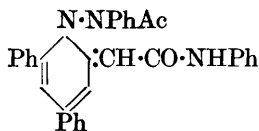
*2-Indoleglyoxyl chloride*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH} \\ \text{NH}\end{smallmatrix}\rangle\text{C}\cdot\text{CO}\cdot\text{COCl}$ , has m. p.  $138\text{--}139^{\circ}$ . *2-Indoleglyoxylic acid*,  $\text{C}_8\text{H}_6\text{N}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , m. p.  $224\text{--}225^{\circ}$  (decomp.), when treated with fused potassium hydroxide at  $200\text{--}205^{\circ}$  yields indole-2-carboxylic acid. *Silver 2-indoleglyoxylate* forms white crystals.

*2-Methyl-3-indoleglyoxyl chloride* forms a brown, crystalline mass and, when heated with neutral solvents, resinifies and yields a magenta-red substance. *2-Methyl-3-indoleglyoxylic acid* (cf. Angeli and Marchetti, A., 1908, i, 207) forms a *methyl ester*, m. p.  $172\text{--}173^{\circ}$ . The *colouring matter* formed together with the chloride separates as a dark red powder, m. p. about  $120^{\circ}$ , decomposes at a slightly higher temperature, dissolves readily in concentrated acids or in alkali solution, and contains 8.22% of nitrogen. T. H. P.

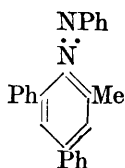
**Pyridine-arylimines.** I. W. SCHNEIDER [with W. DOENHARDT, O. SÜSSENGUTH, H. NITZSCHE, A. ROSS, A. SACK, and E. LEUTHEUSSER] (*Annalen*, 1924, **438**, 115—146).—1 : 4 : 6-*Triphenyl-2-methylpyridinium iodide*, m. p.  $243^{\circ}$ , is obtained by treating

4 : 6-diphenyl-2-methylpyrylium iodide with aniline (cf. Schneider and Seebach, A., 1921, i, 877; Schneider and Ross, A., 1922, i, 1171); when treated with alkali, the corresponding anhydro base, 1 : 4 : 6-triphenyl-2-methylenedihydropyridine, is produced as an unstable, reddish-brown, amorphous substance; this combines instantly, when freshly isolated, with carbon disulphide to yield a dark red substance,  $C_{50}H_{40}O_2N_2S_3$ , m. p.  $200^\circ$  (cf. Schneider, Gaertner, and Jordan, this vol., i, 551), which gives a *perchlorate*, m. p.  $170^\circ$ . The anhydro base also combines with phenylthiocarbimide, affording a red compound,  $C_{24}H_{19}N, Ph \cdot NCS$ , and with phenylcarbimide, an analogous compound, red prisms, m. p.  $233^\circ$ , being produced. 4 : 6-Diphenyl-1-benzyl-2-methylpyridinium iodide, similarly produced from benzylamine and the pyrylium iodide, has m. p.  $212^\circ$ . The corresponding base is again a brown, amorphous substance reacting with the above three reagents; with carbon disulphide a red compound, with phenylthiocarbimide a compound, red needles, m. p.  $193^\circ$ , and with phenylcarbimide a similar product, m. p.  $195^\circ$ , are obtained. 1-Methylamino-4 : 6-diphenyl-2-methylpyridinium iodide, obtained when methylhydrazine is used, forms yellow needles, m. p.  $180^\circ$ . Its anhydro base is very unstable; with carbon disulphide it affords a red substance and with phenylcarbimide and -thiocarbimide greenish-yellow (m. p.  $242^\circ$ ) and red (m. p.  $164^\circ$ ) compounds, respectively. 1-Phenylmethylamino-4 : 6-diphenyl-2-methylpyridinium iodide, obtained by using *as.*-phenylmethylhydrazine, is an orange-yellow substance, m. p.  $167^\circ$ , and gives a yellow, amorphous base which, like its congeners, reacts with carbon disulphide and phenylcarbimide, but gives a definite compound (red needles, m. p.  $171^\circ$ ) only with phenylthiocarbimide. Similarly, 1-diphenylamino-4 : 6-diphenyl-2-methylpyridinium iodide (yellow crystals, m. p.  $137^\circ$ ) affords a yellow, amorphous base, very unstable, the phenylthiocarbimide compound of which forms dark red leaflets, m. p.  $124^\circ$ .

The characteristic properties of the methylenedihydropyridines are illustrated by the above examples. To the blue base obtained by Schneider and Seebach (*loc. cit.*) an analogous constitution was originally ascribed; certainly in some reactions it behaves as if it were 1-phenylamino-4 : 6-diphenyl-2-methylenedihydropyridine, but in other respects it is quite different from the above compounds of this class. Thus, it combines with phenylcarbimide, but with two molecular proportions, to form the compound  $C_{38}H_{30}N_4O_2$ , m. p.  $128.4^\circ$ ; it also reacts with carbon disulphide, but slowly (cf. *loc. cit.*); it yields an *acetyl* derivative, an amorphous mass, resembling the above bases, which again combines with phenylcarbimide to a compound, m. p.  $150^\circ$  (annexed formula), and when treated with ammoniacal silver nitrate it forms a red complex salt,  $(C_{24}H_{20}N_2)_2 \cdot AgNO_3$ , m. p.  $168^\circ$ . On the other hand, the base is intensely blue and crystalline; when treated with methyl iodide it yields, as one product, the 1-phenylmethylamino-4 : 6-diphenyl-2-methylpyridinium iodide described above; its colour depends on



the solvent used to dissolve it, and its stability on the same factor; thus it is blue in benzene or chloroform and loses its colour in a few hours, but in alcohol it is violet and tolerably stable. Experiments are described in which the action of nitrous acid and nitric oxide on this base and on its congeners described below was investigated, but these gave no conclusive results. As the base obtained from 1-methylamino-4 : 6-diphenyl-2-methylpyridinium iodide, described above, resembles its congeners, in this blue



base the presence of the phenyl group in place of the methyl is considered so to affect the valency distribution that the compound should be formulated as a pyridinephenylimine (annexed formula), being thus the first member of a new class of compounds.

This explains satisfactorily the blue colour of the substance, and the properties wherein it resembles the methylene anhydro bases can be referred to tautomeric change.

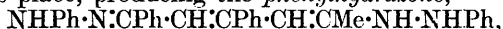
Phenylhydrazine and 2 : 6-diphenyl-4-methylpyrylium iodide (Schneider and Ross, *loc. cit.*) yield, in cold alcohol solution with a little acetic acid, 1-phenylamino-2 : 6-diphenyl-4-methylpyridinium iodide, yellow needles, m. p. 200°. When this is treated with sodium hydroxide, 2 : 6-diphenyl-4-methylpyridinephenylimine, a deep blue substance, needles, m. p. 101°, closely resembling its isomeride, is obtained. This reacts with carbon disulphide and phenylthiocarbimide, and with phenylcarbimide forms an orange compound crystallising in leaflets, m. p. 152°. It also yields a complex salt with silver nitrate, m. p. 172°.

2 : 4 : 6-Triphenylpyrylium iodide (Schneider and Seebach, *loc. cit.*) and phenylhydrazine react in cold alcohol to give ( $\alpha$ -) 2 : 4 : 6-triphenylpyranol phenylhydrazide (cf. following abstract), m. p. 162°, but in hot alcohol an isomeride, the ( $\beta$ -)hydrazide, m. p. 126°, is obtained. When the  $\alpha$ -hydrazide is treated with hot acetic acid, and the solution basified, it is converted chiefly into 2 : 4 : 6-triphenylpyridinephenylimine, dark blue needles, m. p. 182°. This compound resembles its congeners, but is more stable, reacts more slowly, and gives less well-defined products with the customary reagents. When it is treated in dilute acetic acid solution with potassium iodide, 1-phenylamino-2 : 4 : 6-triphenylpyridinium iodide, yellow needles, m. p. 161°, is obtained, whilst with methyl iodide it yields 1-phenylmethylamino-2 : 4 : 6-triphenylpyridinium iodide, m. p. 136°, identical with the product of interaction of phenylmethylhydrazine and the pyrylium iodide. The corresponding amorphous anhydro base appears to suffer conversion into a phenylhydrazide, m. p. 160°, when recrystallised from alcohol (cf. following abstract).  
W. A. S.

### Reaction of Pyrylium Compounds with Phenylhydrazine.

W. SCHNEIDER and W. MÜLLER (*Annalen*, 1924, **438**, 147—154).—When 4 : 6-diphenyl-2-methylpyrylium iodide or sulphoacetate (cf. preceding abstract and earlier references quoted therein) is treated with phenylhydrazine in cold alcoholic solution, the  $\alpha$ -phenylhydrazide, 4 : 6-diphenyl-2-methylpyranolphenylhydrazide, yellow

needles, m. p. 119°, is obtained. In this compound, the pyranol ring is considered to remain intact. It is a comparatively unstable substance; even when dissolved in cold acetic acid it is partly decomposed to the parent pyrylium compound, and partly converted into a 1-phenylamino-4:6-diphenyl-2-methylpyridinium salt, whilst with alkali 4:6-diphenyl-2-methylpyridinephenylimine is obtained. With phenylhydrazine, or if the pyrylium salt be directly treated with an excess of phenylhydrazine, further interaction takes place, producing the *phenylhydrazone*,



orange needles, m. p. 130°.

When the original alcoholic reaction mixture is heated, an isomeride, the  $\beta$ -*hydrazide*, is produced. This is also obtained when an alcoholic solution of the  $\alpha$ -compound is heated for some time. It forms stable, brownish-yellow crystals, m. p. 115°. The pyranol ring is supposed here to have become opened up, but the authors have not yet decided which of the numerous possible formulæ should be attributed to the compound. It is only converted into the pyridinium salt by long treatment with acetic acid. When it is treated with phenylhydrazine, it yields a *phenylhydrazone* isomeric with that described above, yellow needles, m. p. 178°.

W. A. S.

**4-Benzyl-2-methylquinoline.** E. ROSENHAUER (*J. pr. Chem.*, 1924, [ii], **108**, 91—98).—4-Benzyl-2-methylquinoline, obtained by heating *N*-benzylquinaldinium iodide at 230°, has m. p. 63°; *picrate*, decomp. 185°; *hydrochloride*, decomp. 216°; *hydriodide*, decomp. 234°; *methiodide*, decomp. 194°. The base reacts with benzaldehyde, forming 4-benzyl-2-styrylquinoline, m. p. 99°; *picrate*, decomp. 237°; *hydrochloride*, decomp. 231°; *methiodide*, decomp. 224°. The methiodide when heated with alcoholic potassium hydroxide loses hydrogen iodide, forming 1-methyl-4-benzylidene-2-styryl-1:4-dihydroquinoline, brick-red needles, m. p. 140°.

4-Benzyl-2-p-dimethylaminostyrylquinoline forms yellow prisms, m. p. 158°; its halogen acid salts, which are dyestuffs, are of uncertain composition; the *picrate*, decomp. 239°, and *methiodide*, decomp. 261°, giving an intensely red alcoholic solution, were prepared. 4-Benzyl-2-m-nitrostyrylquinoline, crystals, m. p. 182°, forms a *picrate*, decomp. 217°. 4-Benzylquinophthalone, from 4-benzylquinaldine and phthalic anhydride, forms yellow needles, m. p. 236°.

E. H. R.

#### Aryl Substituted Aminoquinolines and their Derivatives.

M. DOHRN, C. ZÖLLNER, and CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 375715; from *Chem. Zentr.*, 1924, i, 967—968).—2-Arylquinoline-4-carboxylamides are treated with salts of hypohalogenous acids at low temperatures. The following compounds are mentioned: 4-Amino-2-phenylquinoline, m. p. 165°; 4-amino-2-phenyl-6-methylquinoline, m. p. 188—189°; 4-amino-2:2'-chlorophenylquinoline, m. p. 166°; 2:2'-chlorophenylquinoline-4-carboxylamide, m. p. 228—229°; 2:2'-chlorophenylquinoline-4-carboxylic acid, m. p. 256—257°; 2:4'-chloro-

*phenylquinoline-4-carboxylic acid*, m. p. 228—229°; *2:4'-chloro-phenylquinoline-4-carboxylamide*, m. p. 238°; and *4-amino-2:4'-chlorophenylquinoline*, m. p. 150—151°. G. W. R.

**Production of Acridinium Compounds.** L. CASSELLA und Co. (Brit. Pat. 218542).—Hydroxy- and alkoxy-acridines are converted into acridinium compounds by the action of alkylating agents, such as methyl and ethyl *p*-toluenesulphonates, benzyl chloride, and ethylene chlorohydrin, in absence of bases, as, for example, in hot nitrobenzene solution. *3:6-Dihydroxy-10-methyl-acridinium chloride*, yellow needles; *3:6-dimethoxy-10-methyl-acridinium chloride*, light yellow scales; *3:6-dimethoxy-10-ethyl-acridinium chloride*, orange-yellow scales, m. p. 198° (decomp.); *3:6-dimethoxy-10-benzylacridinium chloride*, dark yellow needles, m. p. 236° (decomp.); and *3:6-dimethoxy-10-hydroxyethylacridinium chloride*, pale yellow needles, m. p. 240—242°, are described, all of which are strong bactericides of low toxicity and slight tinctorial power. F. G. W.

**Preparation of Colouring Matters.** AKTIEN-GESELLSCHAFT FÜR ANILIN FABRIKATION (W. HERZBERG, and G. HOPPE) (D.R.-P. 384790; from *Chem. Zentr.*, 1924, i, 1110—1111).—The following compounds are mentioned: *hydroxynaphthacridine*, orange-yellow; its *hydrochloride*, yellow; and *dihydroxydinaphthacridine*, orange. G. W. R.

**Unsymmetrical CC-Dialkylbarbituric Acids.** E. LAYRAUD (Fr. Pat. 546997; from *Chem. Zentr.*, 1924, i, 2205; cf. this vol., i, 92—93).—The following compounds, obtained by alkylation of the silver compounds of monoalkylbarbituric acids, are described: *ethylbutylbarbituric acid*, m. p. 126—127°; *butylallylbarbituric acid*, m. p. 118°. G. W. R.

**Unsymmetrical CC-Dialkylbarbituric Acids and their Salts.** E. LAYRAUD (Fr. Pat. [Add.] 26209; from *Chem. Zentr.*, 1924, i, 2205—2206; cf. preceding abstract).—The following new compound is mentioned: *piperazine ethylbutylbarbiturate*, m. p. 150—155°. G. W. R.

**Bromo Derivatives of 1-Methylglyoxaline and Constitution of "Chloroxalmethylin."** I. E. BALABAN and F. L. PYMAN (*J. Chem. Soc.*, 1924, 125, 1564—1572).—The bromination of 1-methylglyoxaline resembles that of glyoxaline (cf. T., 1922, 121, 947). The main product is *2:4:5-tribromo-1-methylglyoxaline*, m. p. 93—94.5° (*hydrochloride*, prisms, m. p. 190—200°). The second product was proved to be *4:5-dibromo-1-methylglyoxaline*, m. p. 79—80°, by its preparation from *4:5-dibromoglyoxaline* and methyl sulphate (*hydrochloride*, m. p. 179°, with previous softening [*dihydrate* also described], *nitrate*, m. p. 153°, *picrate*, m. p. 148—149°). Unlike the unmethylated base, *2:4:5-tribromo-1-methylglyoxaline* is resistant to the action of sodium sulphite, so *4(or 5)-bromo-1-methylglyoxaline* cannot be thus prepared. *5-Bromo-1-methylglyoxaline*, b. p. 128°/ca. 15 mm.,



m. p. 45—46°, is obtained (yield 51%), together with 4-bromo-1-methylglyoxaline (yield 1.5%), by the action of methyl sulphate on 4(or 5)-bromoglyoxaline; the *hydrochloride* (losing  $\frac{1}{2}\text{H}_2\text{O}$ ), m. p. 155°; *nitrate*, m. p. 155°; *hydrogen oxalate* (losing  $\frac{1}{2}\text{H}_2\text{O}$ ), m. p. 147°; *picrate*, m. p. 190°, are described. Its nitration and sulphonation (as for 4-bromoglyoxaline, *loc. cit.*) gave 5-bromo-4-nitro-1-methylglyoxaline (yield 80%), m. p. 180° (*hydrochloride*, m. p. about 155°), and 5-bromo-1-methylglyoxaline-4(?)*-sulphonic acid* (yield 78%), m. p. 284°, hydrolysed to 5-bromo-1-methylglyoxaline. 5-Bromo-1-methylglyoxaline is converted by formaldehyde at 130° into 5-bromo-2-hydroxymethyl-1-methylglyoxaline (yield 42%), m. p. 143° (*picrate*, m. p. 165—166°). Reduction with hydriodic acid and phosphorus gave 1:2-dimethylglyoxaline (cf. Windaus, A., 1909, i, 258). Interaction of *sym.*-dimethyloxamide and phosphorus pentabromide gave 4:5-dibromo-1-methylglyoxaline. Contrary to the conclusion of Sarasin (A., 1923, i, 710), the product (chloroxalmethylin) of the interaction of *sym.*-dimethyloxamide and phosphorus pentachloride (Wallach, A., 1877, ii, 182) is found to be 5-chloro-1-methylglyoxaline and the isomeric base produced by distillation of its methiodide must therefore be 4-chloro-1-methylglyoxaline. The action of methyl iodide on 4(or 5)-bromo-1-methylglyoxaline gave 4(or 5)-bromo-1:3-dimethylglyoxalinium iodide, m. p. 202—204°, which by distillation in a vacuum yielded 4-bromo-1-methylglyoxaline *nitrate*, m. p. 155° (yield 43%); the base itself was an oil (*picrate*, m. p. 179°). Nitration and sulphonation of 4-bromo-1-methylglyoxaline gave 4-bromo-5-nitro-1-methylglyoxaline (yield 54%), m. p. 105°, this being the main product of the action of methyl sulphate on 4(or 5)-bromo-5(or 4)-nitroglyoxaline; 4-bromo-1-methylglyoxaline-5(?)*-sulphonic acid* (yield 77%), prisms (+1H<sub>2</sub>O), m. p. 256° (decomp.), is hydrolysed to 4-bromo-1-methylglyoxaline.

4(or 5)-Bromoglyoxaline does not react with bromobenzene or sodium sulphite, but is reduced by hydriodic acid and phosphorus to glyoxaline. The reactivity of the halogen is increased by the presence of an *o*-nitro group. Thus 4(or 5)-bromo-5(or 4)-nitroglyoxaline on boiling with aqueous sodium sulphite gave 5(or 4)-nitroglyoxaline-4(or 5)-*sulphonic acid* (yield 88%), decomp. 300° (*sodium salt* described). The orientation of 5-chloro-(or bromo)-1-methylglyoxaline was established directly and that of 4-bromo-1-methylglyoxaline indirectly: "Chloroxalmethylin" *nitrate*, m. p. 145°, on heating with concentrated sulphuric acid, gave 5-chloro-4-nitro-1-methylglyoxaline (yield 71%), m. p. 147°. From 5-chloro-(or bromo)-4-nitro-1-methylglyoxaline was obtained 4-nitro-1-methylglyoxaline-5-*sulphonic acid*, m. p. 254° (*sodium salt* described). The latter was hydrolysed by 30% aqueous sulphuric acid at 170° to 4-nitro-1-methylglyoxaline.

F. M. H.

**Tautomerism of Amidines. IV. Methylation of 4(or 5)-Nitroglyoxaline and 4(or 5)-Phenylglyoxaline.** C. E. HAZELDINE, F. L. PYMAN, and (the late) J. WINCHESTER (*J. Chem. Soc.*, 1924, 125, 1431—1441).—The action of methyl sulphate on nitro-

and phenyl-substituted glyoxalines has been studied and the proportions of the two isomeric alkyl derivatives have been determined (cf. T., 1923, **123**, 3359). Glyoxalines having the nitro group in the 4(or 5)-position invariably yield the 5-nitro-1-methyl derivative as main product. The methylation of 4(or 5)-nitroglyoxaline leads to 5-nitro- and 4-nitro-1-methylglyoxalines in the proportions 350:1 (cf. also T., 1922, **121**, 2616; 1923, **123**, 494). The influence of the bromine atom is similar to, but not so powerful as that of the nitro group, the proportions for similar bromo-substituted compounds being 34:1. Substituents of negative polarity, methyl and cyanomethyl (cf. T., 1923, **123**, 367), act in the opposite way. The influence of phenyl as substituent is exceptional and 4(or 5)-phenylglyoxaline yields on methylation 4-phenyl- and 5-phenyl-1-methylglyoxaline in the proportions 4.8:1. On the other hand, the phenyl group affects the results of the distillation of the common methiodides in the same way as a nitro or bromo group. This abnormality may be ascribed more to the structure of the molecule than to its polarity. The orientation of the 4- and 5-nitro-1-methylglyoxalines was determined by the method used for the nitro-1:4- and -1:5-dimethylglyoxalines (cf. T., 1922, **121**, 2616). The differences in physical properties of the two monomethylnitroglyoxalines are paralleled by the above dimethyl derivatives. 4-*p*-Nitrophenyl- and 5-*p*-nitrophenyl-1-methylglyoxalines were obtained on nitrating the corresponding phenylmethylglyoxalines, the positions of the nitro groups being proved by the formation of a mixture of the two bases by the methylation of 4(or 5)-*p*-nitrophenylglyoxalines (T., 1921, **119**, 1893). Further nitration resulted in the formation of 5-nitro-4-*p*-nitrophenyl-1-methylglyoxaline, for which the position of the second nitro group was found by methylation of 4(or 5)-nitro-5(or 4)-*p*-nitrophenylglyoxaline. The dinitro base on reduction gave 5-amino-4-*p*-aminophenyl-1-methylglyoxaline, which on hydrolysis yielded *p*-aminophenylaminoacetic acid, methylamine, and ammonia. The relative positions of the methyl and phenyl groups follow from this. 4(or 5)-Nitroglyoxaline was methylated by treatment with methyl sulphate at 100° and yielded 63.4% of the theoretical of the 5-nitro to 0.24% of the 4-nitro compound. By nitration of 1-methylglyoxaline, 21% of the theoretical of the 4-nitro to 8% of the 5-nitro compound was obtained. 4-Nitro-1-methylglyoxaline has m. p. 133—134°; the *hydrochloride* yields the base when heated at 100°. 5-Nitro-1-methylglyoxaline has m. p. 55°; the *hydrochloride*, after drying at 100°, has m. p. 195° (effervescence); *picrate*, m. p. 153.5°. Reduction of 5-nitro-1-methylglyoxaline by stannous chloride gave methylamine, ammonia, and glycine ethyl ester as hydrochlorides. 4(or 5)-Nitro-1:3-dimethylglyoxalinium iodide, m. p. 181° (effervescence), was obtained by heating 5-nitro-1-methylglyoxaline with methyl iodide. By the action of methyl sulphate on 4-phenylglyoxaline in the cold and completion at 100°, a product was obtained from which (after the removal of unchanged material as nitrate) the 4-phenyl- and 5-phenyl-1-methylglyoxalines were separated as picrates (yields, 29.8 and

6.2% of the theoretical). 4-Phenyl-1-methylglyoxaline has m. p. 110—111°; the *hydrobromide* (+1H<sub>2</sub>O) has m. p. 178—179°; *nitrate*, m. p. ca. 97°; *picrate*, m. p. 245°, microscopic needles. 5-Phenyl-1-methylglyoxaline, m. p. 96—97°, plates; *nitrate*, m. p. 176—177° (decomp.); *picrate*, m. p. 139°. 4(or 5)-Phenyl-1:3-dimethylglyoxalinium iodide forms colourless prisms, m. p. 147—148°. Nitration of 4-phenyl-1-methylglyoxaline took place on heating a solution of the nitrate in concentrated sulphuric acid at 100°. The chief product (56% of the theoretical yield) was 4-*p*-nitrophenyl-1-methylglyoxaline, pale yellow prisms, m. p. 195°. It forms a *nitrate*, cream-coloured, woolly needles, m. p. 197° (decomp.), and a *picrate*, m. p. 258°, microscopic needles. The nitrate of an isomeric base, presumably 4-*o*-nitrophenyl-1-methylglyoxaline, flat, colourless prisms, decomp. 182°, was formed in considerable amount and also a small amount of a dinitro derivative. 5-*p*-Nitrophenyl-1-methylglyoxaline, lemon-yellow needles, m. p. 171—172°, forms a *nitrate*, colourless plates, m. p. 213° (decomp.), and *picrate*, prismatic needles, m. p. 184°. Methylation of 4-*p*-nitrophenylglyoxaline gave 4-*p*-nitro- and 5-*p*-nitro-phenyl-1-methylglyoxalines in yields of 28 and 2.6% of the theoretical, respectively. 5-Nitro-4-*p*-nitrophenyl-1-methylglyoxaline, m. p. 208—209°, was made by warming the nitrate of the mononitro compound with concentrated sulphuric acid (*hydrochloride* described). 4-Nitro-5-*p*-nitrophenyl-1-methylglyoxaline, m. p. 187°, is similar in solubility to the 5-nitro compound. Methylation of 5-nitro-4-*p*-nitrophenylglyoxaline yielded 66% of crude methylated product, consisting mainly of 5-nitro-4-*p*-nitrophenyl-1-methylglyoxaline; none of the 4-nitro-5-*p*-compound could be isolated. Reduction of 5-nitro-4-*p*-nitrophenyl-1-methylglyoxaline by stannous chloride gave 68% of the theoretical yield of 5-*amino*-4-*p*-aminophenyl-1-methylglyoxaline dihydrochloride, which darkens above 200°. It is readily soluble in water. Aqueous solutions give a transient indigo colour with ammonia, reduce ammoniacal silver nitrate, and give a magenta solution with ferric chloride. On hydrolysis with concentrated hydrochloric acid at 170°, *p*-aminophenylaminoacetic acid dihydrochloride, ammonium chloride, and methylamine hydrochloride were obtained. A. C.

**Synthesis of Heteroxanthine from an Iminazole [Glyoxaline] Derivative.** J. SARASIN and E. WEGMANN (*Helv. Chim. Acta*, 1924, 7, 713—719).—5-Chloro-1-methylglyoxaline [the 4-chloro-1-methylglyoxaline of Sarasin (*A.*, 1923, i, 710, 711), the present investigation having shown that the names should be interchanged] is converted into the nitrate and this salt treated with concentrated sulphuric acid, whereupon 5-chloro-4-nitro-1-methylglyoxaline, m. p. 147—148°, is obtained. Reduction, or reduction followed by hydrolysis, of this substance gives abnormal results. When it is treated with potassium cyanide and a little potassium iodide in hot alcoholic solution, 4-nitro-5-cyano-1-methylglyoxaline, m. p. 141—142°, is obtained. This product is converted by the action of sulphuric acid into the *amide*, m. p. 257—258° (decomp.), of

4-nitro-1-methylglyoxaline-5-carboxylic acid, m. p. 160° (decomp.), the latter being obtained by alkaline hydrolysis of the amide, this being unaffected by boiling hydrochloric acid. At 120°, however, hydrolysis and decarboxylation take place, and 4-nitro-1-methylglyoxaline, m. p. 133—134°, is obtained. This is reduced by tin and hydrochloric acid, yielding a *hydrochloride*, presumably of 4-amino-1-methylglyoxaline, which, when heated with hydrochloric acid at 150°, is broken up into ammonia, a little methylamine, and sarcosine, identified as hydrochloride, m. p. 168—169°. The amide of 4-nitro-1-methylglyoxalinecarboxylic acid is reduced to the *amide*, m. p. 184—185°, of 4-amino-1-methylglyoxalinecarboxylic acid, the *hydrochloride* of the amide having m. p. 214—215°. This amino-amide reacts at 160—170° with ethyl carbonate to yield heteroxanthine (7-methylxanthine), m. p. 380° (decomp.), identical with the product obtained from theobromine.

4-Chloro-1-methylglyoxaline (*loc. cit.*) is also readily nitrated, yielding 4-chloro-5-nitro-1-methylglyoxaline, m. p. 77—78°. W. A. S.

**Quaternary Salts of Iminazoles [Glyoxalines]. II.** J. SARASIN and E. WEGMANN (*Helv. Chim. Acta*, 1924, 7, 720—723; cf. A., 1923, i, 710, 711).—5-Chloro-2-methyl-1-ethylglyoxaline, the constitution of which follows from that of 5-chloro-1-methylglyoxaline (cf. preceding abstract), forms a *methiodide*, m. p. 202—203°, which, when heated in a vacuum at 240°, is broken up into ethyl iodide and 4-chloro-1:2-dimethylglyoxaline, m. p. 93—94°, b. p. 258—260° (*picrate*, m. p. 167—168°), which, when reduced with sodium and alcohol, affords 1:2-dimethylglyoxaline. Similarly, 5-chloro-2-methyl-1-ethylglyoxaline *ethiodide*, m. p. 142—143°, yields 4-chloro-2-methyl-1-ethylglyoxaline, b. p. 263—265° (*picrate*, m. p. 154—155°), which on reduction yields 2-methyl-1-ethylglyoxaline; the *propiodide*, m. p. 108—109°, affords 4-chloro-2-methyl-1-propylglyoxaline, b. p. 135—137°/12 mm. (*picrate*, m. p. 152—153°), and, thence, 2-methyl-1-propylglyoxaline, b. p. 222—223° (*picrate*, m. p. 142—143°); the *isobutiodide* affords 4-chloro-2-methyl-1-isobutylglyoxaline, b. p. 144—146°/12 mm. (*picrate*, m. p. 141—142°), and 2-methyl-1-isobutylglyoxaline, b. p. 225—226° (*picrate*, m. p. 151—152°); the *isoamioidide*, m. p. 133—134°, yields 4-chloro-2-methyl-1-isoamylglyoxaline, b. p. 153—155°/12 mm. (*picrate*, m. p. 120—121°), and 2-methyl-1-isoamylglyoxaline, b. p. 242—243° (*picrate*, m. p. 148—149°).

When the nitrate of 5-chloro-2-methyl-1-ethylglyoxaline is heated with sulphuric acid, 4-nitro-5-chloro-2-methyl-1-ethylglyoxaline, m. p. 88°, is obtained. 5-Nitro-4-chloro-2-methyl-1-ethylglyoxaline, m. p. 67°, is prepared in a similar way. W. A. S.

**Compound of Antipyrine with Trichloroacetic Acid.** L. DEBUCQUET (*J. Pharm. Chim.*, 1924, 30, 121—122).—Antipyrine trichloroacetate,  $C_{11}H_{12}ON_2 \cdot CCl_3 \cdot CO_2H$ , forms lustrous plates, m. p. 79—80°, and is dissociated in aqueous solution. W. T. K. B.

**4-Dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone.** CHEMISCHE FABRIK ALTSTETTEN AKTIEN-GES. (Swiss Pat. 99452; from *Chem. Zentr.*, 1924, i, 1272).—4-Dimethylamino-1-phenyl-

2 : 3-dimethyl-5-pyrazolone is prepared from 4-sulphamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone by the action on it of formaldehyde in the presence of formic acid. G. W. R.

**Synthesis of 1 : 2 : 4-Triazole Compounds. VIII. Benzoylformhydroxamic Acid and its Derivatives.** C. GASTALDI (*Gazzetta*, 1924, **54**, 582—589).—As would be expected from the synthesis of 1 : 2 : 4-triazole compounds from the arylhydrazones of pyruvylhydroxamic acid (A., 1923, i, 1236), benzoylformhydroxamic acid,  $\text{Bz}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$  or  $\text{OH}\cdot\text{CBz}\cdot\text{NOH}$ , is converted quantitatively into benzamide and carbon dioxide when heated at its melting point, this reaction being apparently characteristic of free hydroxamic acids, having the grouping  $\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$  or  $\cdot\text{CO}\cdot\text{C}(\text{OH})\cdot\text{NOH}$ ; in the above instance, the formation of benzoylcarbimide as an intermediate compound was assumed, the reaction then proceeding thus:  $\text{NBz}\cdot\text{C}\cdot\text{O} + \text{H}_2\text{O} \rightarrow \text{NHBz}\cdot\text{CO}_2\text{H} \rightarrow \text{NH}_2\text{Bz} + \text{CO}_2$  (cf. A., 1923, i, 1237).

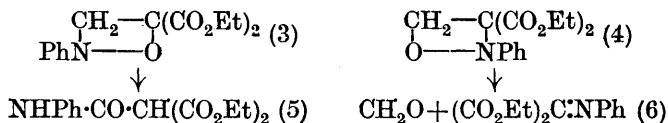
Triazole compounds and benzamide may be obtained by heating at the melting point the acyl derivatives of the arylhydrazones of hydroxamic acids and benzoylformhydroxamic acid, respectively. In these cases, the reaction is determined by the temperature, and may be effected also by heating the acids in neutral solvents of high boiling point, such as naphthalene or  $\alpha$ - or  $\beta$ -methylnaphthalene. If these solvents are replaced by aniline, the symmetrical disubstituted carbamides are formed, the intermediate formation of carbimides being thus proved: (1)  $\text{NPhMe}\cdot\text{N}\cdot\text{CMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{OAc} + \text{NH}_2\text{Ph} \rightarrow \text{NPhMe}\cdot\text{N}\cdot\text{CMe}\cdot\text{N}\cdot\text{C}\cdot\text{O} + \text{NHPhAc} + \text{H}_2\text{O} \xrightarrow{+\text{NH}_2\text{Ph}} \text{NPhMe}\cdot\text{N}\cdot\text{CMe}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh} \xrightarrow{+\text{NH}_2\text{Ph}} \text{NPhMe}\cdot\text{N}\cdot\text{CMe}\cdot\text{NH}_2 + \text{NHPh}\cdot\text{CO}\cdot\text{NHPh}$ . (2)  $\text{Ph}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{Ph}\cdot\text{CO}\cdot\text{N}\cdot\text{C}\cdot\text{O} \xrightarrow{+\text{NH}_2\text{Ph}} \text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ .

*s*-Diphenylcarbamide is formed by the action of aniline on the acetyl derivative of pyruvylhydroxamic acid phenylmethylhydrazone (cf. A., 1923, i, 1237). *s*-Benzoylphenylcarbamide,  $\text{NHBz}\cdot\text{CO}\cdot\text{NHPh}$ , has m. p.  $207^\circ$ . The sodium and silver salts of benzoylformhydroxamic acid are described. T. H. P.

**Additive Formation of Four-membered Rings. V. Formation of Stable Dimethylene-1 : 2-oxaimines from Ethylenes and Nitroso Compounds, with Special Reference to the Direction of the Addition.** C. K. INGOLD and S. D. WEAVER (*J. Chem. Soc.*, 1924, **125**, 1456—1462).—The compounds described

are derivatives of the dimethyleneoxaimine ring:  $\begin{array}{c} \text{C}=\text{O} \\ | \\ \text{C}-\text{N} \end{array}$  (cf. this vol., i, 322, 323; also T., 1922, **121**, 2793; 1923, **123**, 2745), which have been produced by the additive union of unsaturated molecules—in the present case an ethylene derivative and a nitroso compound ( $\text{C}\cdot\text{C} + \text{N}\cdot\text{O}$ ). To ensure the stability of this type of ring, it was found desirable to have a bulky *gem*-grouping attached to one of the ring-bound carbon atoms. The *gem*-substituted ethylenes, (1)  $\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})_2$  and (2)  $\text{CH}_2\cdot\text{CPh}_2$ , were employed

in the formation of these rings, which were found to be amongst the most stable four-membered heterocyclic rings yet produced. The direction of the addition of (1) or (2) with nitrosobenzene was found to be at variance with that required by the "theory of alternate polarities" (cf. Lowry, T., 1923, 123, 822). Thus the ethylene derivative (1) combines readily with nitroso compounds to form rings of the type (3) and not (4), which should not be the case if oxygen key-atoms determine the polarities:  $\text{Ar} \cdot \overset{+}{\text{N}} \cdot \overset{-}{\text{O}}$ ;  $\overset{+}{\text{CH}_2} \cdot \overset{-}{\text{C}}(\overset{+}{\text{CO}_2\text{Et}})$ .



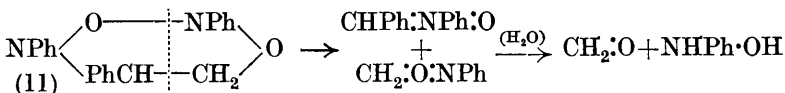
*Ethyl 2-phenyldimethylene-1:2-oxamine-4:4-dicarboxylate* (3), colourless needles, m. p. 98—100°, was obtained when nitrosobenzene in chloroform was added to ethyl methylenemalonate. It exhibits no salt formation with either strong acids or alkalis; it gives no colour with ferric chloride, no copper salt, and is oxidised only with difficulty by alkaline permanganate. Its constitution is proved by the fact that it yields dicarbethoxyacetanilide (5) when heated at 100°, the identity of the latter being settled by a comparison with the condensation product of ethyl malonate and phenylcarbimide. On heating at higher temperatures (best 240—250°) 6-anilino-2:4-diketo-3-phenyl-2:4-dihydro-1:3-oxazine, m. p. 293—294°, is formed by the condensation of (5) with phenylcarbimide. *Ethyl 2-p-chlorophenyldimethylene-1:2-oxamine-4:4-dicarboxylate*, m. p. 122—123°, and the corresponding *p*-bromo compound, m. p. 132—133°, were obtained similarly to (3) on using the *p*-halogen-substituted nitrosobenzenes. Staudinger and Jelagin (A., 1911, i, 215) obtained (7) and only traces of (8) by

the addition of diphenylketen,  $\overset{-}{\text{O}} \cdot \overset{+}{\text{C}}\text{Ph}_2$ , to nitrosobenzene,  $\text{Ph}_2\text{C} - \text{CO}$  (7),  $\text{Ph}_2\text{C} - \text{CO}$  (8), whilst (8) would be expected from

the polarity theory. Diphenylethylene (2) is a compound in which the polarities are oppositely directed with respect to the heavy substituent to those of (1). It may be represented by the polar formula,  $\overset{-}{\text{CH}_2} \cdot \overset{+}{\text{C}}\text{Ph}_2$ . According to the polar theory it should unite with  $\text{O} \cdot \text{NPh}$  to form  $\text{Ph}_2\text{C} - \text{CH}_2$  (9) and not  $\text{CH}_2 - \text{CPh}_2$  (10).

Only (10) was formed. 2:3:3-Triphenyldimethylene-1:2-oxamine (10), m. p. 218—220°, closely resembled the above dimethylene-oxamines. On distillation at 70 mm., it decomposed, yielding benzophenonanil and formaldehyde. As an example of an ethylene derivative in which the *gem*-group is absent, styrene was allowed to react with nitrosobenzene. No dimethyleneoxamine was formed, the product being a six-membered ring (11) which breaks

down into *N*-phenylbenzaldoxime, formaldehyde, and phenylhydroxylamine.



*N*-*p*-Chlorophenylbenzaldoxime, m. p. 172—173°, was obtained from styrene and *p*-chloronitrosobenzene. A. C.

**Anhydrides of Amino-acids and their Derivatives.** P. KARRER and C. GRÄNACHER (*Helv. Chim. Acta*, 1924, 7, 763—780).—When 2:5-dihydroxydihydropyrazine dibenzyl ether (this vol., i, 212) and phthalic anhydride are heated together at 150—200°, glycine and benzylphthalic acid are formed, and when the pyrazine compound and methyl iodide are heated together at 100—120°, sarcosine anhydride and benzyl iodide are produced. The silver salt of glycine anhydride reacts with ethyl  $\omega$ -chloro-*p*-toluate to give 2:5-dihydroxydihydropyrazine di-*p*-carbethoxybenzyl ether, m. p. 196—198°. The corresponding dicarboxylic acid melts and chars at 230—235°; it, like its congener (*loc. cit.*), is readily hydrolysed by dilute hydrochloric acid.

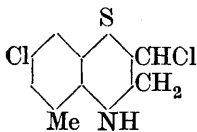
Ethyl hippurate is dehydrated when treated with phosphorus pentachloride (on the water-bath) yielding 5-ethoxy-2-phenyloxazole, b. p. 150—152°/12 mm. (*hydrochloride*, m. p. 115—120°; *picrate*, m. p. 122—123°). Warm, dilute hydrochloric acid readily decomposes this compound to ethyl alcohol and hippuric acid. Methyl acetamidoacetate, similarly dehydrated (in chloroform solution), yields 5-ethoxy-2-methyloxazole, b. p. 60—62°/10—12 mm. (*picrate*, m. p. 98°). The ethyl ester of benzoyl-*l*-leucine yields 5-ethoxy-2-phenyl-4-isobutyloxazole, b. p. 133—134°/2 mm. (*picrate*, m. p. 81°), and that of acetyl-leucine affords 5-ethoxy-2-methyl-4-isobutyloxazole, b. p. 87—89°/20 mm. (*picrate*, m. p. 80—81°). All these oxazoles are easily decomposed by dilute acid.

Hippuric anilide also is dehydrated by treatment with phosphorus pentachloride and thus affords 5-chloro-1:2-diphenylglyoxaline, m. p. 133° (*picrate*, m. p. 157—158°). The compound is stable towards hot hydrochloric acid; the chlorine atom also is firmly attached. 5-Chloro-2-phenyl-1-ethylglyoxaline, m. p. 65—67° (*picrate*, m. p. 160—161°), is obtained in a similar way from hippuric ethylamide, m. p. 147—148°. Hippuramide yields 5-hydroxy-2-phenylglyoxaline, m. p. 141—143°. This compound is decomposed by hot dilute hydrochloric acid.

The relationship of the above investigations to the question of the structure of proteins is discussed. W. A. S.

**Halogenated Ketodihydroaryl-*p*-thiazines.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (K. ZAHN) (D.R.-P. 379318; from *Chem. Zentr.*, 1924, i, 1104—1105).—The following compounds obtained by chlorination of ketodihydroaryl-*p*-thiazines in the methylene group of the thiazine ring are described: *Chloroketodihydrobenz-p*-thiazine, m. p. 212° (decomp.); *dichloroketodihydro-*

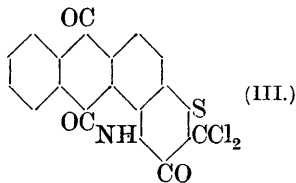
*benz-p-thiazine*, m. p.  $185^{\circ}$  (decomp.); *bromoketodihydrobenz-p-thiazine*; *dibromoketodihydrobenz-p-thiazine*; *chloroketodihydro-5-methyl-7-chlorobenz-p-thiazine* (I), m. p.  $240^{\circ}$ ; *2-dichloroketodihydro-5-methyl-7-chlorobenz-p-thiazine*, m. p.  $205^{\circ}$ ; *monochloroketodihydronaphth-p-thiazine*, blackening at  $210^{\circ}$ ; *dichloroketodihydronaphth-p-thiazine* (II), m. p. about  $230^{\circ}$  (decomp.); *dichloroketodihydroanthraquinonyl-p-thiazine* (III).



(I.)



(II.)



(III.)

G. W. R.

**4-Nitro-2-sulphophenyldehydrothio-*p*-toluidinesulphonic Acid.** D. H. PEACOCK (*J. Chem. Soc.*, 1924, **125**, 1547).—This compound was prepared by condensing sodium dehydrothio-*p*-toluidinesulphonate with sodium 6-chloro-3-nitrobenzenesulphonate. The *potassium* salt,  $C_{20}H_{13}O_8N_3S_3K_2$ , dyes cotton in bright yellow shades tinged with green. The *silver*, *lead*, and *barium* salts have been prepared. The potassium salt with strong alcoholic potassium hydroxide yields a bronze, crystalline powder which appears to contain the :NK group.

4-Amino-2-sulphophenyldehydrothio-*p*-toluidinesulphonic acid, obtained on reducing the nitro compound, dyes cotton very pale shades. The diazo compound couples on the fibre with  $\beta$ -naphthol to produce a bright rose, and with *m*-phenylenediamine a full brown shade.

A. C.

**Condensation of Aryldiazonium Salts and of Alkyl Nitrites with Derivatives of Cyanoacetic Acid.** T. K. WALKER (*J. Chem. Soc.*, 1924, **125**, 1622—1625; cf. T., 1923, **123**, 2775).—Difficulties in preparing benzylcyanoacetic ester were overcome (yield 60%) by use of excess of cyanoacetic ester (cf. A., 1893, i, 16; 1899, i, 897), and treatment with sodium hydroxide gave the acid. Ice-cold solutions of alkylcyanoacetic acids reacted with aryldiazonium salts according to the equation  $CHR(CO_2H) \cdot CN + Ar \cdot N_2 \cdot OH \rightarrow CR(N \cdot NHAr) \cdot CN + H_2O$  (where  $R = CH_2Ph$ ,  $Ph$ , or  $Et$ ); the following hydrazones were thus obtained: *phenylpyruvonitrilephenylhydrazone* (100% yield), m. p.  $157^{\circ}$ , converted by boiling alcoholic potassium hydroxide into *phenylpyruvic acid phenylhydrazone*, m. p.  $161^{\circ}$ ; *phenylpyruvonitrile-p-tolylhydrazone* (yield 25%), m. p.  $113^{\circ}$ ; *phenylpyruvonitrile-p-nitrophenylhydrazone* (small yield), m. p.  $167$ — $168^{\circ}$ ; *methylpyruvonitrile-p-tolylhydrazone*, m. p.  $143$ — $144^{\circ}$ ; *methylpyruvonitrile-p-chlorophenylhydrazone*, m. p.  $172^{\circ}$ ; *phenylglyoxylo-nitrilephenylhydrazone*, m. p.  $152^{\circ}$ .

Nitrous acid and alkyl nitrites were without action on mono-alkylcyanoacetic acids, whilst the esters only yielded oximino derivatives,  $CN \cdot CR \cdot NOH$ , when treated with potassium ethoxide



at 0° in dry ethereal solution. Thus ethyl benzylcyanoacetate reacted with amyl nitrite; cautious acidification yielded *phenylpyruvonnitrile oxime*, an unstable red oil (*silver salt* described). Its constitution was established by hydrolysing with acid to hydroxylamine, whilst heating with alcoholic potassium hydroxide gave  $\alpha$ -oximino- $\beta$ -phenylpropionic acid. Similarly, from ethyl ethylcyanoacetate there was prepared *methylpyruvonnitrile oxime*, a red oil (*potassium, sodium, and silver salts* described); ethyl phenylcyanoacetate gave *phenylglyoxylnitrile oxime* (small yield), m. p. 129°.

The general conclusion from these and previous results is that an aryl diazonium salt condenses with a compound CHRXY (where  $X=CO_2H$ ,  $CO_2R'$ ,  $COR'$ ,  $CN$  and  $Y=CO_2H$ ,  $CO_2R'$ ); alkyl nitrites condense similarly except when, simultaneously,  $X=CN$  and  $Y=CO_2H$ . Nitrosobenzene does not react with CHRXY, although it usually condenses readily with  $CH_2XY$ . F. M. H.

**Preparation of Aminoazo Compounds.** FARBENFABR. VORM. F. BAYER U. CO. (J. HALLER) (D.R.-P. 381916; from *Chem. Zentr.*, 1924, i, 1592).—Negatively substituted *o*-aminodialkylanilines are diazotised and the diazo compounds coupled with diazotisable amines. Compounds are thus prepared from diazotised 4-nitro-2-amino-1-dimethylaniline or 2-amino-4-methoxytoluene and *p*-xylydine, from diazotised 4-chloro-2-amino-1-dimethylaniline and 2-amino-4-methoxytoluene, and finally from diazotised 4-nitro-2-amino-*N*-methyl diphenylamine and *m*-aminoacetanilide. 4-Nitro-2-amino-*N*-methyl diphenylamine has m. p. 69–70°. G. W. R.

**Halogen-substituted Aromatic Hydrazines. II. 2:3-, 2:5-, 2:6-, and 3:5-Dibromophenylhydrazines and *p*-Bromophenylmethylhydrazine and their Reaction Products with Aldehydes and Ketones.** E. VOTOČEK and R. LUKES (*Bull. Soc. chim.*, 1924, [iv], 35, 868–879).—Of the above hydrazines, only the 2:5- and 3:5-dibromophenylhydrazines have been previously prepared. The 2:5-dibromophenylhydrazones of the following are described: *acetone*, m. p. 93°; *benzaldehyde*, m. p. 79°; *furfuraldehyde*, m. p. 104°; *arabinose*, m. p. 170–175°; *galactose*, m. p. 207°; *rhamnose*, m. p. 184°; *glucose* 2:5-dibromophenylosazone, m. p. 228–229°. The corresponding osazone of galactose could not be prepared in a pure state.

3:5-Dibromophenylhydrazones of the following are described: *acetone*, m. p. 85–86°; *benzaldehyde*, m. p. 106–107°; *furfuraldehyde*, m. p. 116°; *glucose*, m. p. 158–159°; *rhamnose*, m. p. 195–196°; *galactose*, m. p. 172°. The corresponding osazones of dextrose and galactose were isolated in an impure state.

2:3-Dibromophenylhydrazine, m. p. 112°, was prepared from 2:3-dibromoaniline by diazotisation and subsequent reduction with stannous chloride. *Acetone* 2:3-dibromophenylhydrazone, *benzaldehyde* 2:3-dibromophenylhydrazone, m. p. 106°, and the corresponding osazones of dextrose and galactose, which are both difficult to purify, are described.

2:6-Dibromophenylhydrazine, m. p. 110°, was similarly obtained

from 2 : 6-dibromoaniline. *Acetone 2 : 6-dibromophenylhydrazone* (oil), *benzaldehyde 2 : 6-dibromophenylhydrazone*, m. p. 51—52°, unstable, and *furfuraldehyde 2 : 6-dibromophenylhydrazone*, m. p. 62°, are described. This hydrazine forms no characteristic hydrazones or osazones with the sugars.

as-*p-Bromophenylmethylhydrazine*, m. p. 33°, was obtained by bromination of phenylmethylhydrazine in cold concentrated hydrochloric acid solution. *Benzaldehyde p-bromophenylmethylhydrazone*, m. p. 106—107°, *acetone p-bromophenylmethylhydrazone*, an unstable oil, and *levulose p-bromophenylmethyllosazone*, m. p. 153°, are described.

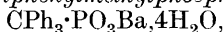
It is proved by two methods that bromination of phenylmethylhydrazine under the above conditions leads to a *p*-bromo derivative. Methylation of *p*-bromoaniline followed by the formation and reduction of the corresponding nitrosoamine gives *p*-bromophenylmethylhydrazine identical with the compound produced by direct bromination of phenylmethylhydrazine. *p*-Bromophenylmethylhydrazine was also reduced to *p*-bromomethylaniline, giving a nitroso compound identical with that produced by the first method. In the bromination of phenylmethylhydrazine no *o*-bromophenylmethylhydrazine can be detected.

A. E. C.

**Formation of Triphenylmethylphosphinic Acid from Triphenylmethoxyphosphorus Dichloride.** D. R. BOYD and F. J. SMITH (*J. Chem. Soc.*, 1924, **125**, 1477—1480).—Alcoholic potassium hydroxide converts triphenylmethylphosphorus dichloride into an acid, which was assumed by Boyd and Chignell (T., 1923, **123**, 813) to have the formula  $\text{CPh}_3 \cdot \text{O} \cdot \text{P}(\text{OH})_2$ . Alkylphosphorous acids of this type are monobasic, but if the above acid dissolved in one equivalent of sodium hydroxide is titrated with more alkali, the curve showing the change of  $p_{\text{H}}$  with increase of alkali concentration indicates the presence of a second salt. The alternative formula,  $\text{CPh}_3 \cdot \text{PO}(\text{OH})_2$ , is more in harmony with the dibasic character of the acid. The latter forms triphenylmethane when heated with soda-lime, a reaction characteristic of phosphinic acids. There is evidently a molecular rearrangement during which tervalent phosphorus becomes quinquivalent. (1)  $\text{CPh}_3 \cdot \text{O} \cdot \text{PCl}_2 \rightarrow \text{CPh}_3 \cdot \text{PO}(\text{OEt}) \cdot \text{OK}$ .

In the case of the reaction between phosphorus trichloride and triphenylcarbinol, the reaction proceeds according to equation (2) to the extent of 78% of the carbinol employed (the normal reaction between phosphorus trichloride and an alcohol; Menshutkin, 1866) whilst about 5% of the carbinol appears to react according to (3): (2)  $\text{R} \cdot \text{OH} + \text{PCl}_3 = \text{PHCl}_2 \cdot \text{OR} = \text{PCl}_2 \cdot \text{OR} + \text{HCl}$ . (3)  $\text{R} \cdot \text{OH} + \text{PCl}_3 = \text{PHCl}_3 \cdot \text{OR} = \text{PCl}_2 \cdot \text{R} \cdot \text{O} + \text{HCl}$ . Reaction (3) will tend to take place where the alcohol is pronouncedly basic with a tendency to dissociate into  $\text{R} \cdot$  and  $\cdot \text{OH}$ . It is important to notice that  $\text{CPh}_3 \cdot \text{O} \cdot \text{PCl}_2$  is specially stable towards water whilst compounds of the type  $\text{R} \cdot \text{O} \cdot \text{PCl}_2$  are usually readily hydrolysed by water. It is suggested that alcohol is first added on to the unsaturated phosphorus atom, then, under the influence of the hot alcoholic potassium hydroxide

the disturbance of the molecule due to this and to the splitting off of hydrogen chloride may produce a state favourable to the migration of the triphenylmethyl group from oxygen to phosphorus as in (1) above. Directions are given for improving the yield of triphenylmethylphosphorus dichloride. Triphenylmethylphosphinic acid prepared as previously described was found to contain about 50% of its monoethyl ester; the pure acid has m. p. 275°. The yield was increased to 80% of theory by using 5—6 mols. of potassium hydroxide (in place of 3). *Dipotassium triphenylmethylphosphinate* ( $+3\text{H}_2\text{O}$ ) and *barium triphenylmethylphosphinate*,



are described.

A. C.

**Chemistry of the Blood Colouring Matter. II. Chemical Character of Kathæmoglobin.** F. HAUROWITZ (*Z. physiol. Chem.*, 1924, **137**, 62—77).—Mainly from spectroscopic and magnetic investigations of kathæmoglobin, the latter is shown to behave as if it were a Zsigmondy "colloid-compound" of hæmatin and globin.  $\alpha$ -Hæmin (and from this, crystalline chlorohæmin) was obtained by digesting kathæmoglobin with pepsin and hydrochloric acid.

B. F.

**Products of the Catalytic Hydrolysis of Goose Feathers.** W. S. SSADIKOV and N. D. ZELINSKY (*Biochem. Z.*, 1924, **147**, 30—69).—A highly detailed experimental account of the application to goose feathers of the authors' catalytic method of fragmenting proteins of which a preliminary announcement has already been made (*A.*, 1923, i, 492). The isolation of many substances of the type of peptin and piprin anhydrides is described and the results of analyses are detailed. Such complex cyclic compounds are regarded as precursors of the amino-acids obtained on ultimate hydrolysis, the peptins giving rise to peptides as intermediates, and the piprins to piperidones. Many other complex derivatives, several of which are described, formed by secondary changes of the real protein units, may arise in the course of catalytic hydrolysis of ring structures.

J. P.

## Biochemistry.

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**Pharmacology of Cell Respiration. V. Influence of  $\gamma$ -Rays on Cell Respiration.** F. HAZAMA (*Z. physiol. Chem.*, 1924, **138**, 102—107).—Small doses of  $\gamma$ -rays usually cause a transitory increase in the oxygen consumption of the erythrocytes of the goose, provided that at least 4 hours have elapsed since the removal of the erythrocytes from the body; large doses are without effect.

E. S.

**Chondroitinsulphuric Acid in Serum.** K. DRESEL (*Klin. Woch.*, 1923, **2**, 2344—2345; from *Chem. Zentr.*, 1924, i, 1554—1555).—Chondroitinsulphuric acid, normally excreted in the urine, may be retained in certain pathological conditions. G. W. R.

**Adsorption of Sodium Salicylate by Blood-serum.** R. COQUOIN (*Compt. rend. Soc. Biol.*, 1923, **89**, 1259—1261; from *Chem. Zentr.*, 1924, i, 1558).—On long-continued dialysis an equilibrium is established with respect to salicylate between serum and a physiological salt solution. No adsorption of sodium salicylate by serum takes place. This is contrary to the view of Chabanier, Lebert, and Lobo-Onell (*Compt. rend. Soc. Biol.*, 1923, **88**, 178).  
G. W. R.

**Serum Proteins. (Method of Obtaining Serum and Criticism of Rohrer's Method of Determining the Albumin-Globulin Value.)** W. VON FREY (*Biochem. Z.*, 1924, **148**, 53—60).—The differences between plasma-serum and ordinary blood-serum (from a clot) are not evident if alterations of carbon dioxide tension are prevented by keeping the preparations under a layer of paraffin (cf. Leendertz, *Arch. klin. Med.*, 1922, **140**). Refractometric methods of determining serum proteins do not give trustworthy results, these being in general higher than those obtained by chemical methods. The Hammarsten and Rohrer methods of determining the albumin-globulin value do not give concordant results, a finding which is ascribed to the untrustworthiness of the latter method.  
J. P.

**Effect of Exercise on Sugar and Residual Nitrogen in Blood.** CÄSAR and SCHAAL (*Z. klin. Med.*, 1924, **98**, 96—99; from *Chem. Zentr.*, 1924, i, 1553).—The blood-sugar was more than doubled after a foot race. The effect is reached 20—46 minutes after the event. No marked effect on the residual nitrogen of the blood was noted.  
G. W. R.

**Changes in Blood-sugar.** I. S. NAKAHAYASHI and J. ABELIN (*Biochem. Z.*, 1924, **147**, 544—556).—From determinations of the polarimetric and copper-reducing values (Bertrand) of deproteinised aqueous blood filtrates the authors claim to substantiate the results of Winter and Smith (*J. Physiol.*, 1922, **57**, 100). Although the figures published show a general tendency of the polarimeter value to rise, this is irregular and falls are sometimes recorded. In four normal cases (sheep's blood), the initial polarimeter value instead of being below the copper-reducing value, as the authors state, is above the latter or insignificantly below it. The feeding of thyroid material does not influence the behaviour of the blood filtrate, but after adrenaline injections this shows a polarimeter value above that of the copper-reducing value—exceptions again occur—and the general tendency is for the former to fall. Some days after the adrenaline injection the blood filtrates again show "normal" behaviour.  
J. P.

**Distribution of Blood-sugar between Corpuscles and Plasma.** F. HÖGLER and K. UEBERRACK (*Biochem. Z.*, 1924, **148**, 150—159).—In the rabbit, the ratio of corpuscle sugar to plasma sugar is very small. In human plasma, from blood to which anti-coagulant has been added in deficient amount, the blood-sugar results are too low. Hæmolysis leads to high results. Using sufficient anti-coagulant and avoiding hæmolysis, plasma and sera prepared by various methods give concordant blood-sugar results. Human corpuscles contain 50—80 mg. % of sugar. J. P.

**Determination of Blood-sugar.** L. PINCUSSEN and N. KLISSIUNIS (*Biochem. Z.*, 1924, **150**, 44—48).—Comparative determinations of blood-sugar from different parts of the circulation show that higher values may sometimes be obtained in blood from the right hand than in blood from the left, and in blood from either hand than in that from the lobe of the ear. It is suggested that blood obtained by capillary puncture (as from the ear) must always be diluted with tissue fluids; also that the blood is richer in sugar when circulating through active parts. The latter assumption is supported by the observation that the blood of a paralysed limb always contains less sugar than blood from other parts of the same individual's body. C. R. H.

**Blood-sugar of Rabbits under Various Conditions.** N. MOCHIZUKI (*Biochem. Z.*, 1924, **150**, 123—143).—Ligature of the pancreatic duct produces a gradually increasing degree of hyperglycæmia in rabbits; animals thus treated show a greater hyperglycæmia after feeding with dextrose and after injection of adrenaline than do normals; during the first 10 days after operation an increased proportion of the total blood-sugar is contained in the corpuscles. The slight rise in blood-sugar which follows administration of pilocarpine and of phloridzin in normal animals is replaced by a fall in the operated animals in the case of the latter substance, whilst in the case of the former no effect at all is observed. C. R. H.

**Action of Uranyl Acetate. III. Action on Red Blood-corpuscles. III.** Y. MIKAWA (*Biochem. Z.*, 1924, **149**, 550—555).—Uranyl acetate agglutinates the red corpuscles of rabbit blood without hæmolysing them. Such agglutinated corpuscles are not hæmolysed by saponin. This is probably due to a fixation of the hæmoglobin by the uranyl acetate. Small amounts of this salt damage the structure of the cells, as is shown by their increased sensitiveness to physiological saline solution. S. S. Z.

**Partition of Chlorides between Plasma and Corpuscles in Human Blood.** F. HÖGLER and K. UEBERRACK (*Biochem. Z.*, 1924, **150**, 18—22).—No difference could be detected between the chlorine content of serum and of plasma; the ratio of corpuscle-chlorine to plasma-chlorine is approximately constant both in normal individuals and in those suffering from nephritis, and is of the same magnitude as the ratio of the sugar of the corpuscles to the sugar of the plasma. C. R. H.

**Changes in Chlorine Content of Whole Blood and Blood-serum of Infants in Relation to Gastric Secretion.** W. SCHÖBER (*Monatschr. Kinderheilk.*, 1923, **26**, 297—307; from *Chem. Zentr.*, 1924, i, 1948).—The chlorine content of the serum of suckling infants falls 2 hours after feeding, rising again after 3 hours. The chlorine content of the whole blood generally increases after feeding. The chlorine in the hydrochloric acid of gastric juice is not supplied entirely by the blood, but must come, in part, from chlorine reserves in the tissues. G. W. R.

**Action of Intravenous Infusions of Sodium Chloride and Sugar on the Alkali Reserve of the Blood.** Y. FUJIMAKI (*Arch. exp. Path. Pharm.*, 1924, **103**, 178—187).—One and a half hours after the injection of sodium chloride and sugar into the rabbit a rise in temperature is produced which is associated with diminished lung ventilation and a resulting retention of carbon dioxide. This is in turn compensated by an increase in the alkali reserve. J. P.

**Acid-Base Equilibrium of the Blood of Normal Guinea Pigs, Rabbits, and Rats.** J. A. HAWKINS (*J. Biol. Chem.*, 1924, **61**, 147—155).—Guinea pigs and rabbits, which show large variations in body temperature, show also variations in the acid-base equilibrium of their blood; rats, on the other hand, both in body temperature and in acid-base equilibrium, are relatively stable. C. R. H.

**Effect of Methylamine Hydrochloride and Ammonium Chloride on the Physiological Osmotic Pressure of Sodium Chloride Solutions.** M. DUVAL (*Compt. rend. Soc. Biol.*, 1923, **89**, 1268—1270; from *Chem. Zentr.*, 1924, i, 1558).—With rabbit blood-corpuscles methylamine hydrochloride and ammonium chloride behave like acetamide (Duval, *Compt. rend. Soc. Biol.*, 1923, **88**, 1196). In solutions poor in sodium chloride but rich in methylamine, hæmolysis occurs. Hæmolysis is due to the lowering of the physiological osmotic pressure of the solution against that of the blood-corpuscles. G. W. R.

**Non-coagulable Nitrogen of Blood, and Muscular Work.** G. AIELLO (*Rif. med.*, 1923, **39**, 721—722; from *Chem. Zentr.*, 1924, i, 1945).—Muscular work, involving protein decomposition and increase in blood concentration, resulted in an increase in the residual nitrogen of the blood. No relationship was observed between blood pressure and residual nitrogen. G. W. R.

**Globulin and Albumin Coefficients of Serum especially during Pregnancy.** H. KÜRTEN (*Arch. exp. Path. Pharm.*, 1924, **103**, 237—238).—A citation of the author's previous work (*Biochem. Z.*, 1922, **133**, 126; 1923, **135**, 536) in relation to that of Hafner (*Arch. exp. Path. Pharm.*, 1924, **101**, 336). J. P.

**Investigations of the Blood of Individual Animals. III.** W. KÜSTER (*Z. physiol. Chem.*, 1924, **138**, 21—37).—The preparation and alkylation of hæmins from the blood of different animals

are recorded. The results indicate that the crude hæmin consists of a mixture and suggest that various hæmoglobins occur in one and the same blood. E. S.

**Formation of Porphyrin from "Carbon Dioxide Blood."** P. LIST (*Z. physiol. Chem.*, 1924, **138**, 164—170; cf. *ibid.*, 1924, **135**, 95).—From blood which has been saturated with carbon dioxide and subsequently treated with 25% hydrochloric acid there was obtained a substance of the nature of porphyrin which could be further separated into two components, one of which could be extracted from hydrochloric acid solution with chloroform whilst the other could not. Both components could be extracted together by means of ether after neutralising the solution and acidifying with acetic acid. Details are given of spectroscopic observations on the mixture and the two components separately. C. R. H.

**Ammonia Content of Blood.** V. HENRIQUES and E. GOTTLIEB (*Z. physiol. Chem.*, 1924, **138**, 254—261).—A series of experiments on the amounts of ammonia recoverable from blood by prolonged aëration leads to the conclusion that the circulating blood contains no preformed ammonia, and that any which may be found is the product of *in vitro* reactions in the drawn blood. C. R. H.

**Distribution of Carbamide in Blood and in Cerebrospinal Fluid.** M. POLONOVSKI and C. AUGUSTE (*J. Physiol. pathol. gén.*, 1923, **21**, 267—282; from *Chem. Zentr.*, 1924, i, 1945—1946).—Plasma and serum have the same content of carbamide, but the erythrocytes contain 5 to 8% less. For every type of blood there is a characteristic distribution of carbamide, which is quickly restored if a part of the plasma is replaced by sodium chloride solution or by concentrated carbamide solution. Cerebrospinal fluid contains from 1 to 25% less carbamide than peripheral venous blood. G. W. R.

**Fats and Lipoids in Blood. I. Distribution of Cholesterol and other Lipoids in the Blood of Different Animals.** R. IWATSURU (*Pflüger's Archiv*, 1924, **202**, 194—199; from *Chem. Zentr.*, 1924, i, 1947).—The cholesterol, fat, and lipid content is practically constant in the corpuscles of various mammals. The values obtained were 215 mg. of cholesterol, and 580 mg. of fats and lipoids (calculated as triolein) per 100 c.c. of blood. Variations of these substances in the whole blood of various species and individuals are due to differences in the amounts appearing in the plasma. G. W. R.

**New Basic Crystalline Constituent of Blood. I. A.** LEIMDÖRFER (*Biochem. Z.*, 1924, **149**, 513—524).—A new basic substance is described which can be obtained from the blood-corpuscles of human and mammalian blood by boiling with dilute acetic acid, extracting with alcohol, and precipitating with alcoholic cadmium chloride. It is present in the erythrocytes only. It gives a diazo reaction when sodium or potassium hydroxide is



employed but not when ammonia or sodium carbonate is used. It is obtained from the cadmium compound by removing the metal with hydrogen sulphide, dissolving in alcohol, and precipitating with ether. It can also be precipitated directly from the alcoholic extract of the corpuscles with ether. The substance has not yet been prepared in a pure condition; the analyses suggest so far that it contains N, C, and H in the approximate proportions 1 : 3·5 : 7·9.

S. S. Z.

**Transformation of Blood Pigment into Bile Pigment.** T. BRUGSCH and E. POLLAK (*Biochem. Z.*, 1924, **147**, 253—254).—It is claimed that by the action of pyrocatechol, hæmin and its derivatives are converted into bile pigment (bilirubin). Quinol and resorcinol do not act in this way.

J. P.

**Blood Pigments. III. Methæmoglobin and its Derivatives.** F. HAUROWITZ (*Z. physiol. Chem.*, 1924, **138**, 68—99).—Both colorimetric and spectroscopic methods show that methæmoglobin exists in two forms in aqueous solution. When the reaction of the medium is more alkaline than  $p_H$  10·0 it is present entirely as alkaline methæmoglobin, and when more acid than  $p_H$  6·0 entirely as acid methæmoglobin; between these hydrogen-ion concentrations equilibrium mixtures exist.

Pure, crystalline methæmoglobin is best prepared by allowing pure oxyhæmoglobin to stand for 6—8 weeks in 20% alcohol in the presence of air; its formation by means of other reagents has been studied. The action of nitrite on oxyhæmoglobin results in the formation of a mixture of nitric oxide-hæmoglobin and methæmoglobin and not, as stated by Hartridge (A., 1921, i, 135), of nitrite-hæmoglobin. Pure fluormethæmoglobin has been found to contain one atom of fluorine to one of iron.

E. S.

**Mechanism of Hæmolysis in Hypertonic Salt Solutions.** D. ACÉL and L. LORBER (*Biochem. Z.*, 1924, **147**, 557—562).—Strongly hypertonic salt solutions (5—50%), except those with physiologically inactive anions (citrate, sulphate), hæmolyse red blood-corpuscles. The order of activity of the anions for salts with the same cation conforms to the Hofmeister series. In the salts of multivalent metals the activity of the cation is important. The process is regarded as being similar to hypotonic hæmolysis and support is thereby gained for the view that the erythrocyte is a colloidal structure containing hæmoglobin in its interstices, and not a closed semi-permeable membrane filled with the pigment. In weakly hypertonic solutions osmosis predominates, whilst in stronger salt solutions the imbibition of water by the colloid substance of the cells begins to play a part.

J. P.

**Influence of Sunlight on Protein Metabolism.** L. PINCUSSEN (*Biochem. Z.*, 1924, **150**, 36—43).—Irradiation causes an increase in the general metabolism of rabbits, as shown by an increase in nitrogenous excretion, which is increased by the use of sensitisers, such as various dyestuffs and potassium iodide. Differences in the action of the various sensitisers may be observed

in their effect on individual constituents of the total excreted nitrogen. C. R. H.

**Nitrogen Metabolism in Avitaminosis.** S. YOSHIE (*Biochem. Z.*, 1924, **148**, 1—48).—In avitaminosed dogs, a diminution in intestinal absorption leads to a lessened urea formation and an increased excretion of amino-nitrogen and ammonia, a disturbance which can be reduced in intensity by any condition bringing about increased absorption. This condition of acidosis may appear at all stages of avitaminosis and is often apparently of a temporary nature and not directly associated with the latter, whilst at other times it is due to a progressive deterioration in the condition of the gastro-intestinal tract. An increase in protein metabolism, leading ultimately to a breakdown of cell proteins, is a primary result of avitaminosis. The rapidity with which the effects of avitaminosis become manifest is much greater in young than in old animals, varying more or less inversely with the age. J. P.

**Pancreas and Carbohydrate Balance.** E. TOENNIESSEN (*Klin. Woch.*, 1924, **3**, 212—213; from *Chem. Zentr.*, 1924, i, 1557).—It is held that the pancreas does not take part in the catabolism of carbohydrates to lactic acid, but is concerned only in the later stages of degradation. G. W. R.

**Lactic Acid Formation in Muscular Contraction.** O. MEYERHOF, H. E. HIMWICH, and MATSUOKA (*Klin. Woch.*, 1924, **3**, 392—395; from *Chem. Zentr.*, 1924, i, 2174).—Contraction of isolated muscle caused by chloroform, caffeine, or heat is accompanied by the formation of lactic acid and is analogous in this respect to natural or electrically produced contraction. Contraction due to acetylcholine is not accompanied by lactic acid formation. Chloroform contraction can be inhibited by novocaine. G. W. R.

**Muscular Exercise, Lactic Acid, and the Supply and Utilisation of Oxygen.** I—III. A. V. HILL, C. H. N. LONG, and H. LUPTON (*Proc. Roy. Soc.*, 1924, **B**, **96**, 438—475).—I. *Introduction.* Previous work (A., 1923, ii, 977) and the various aspects of the problem as presented in skeletal and heart muscle, are discussed.

II. *Determination of lactic acid in biological fluids.*—Clausen's permanganate method (A., 1922, ii, 593) with slight modifications is considered suitable for blood and urine. In blood to which zinc lactate has been added about 85% of the lactic acid is found by this method. Resting human blood contains 10 to 20 mg.% and urine 3 to 14 mg.%. Oxidation with 50% sulphuric acid at 140° as described by Clausen (*loc. cit.*) does not give good results and even with 60% acid at 155° only 80% of the lactic acid is accounted for.

III. *Lactic acid in blood and the respiratory quotient.*—During steady, moderate exercise the variations in both respiratory quotient and total lactic acid of the blood are small. During and for a short time after severe exercise the lactic acid concentration in-

creases to a maximum. The value then falls, owing to the diffusion of lactate ions into the blood stream and oxidative recovery. In blood to which lithium lactate has been added, the plasma attains a concentration of lactic acid about 50% higher than that of the blood as a whole, and in human blood after muscular exercise about 30% higher. The concentration in the corpuscles is considerably less than that in the plasma. The variations in the lactic acid concentration of muscle during exercise and in recovery lead to wide variations in the respiratory quotient. This increases with increase in vigour of the exercise and may reach the value of 2. It then falls to low values for a considerable period before returning finally to a normal resting value. All these changes depend merely on the liberation of lactic acid and its removal in recovery. O. O.

**Degradation of Carbohydrates in Striped Muscle. IV. Biochemistry of  $\alpha$ - and  $\beta$ -Glucose.** F. LAQUER and K. GRIEBEL (*Z. physiol. Chem.*, 1924, **138**, 148—155).—The formation of lactic acid by a suspension of chopped muscle, already known (A., 1922, i, 1089; 1923, i, 268) to be increased by the addition of glycogen, is increased more by  $\alpha$ -glucose than by  $\beta$ -glucose, the effect of ordinary dextrose being intermediate. In view of this it is suggested that  $\alpha$ -glucose may be the particular form in which carbohydrate is actively metabolised in the organism. C. R. H.

**Calcium Content of Normal and Diseased Skin.** GANS (*Arch. Dermat. Syphilis*, 1924, **145**, 135—137; from *Chem. Zentr.*, 1924, i, 2162).—In normal skin, calcium occurs in the cutis, in rather less amount in the papillary bodies, with practically none in the epidermis. Changes in distribution occur in pathological conditions. In eczema, the calcium content of the epidermis greatly exceeds that of the papillary bodies and the cutis. A similar change is shown in the potassium content, principally on account of the exudative processes involved. G. W. R.

**Retention of Lime by Animal Tissues. II.** R. E. LIESEGANG (*Biochem. Z.*, 1924, **149**, 605).—Polemical. S. S. Z.

**Calcium Fixation in the Development of Bone.** E. FREUDENBERG and P. GYÖRGY (*Ergeb. inn. Med. Kindersheilk.*, 1923, **24**, 17—28; from *Chem. Zentr.*, 1924, i, 1952; cf. A., 1922, i, 608).—The physiological fixation of lime takes place in three stages which may be represented as follows: (1) cartilage protein + Ca = Ca-cartilage protein; (2) Ca-cartilage protein + phosphate = Ca-cartilage protein-phosphate; (3) Ca-cartilage protein-phosphate = calcium phosphate + cartilage protein. G. W. R.

**Natural Porphyrins. VII. Urinoporphyrinogen Heptamethyl Ester and a New Conversion of Urino- into Coproporphyrin.** H. FISCHER and W. ZERWECK (*Z. physiol. Chem.*, 1924, **137**, 242—264).—The two main porphyrins present in porphyrinuria, urino- and copro-porphyrin, have been separated by means of hot glacial acetic acid in which coproporphyrin is readily

soluble whilst urinoporphyrin is practically insoluble. Further, by esterifying with methyl sulphate a new *porphyrin* has been isolated. The crystalline *methyl* ester has m. p. 255—257°. The new porphyrin forms a crystalline *copper* salt, m. p. 292°. On hydrogenating urinoporphyrin methyl ester in the presence of platinum, it takes up 4 atoms of hydrogen, and yields the leuco compound,  $C_{47}H_{54}O_{16}N_4$  (colourless prisms, m. p. 148°). It is easily reconverted into urinoporphyrin by atmospheric oxidation. Urinoporphyrin, on oxidation with chromic acid, gives an inactive, crystalline carboxylated hæmatic acid. On reduction with hydriodic acid and phosphorus iodide, it yields a pyrrole acid giving an intense Ehrlich reaction. When the reduction is carried out in the cold ammonia is formed to the extent of one-third of the total pyrrole nitrogen. This is in harmony with the assumption that urinoporphyrin contains two hydroxypyrrole nuclei. The conversion of urinoporphyrin into coproporphyrin (A., 1916, i, 775) has been effected by heating it with 1% hydrochloric acid for 3 hours at 180—185°.

D. R. N.

**Natural Porphyrins. VIII. Occurrence of Urinoporphyrin (as Copper Salt, Turacin) in Turakoo Birds and the Demonstration of Coproporphyrin in Yeast.** H. FISCHER and J. HILGER (*Z. physiol. Chem.*, 1924, **138**, 49—67).—The identity of turacin (A., 1923, i, 964) with the copper salt of urinoporphyrin has been confirmed by a comparison of the two salts; moreover, removal of the metal from turacin by reduction with sodium amalgam and subsequent oxidation in the air yields urinoporphyrin.

When the copper salts of coproporphyrin and urinoporphyrin are submitted to dry distillation, the products, which in each case consist of a new copper salt, have been shown by crystallographic and spectroscopic examination to be identical. That a relationship exists between coproporphyrin and urinoporphyrin is thus established.

Coproporphyrin, identified as its crystalline ester, has been isolated from putrefying yeast. This is the first occasion on which an animal porphyrin has been isolated from plant material. E. S.

**Natural Porphyrins. IX. Ooporphyrin from Plovers' Egg Shells and its Relationship to Blood Pigments.** H. FISCHER and F. KÖGL (*Z. physiol. Chem.*, 1924, **138**, 262—275).—The authors have isolated from plovers' egg shells a methyl ester which proves to be identical with the ooporphyrin dimethyl ester previously obtained from gulls' egg shells (this vol., i, 230). On boiling for 1 minute with a mixture of glacial acetic acid and hydriodic acid, this ester gives mesoporphyrin; with glacial acetic and hydrobromic acids it gives hæmatoporphyrin. These two reactions show that ooporphyrin belongs to the hæmoglobin group of pigments. The identity of ooporphyrin with Kämmerer's porphyrin and with the porphyrin obtained by Papendieck (this vol., i, 894) from blood treated with hydrogen sulphide, has been proved by the fact that the latter also undergo the two reactions mentioned above, and further by the identity of the complex

salts with iron ("hæmin esters") prepared from the dimethyl esters of all three porphyrins. C. R. H.

**Natural Porphyrins. X. Blood Pigments in Yeast. Detection of Porphyrin in Plants.** H. FISCHER and J. HILGER (*Z. physiol. Chem.*, 1924, **138**, 288—306).—In the autolysis of yeast there was obtained, besides the coproporphyrin already described (this vol., i, 894) as resulting from the bacterial putrefaction of yeast, Kämmerer's porphyrin, which was identified spectroscopically; after removing the porphyrin with 5% hydrochloric acid the solution of the remaining products of autolysis gave the hæmin spectrum, and on evaporation to dryness and treatment with pyridine, a definite hæmochromogen spectrum. The latter result was also obtained after plasmolysis of the yeast with ether and glacial acetic acid. Kämmerer's porphyrin was also obtained when blood was added to a fermenting mixture of sucrose and yeast, and after fermentation had ceased the whole was submitted to autolysis. Kämmerer's porphyrin was found in a sample of brewer's wort; coproporphyrin (probably) in hops. The spectra of porphyrins (unidentified) were obtained not only from grasses, by treating an alcoholic extract with glacial acetic acid, but also from chlorophyll-free coconut milk. C. R. H.

[Spectroscopic Chemical Reactions of Porphyrins and their Derivatives.] H. FISCHER (*Z. physiol. Chem.*, 1924, **138**, 307—313).—Polemical; reply to criticisms by Papendieck and Schumm (this vol., i, 460, 893) of the author's position with regard to the value of the spectroscopic method of analysis. C. R. H.

**Compounds Extracted from Human Skeletal Muscle. Reply to J. A. Smorodinzev.** R. ENGELAND and W. BIEHLER (*Z. physiol. Chem.*, 1924, **138**, 118).—Polemical (cf. this vol., i, 456). E. S.

**Chemical Composition of Cardiac Muscle in Different Diseases.** G. DOMAGK (*Z. klin. Med.*, 1924, **98**, 171—219; from *Chem. Zentr.*, 1924, i, 1551—1552).—Observations are recorded of the effect of certain pathological conditions on the content of non-protein nitrogen, fat, and water in cardiac muscle.

G. W. R.

**Metabolism of the Heart. I. Carbohydrate Balance of the Heart.** P. SCHENK (*Pflüger's Archiv*, 1924, **202**, 315—328; from *Chem. Zentr.*, 1924, i, 2173).—The glycogen content of dogs' hearts is fairly constant. At any instant the content of carbohydrates intermediate between glycogen and lactic acid and including glucose and sugars of equal reducing power, forms a fairly constant proportion, approximately one-fifth, of the total carbohydrate present. The amount of lactic acid is extremely small and is probably due to the manipulations involved. It is improbable that lactic acid is a normal constituent of the resting muscle of warm-blooded animals.

G. W. R.

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**Metabolism of the Heart. II. The Phosphoric Acid Balance of the Heart.** P. SCHENK (*Pflüger's Archiv*, 1924, **202**, 329—336; from *Chem. Zentr.*, 1924, i, 2173; cf. preceding abstract).—The total phosphoric acid and lactacidogen phosphoric acid contents of heart muscle are appreciably higher than those of skeletal muscle.  
G. W. R.

**Metabolism of the Heart. III. Carbohydrate and Phosphoric Acid Balance of the Heart after Injury.** P. SCHENK (*Pflüger's Archiv*, 1924, **202**, 337—355; from *Chem. Zentr.*, 1924, i, 2173—2174; cf. preceding abstracts).—Data are given as to the effect of narcosis, hydrocyanic acid poisoning, and electrical stimulation on the carbohydrate and phosphoric acid balance in heart muscle.  
G. W. R.

**Sulphuric Acid Content of Body Fluids in Normal and Pathological Conditions.** R. MEYER-BISCH (*Biochem. Z.*, 1924, **150**, 23—35).—The concentration of total sulphuric acid in the blood-serum of normal individuals is about 18 mg. %. This amount is altered to a variable extent in nephritis and constantly raised in diabetes. The sulphuric acid content of the cerebrospinal fluid is greater than that of the serum, and is raised in meningitis, syphilis of the central nervous system, and encephalitis. Pleural exudates and cedema fluids contain about the same amount of sulphuric acid as the blood serum; lymph from the thoracic duct contains a variable amount but greater than the blood.  
C. R. H.

**Solubility of Uric Acid. I.** K. HARPUDE and H. ERBSEN (*Biochem. Z.*, 1924, **148**, 344—354).—In phosphate buffers uric acid is partly converted into urate, the amount of free uric acid in solution being independent of the hydrogen-ion concentration and practically constant about the true solubility value, whilst the proportion of urate depends on this constant concentration of free uric acid and on the hydrogen-ion concentration. The limiting degree of supersaturation of uric acid is partly dependent on the nature of the buffer acid present.  
J. P.

**Solubility of Uric Acid. II.** K. HARPUDE (*Biochem. Z.*, 1924, **148**, 355—369).—The behaviour of a supersaturated monourate solution at a  $p_H$  greater than 6.7 is ascribed to the presence of both undissociated uric acid and diurate, whilst in acid acetate and lactate buffers a supersaturation of undissociated uric acid is inferred. Non-electrolytes (dextrose, urea, glycine) and colloids (glycogen, globulin) increase the range of solubility of uric acid.  
J. P.

**Groups Responsible for the Nucleal Coloration and Nucleal Reaction.** R. FEULGEN and K. VOIT (*Z. physiol. Chem.*, 1924, **137**, 272—286).—Thymus-nucleic acid on mild partial hydrolysis gives rise to purines and substances which give an intense violet coloration with fuchsin-sulphurous acid and also the green pine-shaving reaction. The carbohydrate residue of thymus-nucleic acid

is not a hexose, but a substance of unknown constitution. The nucleal reaction is not caused by furfuraldehyde, but is absolutely specific for (partly hydrolysed) thymus-nucleic acid. The substance which gives these reactions is very sensitive to acids, and on further hydrolysis ceases to give the colorations. It appears to be of the nature of thyminic acid (A., 1918, i, 413), which gives intense colorations with these tests (cf. this vol., i, 438). The isolation and determination of the nature of the carbohydrate residue in thymus-nucleic acid is rendered difficult as it readily decomposes, unlike the pentoses, under the influence of acids. The carbohydrate, like the furfuraldehyde derivatives (A., 1896, i, 144), gives the green pine-shaving reaction. This reaction is due to the presence of a free aldehyde grouping in thyminic acid, and is not given when the latter is oxidised or combined with another group, and therefore thymus-nucleic acid itself does not give this coloration. D. R. N.

**Nature and Significance of the Lipoids of Protoplasm.** W. BIEDERMANN (*Pflüger's Archiv*, 1924, **202**, 223—258; from *Chem. Zentr.*, 1924, i, 2151).—Plant and animal protoplasts contain considerable quantities of lipoids, principally phosphatides of the lecithin type. They are probably held in adsorptive combination. Artificial digestion may be used to liberate them for analytical purposes. Lipoids exerting a protective effect against digestion occur not only in limiting membranes, but also within the protoplasm of plants. Animal protoplasm loses its resistance to digestion after death or injury. Plant protoplasm, however, retains this property so long as the lipoids are not extracted. G. W. R.

**Molecular Stability of Acetic-choleic Acid.** C. T. MÖRNER (*Z. physiol. Chem.*, 1924, **138**, 177—183).—Two samples of acetic-choleic acid were kept for a prolonged period in desiccators, one over sulphuric acid, and the other over sulphuric acid and quicklime. In both there were observed (1) a continuous decrease in weight, (2) at first a fall and then a rise in the melting point. The molecular weight increased in the course of the experiment (306 days) from 226 to 353. These changes indicate a continuous decomposition with loss of acetic acid, and the result is in contradiction to the claim of Wieland and Sorge (A., 1916, i, 710) regarding the extreme stability of acetic-choleic acid. C. R. H.

**Fugutoxin.** F. ISHIWARA (*Arch. exp. Path. Pharm.*, 1924, **103**, 209—222).—Pure fugutoxin from the ovary of *Spheroides* melts at 120°, has  $[\alpha]_D^{20} +17^\circ$  to  $+27^\circ$ , and exhibits chemical properties which suggest that it is a glucose ester and not a glucoside. It yields an osazone of m. p. 207.5°. J. P.

**Spermine.** III. F. WREDE (*Z. physiol. Chem.*, 1924, **138**, 119—135; cf. this vol., i, 77, 78).—From human semen the author has isolated the *chloroaurate* of a base which proves to be identical with the spermine described by Schreiner (A., 1879, 72). This salt crystallises in leaflets which darken at 210° and melt at 216—218° (decomp.). The *chloroplatinate* forms orange plates which darken at 235° and melt at 242°. The *picrate* sublimes at 200° and melts

at 240° (decomp.); the *picrolonate* sublimes at 240° and decomposes at 280°. The *m*-nitrobenzoyl derivative has m. p. 171°. Molecular-weight determinations on the *m*-nitrobenzoyl derivative give values about 800, whence the formula of the base becomes  $C_{10}H_{26}N_4$ .  
C. R. H.

**Lignoceric Acid.** P. A. LEVENE, F. A. TAYLOR, and H. L. HALLER (*J. Biol. Chem.*, 1924, **61**, 157—161).—The earlier conclusions (A., 1913, i, 1151; 1914, i, 1123) that lignoceric acid differs in constitution from *n*-tetracosanic acid, subsequently criticised by Brigl and Fuchs (A., 1922, i, 712), are now confirmed by the preparation from distinct sources of two samples of the acid, which, separately and when mixed, melted at 80·5—81°, both before and after the fractional crystallisation described by Brigl and Fuchs.  
C. R. H.

**Egg of *Bombyx Mori*—Proteins, Reactions.** L. PIGORINI (*Arch. Farm. sper. Sci. aff.*, 1924, **37**, 221—230).—The eggs of the silkworm appear to contain (1) albumins, (2) globulins, (3) vitellins and nucleo-proteins, and (4) a substance allied to the ovomucoid of birds' eggs. During incubation of the eggs, the compounds of group (1) remain practically constant in amount until two days before hatching and then diminish considerably, those of groups (2) and (4) decrease slightly throughout the whole period of incubation and to a greater extent during the last two days, and those of group (3) increase continuously during the incubation; apparently the last compounds are those which are utilised principally in the formation of cytoplasm in the embryo. Except during the last two days of the incubating period, the ratio of the amount of albumins to that of globulins in the egg has the approximate value 1:0·7. The acidity of the alcoholic extract of the eggs, calculated as grams of oxalic acid per 100 g. of the eggs, increases from 4·536 before incubation to 5·166 at the seventh to ninth day and then falls to 2·709 at the end of the incubation on the twentieth day.

T. H. P.

**Imitation of Nervous and Cellular Tissue by means of Potassium Hydroxide, Silica, and Alcohol.** L. A. HERRERA (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 510—512).—A solution of 1 g. of potassium hydroxide and 1 g. of lactose in 50 g. of absolute alcohol dissolves the silica gel prepared by adding alcohol to potassium silicate. When such solutions are suitably dried, almost exact imitations of nervous and cellular tissues are obtained.

T. H. P.

**Precipitation of the Casein of Human Milk.** F. DEMUTH (*Biochem. Z.*, 1924, **150**, 144—148).—In the presence of suitable buffer mixtures the precipitation of the casein of human milk can be brought about constantly and rapidly, the optimum  $p_H$  being about 4·5.

C. R. H.

**Presence of a Hitherto Undescribed form of Urea in Human Urine.** W. O. MOOR (*Biochem. Z.*, 1924, **149**, 575—584).—In preparing urea from human urine a non-crystalline residue is



obtained which consists of two substances, namely a crystalline urea and another non-crystalline substance isomeric with urea. This residue is soluble in water, in absolute alcohol, and in methyl and amyl alcohols, but is insoluble in ether and in chloroform. It contains a basic and an acidic substance. The former combines with oxalic acid, the latter with barium oxide. The barium salt of the acid substance contains nitrogen and sulphur. On shaking the residue with charcoal, the acid substance is adsorbed, whilst the other substance is converted into ordinary crystalline urea. The blue reaction given by urine with ammonia and phosphotungstic acid is due to the presence of the above residue. S. S. Z.

**Ionic Acidity in Normal Human Urine. Influence of Food.**

P. LE NOIR and A. M. DE FOSSEY (*Compt. rend.*, 1924, **178**, 2008—2010).—The hydrogen-ion concentration of the urine of a normal person varies as a result of ingestion of food. During a meal, gastric secretion is accompanied by a decrease in urinary acidity in all cases where a normal mixed diet is taken. This phase is succeeded by increase of acidity, the extent and duration of which vary with different subjects and are not constant even in the same individual. H. J. E.

**Effect of Phosphoric Acid on Excretion of Chlorine.**

W. RÖCKEMANN (*Arch. Kinderheilk.*, **72**, 161—171; from *Chem. Zentr.*, 1924, i, 1405).—The excretion of chlorine in urine and faeces is diminished after administration of sodium dihydrogen phosphate. G. W. R.

**Uric Acid Excretion in the Dog.**

L. ROSENFELD (*Z. physiol. Chem.*, 1924, **138**, 276—279).—The oral administration of 15 g. and 7.5 g. of uric acid on two separate occasions led to approximately the same (small) increase in excretion of uric acid and total nitrogen, which bears no relation to the amount of uric acid ingested. C. R. H.

**Influence of Guanylic and Adenylic Acids on Uric Acid Excretion.**

L. ROSENFELD (*Z. physiol. Chem.*, 1924, **138**, 280—287).—Intravenous administration of the sodium salts of guanylic and adenylic acids to dogs and rabbits led to a smaller increase in uric acid excretion and a larger increase in total nitrogen excretion than could be accounted for theoretically by the amount of substance injected. C. R. H.

**Effect of Salts of the Rare Earths on the Excretion of Uric Acid.**

POMPEANI (*Compt. rend. Soc. Biol.*, 1924, **90**, 2—4; from *Chem. Zentr.*, 1924, i, 1557).—Salts of thorium, caesium, and didymium, subcutaneously administered, were without effect on the excretion of uric acid. Some effect was observed with salts of samarium and yttrium. G. W. R.

**Creatinine Content of the Urine of Healthy and Sick Children.** A. LORENZINI (*Bull. Sci. Med.*, 1922, **10**, 245—264; from *Chem. Zentr.*, 1924, i, 1555).—The creatinine content of the

urine is generally smaller in children than in adults. Data are given for the influence of certain diseases on the amounts of creatine and creatinine found in the urine.

G. W. R.

**Creatinine Excretion of Various Domestic Mammals.** J. SZENDE (*Biochem. Z.*, 1924, **149**, 566—571).—The following are the average figures for the creatinine content of 1000 c. of urine: dog 1.87 g., cat 1.76 g., cattle (stall) 3.98 g., cattle (after killing in slaughter-house) 9.41 g., horse 3.59 g. Paralytic hæmoglobinaemia and tetanus raise considerably the creatine content of horse's urine.

S. S. Z.

**Urinary Pigment in Normal and Pathological Conditions.**

H. FISCHER and W. ZERWECK (*Z. physiol. Chem.*, 1924, **137**, 176—241).—Urochrome can be prepared in quantity by concentrating in vacuum to a syrup large volumes of normal urine. The crystalline mass is filtered off and the syrupy mother-liquor containing most of the pigment submitted to dialysis. The pigment, which is not dialysable, is then isolated from the dialysed solution by acidification, when it is obtained in amorphous flocks. Analysis gave C=52%, H=6%, N=11%, and S=2% (cf. A., 1907, i, 993; 1909, i, 920; 1923, i, 417). It is sparingly soluble in water and most organic solvents. On hydrolysis with hydrochloric acid, it yields tyrosine, leucine, histidine, and arginine. Contrary to previous observations, pyrrole does not appear to be present in the pigment and also Ehrlich's aldehyde reaction in both acid and basic fractions of the hydrolytic products was negative. Trypsin had no effect on the pigment. The amino-nitrogen content of the pigment according to Van Slyke's method amounted to 10% of the total nitrogen. The conclusion is drawn from these results that the colouring matter is definitely a protein derivative. A brown pigment from a case of porphyrinuria was also isolated. It differs from the pigment in normal urine in that it is readily adsorbed on aluminium hydroxide, from which it can be removed by means of ammonia, and precipitated from the ammoniacal solution by acidification as in the case of the normal pigment. Its elementary composition and the examination of its products of hydrolysis suggest that the two are very closely related. The content of the brown pigment is always dependent on the porphyrin content of the urine and the two vary together. It is believed that both pigments are derived from a chromoprotein present in muscle, the porphyrin originating from its prosthetic constituent and the brown pigment from the protein moiety.

D. R. N.

**Conversion of Urobilinogen into Urobilin.** S. BIRO (*Biochem. Z.*, 1924, **149**, 459—467).—Urobilin cannot be detected in freshly collected urine containing urobilinogen. The latter becomes gradually converted into urobilin both in the presence and in the absence of light. This conversion takes place also when Ehrlich's reagent is added to the urine, and can be followed spectroscopically.

S. S. Z.

**Volatile Fatty Acids in Fæces.** A. CECCHINI (*Arch. patol. clin. med.*, 1923, **2**, 361—392; from *Chem. Zentr.*, 1924, **i**, 2166—2167).—Volatile fatty acids in fæces are not necessarily derived from fats and carbohydrates, but can arise from the bacterial decomposition of amino-acids. They are generally present in inverse relationship to indican in the urine. Acetic and butyric acids are commonly present but formic acid is never found. Saline aperients do not alter the bacterial flora of the intestine. From the occurrence, in certain cases, of butyric acid in urine, it is concluded that resorption of the toxic products of intestinal fermentation can take place.  
G. W. R.

**Elimination of Methyl Alcohol and the Conditions for its Accumulation.** E. M. P. WIDMARK and N. V. BILDSTEN (*Biochem. Z.*, 1924, **148**, 325—335).—The rabbit excretes methyl alcohol in constant amount in unit time independently of the concentration in the blood in such a way that the amount present in the latter,  $y$ , at a time,  $t$ , after the injection is expressed by the equation  $y = (b - \beta)t$ , where  $b$  is the amount administered and  $\beta$  the amount eliminated. The conditions for the accumulation of the alcohol in man are discussed.  
J. P.

**Content of Calcium and Magnesium in Cancerous Blood.** L. BLUM and A. KLOTZ (*Compt. rend. Soc. Biol.*, 1923, **89**, 1335—1336; from *Chem. Zentr.*, 1914, **i**, 1553).—In the majority of cases cancer had no effect on the calcium and magnesium content of blood.  
G. W. R.

**Composition of Blood in Epilepsy.** G. PEZZALI (*Rif. med.*, 1923, **39**, 433—437; from *Chem. Zentr.*, 1924, **i**, 929).—In epileptic blood there is no marked change in residual nitrogen, sugar, and chlorine. A definite decrease in cholesterol and fat, succeeded by a slight increase, and a marked increase in calcium and, frequently, of indican occur during the attack.  
G. W. R.

**Deficiency of Calcium Ions in the Blood of Epileptics.** E. J. BIGWOOD (*Compt. rend. Soc. Biol.*, 1924, **90**, 98—100; from *Chem. Zentr.*, 1924, **i**, 1947; cf. this vol., **i**, 680).—The relationship between  $p_H$  and  $p_{Ca}$  is not affected by epilepsy. After administration of sodium borotartrate alkalosis persisted whilst  $p_{Ca}$  remained within physiological limits. In such cases, convulsions do not occur. They are associated more with calcium shortage than with alkalosis. Similar conditions obtain in tetany.  
G. W. R.

**The Amount of Calcium in the Blood and of Amino-acids in the Serum in Cases of Struma and Myositis Ossificans.** A. SZENES (*Mitt. Grenzgeb. Med. Chirurg.*, 1923, **36**, 591—605; from *Chem. Zentr.*, 1924, **i**, 2164—2165).—The effect of different types of struma on the calcium content of the total blood and the refractive index of the serum is described. In general, the former is above normal and the latter lower with large than with small tumours and highest with malign tumours. The amino-acid content of the serum was above normal in two cases of large tumours.

In a case of myositis ossificans a high calcium content in the blood was observed.  
G. W. R.

**Significance of Ions in Muscle Function. III. Influence of Various Cations on the Chemical Activity of Striated Frog Muscle.** H. LANGE (*Z. physiol. Chem.*, 1924, **137**, 105—153).—Muscular contraction is accompanied by a series of changes of chemical and colloidal nature. Lactacidogen is converted by enzymic decomposition into free phosphoric and lactic acids which further bring about physical transformations in the muscle fibre and the covering membrane. This dissimilatory phase is followed by a rapid re-synthesis of the active substance. The chemical transformations in the muscle fibre for the time being control the absorptive condition of the sarcoplasm, and similar processes in the latter regulate the lactacidogen metabolism in the fibre. The cations may be divided into two groups according to their influence on the lactacidogen metabolism in fresh muscle. The first group, which displaces the enzyme equilibrium towards the synthetic side, comprises calcium, barium, and strontium and the second group, which does not possess this property or exhibits a contrary effect, comprises sodium, potassium, ammonium, and magnesium. The action of calcium at different concentrations varies remarkably, promoting synthesis strongly at some, and at others even showing a feeble contrary effect. On the other hand, magnesium, potassium, and sodium, especially at higher concentrations, inhibit the decomposition of lactacidogen, whilst potassium even promotes its synthesis. Calcium ions behave differently from other ions ( $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{++}$ ) in inhibiting the formation of lactic acid. Calcium ions strongly accelerate the decomposition of glycogen, and sodium, potassium, and magnesium ions act similarly, although to a much smaller extent. Calcium ions inhibit strongly oxidative processes, whilst potassium chloride behaves differently in producing at first a very rapid transitory increase in respiratory activity. The action of all these ions is controlled very largely by the hydrogen-ion concentration. The action of salts is due to their influence on the colloidal conditions of the tissue as well as to their effect on the enzymes.  
D. R. N.

**Significance of Ions in Muscle Function. IV. Enzymic Synthesis of Lactacidogen under the Influence of Ions.** G. EMBDEN and C. HAYMANN (*Z. physiol. Chem.*, 1924, **137**, 154—175).—The course of lactacidogen metabolism in the press juice of frog's muscle is influenced strongly by the addition of inorganic salts, both by the anions as well as the cations;  $\text{CNS}'$ ,  $\text{I}'$ , and  $\text{Cl}'$  accelerate the degradation of lactacidogen, whilst fluorine, citrate, and calcium ions induce strongly the synthesis of lactacidogen. Thus lactacidogen synthesis under the influence of fluorine ions can be easily followed by the almost complete disappearance of inorganic phosphoric acid and by the isolation of its characteristic osazone. By the simultaneous addition of glycogen the lactacidogen synthesis is so strongly favoured that inorganic phosphoric acid, even when present in minute amounts, disappears; dextrose and

maltose have no such influence. The maximum amount of synthesis of lactacidogen under the influence of fluorine ions is obtained within the first few hours and thereafter the inorganic phosphoric acid content again gradually increases. D. R. N.

**Diffusion of Glucose in the Organism.** A. CHAUFFARD, P. BRODIN, P. ZIZINE, and A. GRIGAUT (*Compt. rend. Soc. Biol.*, 1923, **88**, 1022—1024; from *Chem. Zentr.*, 1924, i, 1408).—The diffusibility of glucose through animal membranes is considerably less than that of sodium chloride, sodium urate, and carbamide, respectively. The content of different physiological fluids in diffusible substances is compared. G. W. R.

**Electrolytes of High Molecular Weight and their Significance in the Cell.** H. HAMMARSTEN (*Biochem. Z.*, 1924, **147**, 481—543).—Pure disodium guanylate was prepared by hydrolysis of sodium (yeast) nucleinate ("Astra") in an autoclave with 5% sodium hydroxide for 30 minutes at 100° in the presence of sodium acetate. Disodium guanylate was completely precipitated at 0° by the addition of acetic acid, and was further purified by Feulgen's method. From the disodium salt guanylic acid was obtained by precipitation as the copper salt and treatment of the latter with hydrogen sulphide. The partly precipitated acid was separated from copper sulphide by means of barium hydroxide solution and was finally liberated from the barium salt by sulphuric acid. Guanylic acid has a dissociation constant of  $4.45 \times 10^{-3}$ . Disodium guanylate dissociates as does a normal inorganic bivalent salt, and the migration velocity of the bivalent guanylate ion at 20° is 48.3. The free acid and its sodium salt have osmotic pressures which agree with the Arrhenius-van't Hoff theory, and that of the salt is lowered by sodium and magnesium chlorides, more especially by the latter. Guanylic acid only shows typical amphoteric behaviour in strongly acid solutions or when present in large excess. Strongly basic amino-acids or proteins (lysine, histone chloride) form salt-like combinations with guanylic acid which are readily split up by dialysis in the presence of neutral salts. Glycocholic acid has  $k = 4.0 \times 10^{-5}$ , whilst taurocholic acid is a much stronger acid. Extending these investigations to histone and protamine chlorides, and to the sodium and alkylammonium salts of glycocholic, taurocholic, and thymus-nucleic acids and of Congo-red and related dyestuffs, it is concluded that in such electrolytes of high molecular weight, osmotic pressure is dependent not only on the degree of dissociation, but also on the molecular volume of the substance, and is often less than the Arrhenius-van't Hoff and Bjerrum-Debye theories demand. The amount of this abnormality in osmotic pressure is a function of the ratio of the ionic volume of the larger ion to that of the smaller—if the latter is increased the osmotic pressure rises. Importance is attached to such osmotic studies in relation to the biochemistry of the living cell. J. P.

**Effect of Phosphates in (Magnesium) Narcosis.** K. SPIRO (*Klin. Woch.*, 1923, **2**, 2039; from *Chem. Zentr.*, 1924, i, 1410).—Injection of phosphates neutralises magnesium narcosis. G. W. R.

**Effect of Veratrine on the Intestines and the Uterus and Importance of Potassium and Calcium Ions in this Connexion.** E. L. BACKMAN (*Compt. rend. Soc. Biol.*, 1924, **90**, 128—131; from *Chem. Zentr.*, 1924, i, 1560—1561).—Veratrine raises the tone of the musculature of the surviving intestine and uterus of rabbits and guinea pigs. Calcium in small doses strengthens this action whilst in large doses it acts in the opposite sense. Potassium also antagonises the effect of veratrine. G. W. R.

**Action of *p*-Dihydroxycamphane (Bredt).** H. LEO (*Arch. exp. Path. Pharm.*, 1924, **103**, 135—137).—The increased action on the heart and on respiration of *p*-hydroxycamphor as compared with camphor and diketocamphane is not shown on introducing a second hydroxyl group, as in *p*-dihydroxycamphane, but is, on the contrary, abolished, and this new compound exhibits, indeed, a strong paralysing effect. J. P.

**Diuretic and Antidiuretic Effects of Pituitary Extract.** W. G. MACKERSIE (*J. Pharm. Exp. Ther.*, 1924, **24**, 83—99).—It is suggested that the effect of pituitary extract on the rate of urinary secretion may be of use as a supplement to the uterine test for this substance, since such substances as histamine and ergotoxin, the presence of which may lead to confusion in the uterine test, have no effect on the secretion of urine. C. R. H.

**Increased Absorption of Cholesterol in the Presence of Deoxycholic Acid.** R. SCHÖNHEIMER (*Biochem. Z.*, 1924, **147**, 258—263).—The administration to rabbits and guinea-pigs of sodium deoxycholate along with fat produces a marked increase in the rate of absorption of the latter and a pronounced lipæmia. Rabbits on a cholesterol-fat diet to which the bile salt is added show a marked increase in serum cholesterol, which is not evident if no sodium deoxycholate, or if it alone, is given. J. P.

**Chemistry and Pharmacology of Kawa-kawa (*Piper methysticum*).** K. SCHÜBEL (*Arch. exp. Path. Pharm.*, 1924, **102**, 250—282).—Kawa resin has a weak narcotic action, paralyses sensory nerves, and first stimulates and then paralyses smooth muscle. The hydrolysis products of the resin show similar actions. The local anæsthetic action is ascribed to compounds of the benzoic and cinnamic acid group. Kawa root contains no glucosides, nor were alkaloids detected in the resin, although nitrogen is present. From the hydrolysis products of the resin was isolated kawaic acid,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , yellow needles or plates from benzene, m. p.  $165^\circ$  (decomp.) (cf. Borsche and Roth, A., 1921, ii, 862). The ethyl ester, tasting of pepper, was prepared. Kawaic acid produces an increased reflex excitability and a diminished blood pressure. By vacuum distillation of the residue from the crystallisation of kawaic acid were obtained (1) a pale yellow oil containing nitrogen and tasting of pepper, which possessed a weak narcotic action, and stimulated the digestive glands, and (2) a crystalline, unsaturated acid, m. p.  $51$ — $53^\circ$ , with no narcotic action. J. P.

**Mechanism of Catalytic Action of Iron Salts. I.** O. BAUDISCH and L. A. WELO (*J. Biol. Chem.*, 1924, **61**, 261—274).—A review of previously published work by the author and others on the catalysis of oxidations and reductions by iron salts.

C. R. H.

**$\beta$ -Oxidation in the Kidneys.** I. SNAPPER and A. GRÜNBAUM (*Biochem. Z.*, 1924, **150**, 12—17).—After perfusion of the isolated kidneys of various animals with blood to which had been added phenylacetic acid or phenylbutyric acid there was obtained in the perfusion fluid phenylaceturic acid, whereas the perfusion of phenylpropionic acid or phenylvaleric acid led to the formation of hippuric acid, thus showing that  $\beta$ -oxidation (Knoop, A., 1905, ii, 46) can take place in this organ.

C. R. H.

**Copper, Enzymes, and Fertilisation.** O. GLASER (*Biol. Bull. Marine Biol. Lab.*, 1923, **44**, 79—104; from *Chem. Zentr.*, 1924, i, 2281—2282).—Eggs of *Arbacia* absorb copper ions from sea-water to which copper sulphate is added. Copper is also a normal constituent of *Arbacia* eggs and increases in amount up to maturity. After fertilisation the copper content decreases probably owing to secretion of pigment.

G. W. R.

**Hydrolysis of Nucleic Acid by Takadiastase.** J. NOGUCHI (*Biochem. Z.*, 1924, **147**, 255—257).—Takadiastase contains nucleinase and nucleotidase, capable of hydrolysing yeast and thymus-nucleic acids with the liberation of phosphoric acid and purine bases.

J. P.

**Effect of  $\alpha$ - and  $\beta$ -Methylglucosides on Taka-invertase.** Y. HATTORI (*Biochem. Z.*, 1924, **150**, 150—158).—The hydrolysis of sucrose by the invertase of takadiastase is inhibited by  $\beta$ -methylglucoside and unaffected by  $\alpha$ -methylglucoside, whereas the reverse is true of yeast invertase. The type of inhibition, as shown by the time relations of the reaction, resembles that brought about by *lævulose*.

C. R. H.

**Participation of Co-enzyme in the Degradation of Sugar.** K. MYRBÄCK and H. VON EULER (*Ber.*, 1924, **57**, [B], 1073—1076).—The co-enzyme content of a bottom yeast was diminished by about 55% by desiccation under the conditions usual in practice, but remained almost unchanged when the specimen was rapidly spread in a thin layer on porous clay. The presence of co-enzyme was established in a *Torula* from kefir, which produces alcohol, in a product from the same source which ferments lactose, yielding unknown substances, and in *Streptococcus lactis*. Its presence could not be established in *Penicillium glaucum* or *Bacillus lactis aerogenes*.

H. W.

**Fermentation Co-enzyme (Co-enzyme) of Yeast. IV.** K. MYRBÄCK and H. VON EULER (*Z. physiol. Chem.*, 1924, **138**, 1—10).—Further experiments on the purification of the co-enzyme, using mainly the lead acetate method (this vol., i, 918), are recorded. Baryta, in contrast to lead acetate, precipitates

only insignificant amounts of the co-enzyme. Adsorption by alumina gave inconclusive results. Tholin's results (A., 1922, i, 305) on the inactivation of the co-enzyme by heat at varying degrees of acidity have been confirmed with more active preparations.

E. S.

**Formation of *l*-Malic Acid in Alcoholic Fermentation by Yeast.** H. D. DAKIN (*J. Biol. Chem.*, 1924, **61**, 139—145).—*l*-Malic acid is a constant product of the action of yeast on pure sucrose solutions; the amount formed is increased by the addition of sodium hydrogen carbonate to the medium; it is diminished by the addition of monoamino-acids, and of glutamic, aspartic, and hydroxyaspartic acids, also by the products of hydrolysis of yeast; it is little affected by proline and hydroxyproline and is sometimes increased by hydroxyglutamic acid; it is markedly increased by sodium fumarate, but is not affected by sodium succinate. C. R. H.

**"Limit" Dextrin and a Complement of the Amylases.** III. H. PRINGSHEIM and A. BEISER (*Biochem. Z.*, 1924, **148**, 336—343).—In continuation of previous observations (this vol., i, 106), it is found that amylose is hydrolysed by amylases much more quickly than is amylopectin. The presence of complement does not influence the hydrolysis of amylose, whilst it has a marked accelerating effect on that of amylopectin. "Limit" dextrin ("Grenzdextrin") is a trisaccharide derived from amylopectin (cf. Pringsheim and Wolfsohn, this vol., i, 714). Amylase complement has a marked effect on the hydrolysis of glycogen, a fact supporting the view that amylopectin and glycogen may be related (Pringsheim and Goldstein, A., 1922, i, 633). Complement is associated with malt amylase in the natural state. J. P.

**Dextrin-producing Power of Malt Amylase and the Re-activation of Amylase Inactivated by Heat.** T. CHRZĄSZCZ (*Biochem. Z.*, 1924, **150**, 60—92).—The preparations of amylase were obtained from barley, wheat, and millet, and showed only quantitative differences in their behaviour. The hydrolysis of starch by this amylase proceeds best at  $p_H$  4.66—5.28. The speed of the reaction is increased by using large amounts of enzyme in concentrated solution and by keeping the starch paste as thick as is consistent with thorough mixing with the enzyme. The starch paste is best prepared by heating at a temperature above 80°. The optimum temperature for the reaction is not fixed, but depends on the amount of enzyme present; with small amounts it is 30—50°; with large amounts 50—70°. Amylase is completely inactivated by heating for 2 hours at 90°; such a preparation may be partly reactivated by shaking with air; shaking with oxygen, hydrogen peroxide, or carbon dioxide does not increase the reactivation.

C. R. H.

**Isoelectric Point of Malt Amylase.** H. C. SHERMAN, A. W. THOMAS, and M. L. CALDWELL (*J. Amer. Chem. Soc.*, 1924, **46**, 1711—1717).—Working with purified enzyme preparations in solutions adjusted to a wide range of hydrogen-ion concentrations



by means of buffer solutions, and using the U-tube apparatus of Michaelis (A., 1909, i, 277) suitably modified, the isoelectric point of malt amylase has been determined by electrophoresis to be  $p_H$  4.3—4.5, a point which coincides with its maximum activity towards starch (Sherman, Thomas, and Baldwin, A., 1919, i, 181). On the acid side of this range, the enzyme migrates towards the cathode, on the alkaline side towards the anode. The relative concentration of the enzyme in the anodic and cathodic arms was determined by a modification of Sherman's gravimetric method (A., 1910, ii, 1012; 1922, i, 283). These results show that the enzyme is either an ampholyte or associated with an ampholyte and support the view previously advanced that amylase is either protein in nature or intimately associated with protein. The results are in accord with the observation (Sherman and Thomas, A., 1915, i, 183) that the amylolytic activity of malt amylase is increased by the addition of neutral salts. R. B.

**Invertase in Honey.** J. M. NELSON and D. J. COHN (*J. Biol. Chem.*, 1924, **61**, 193—224).—Honeycombs were extracted with water and the filtered solution was treated with alcohol; the viscous precipitate was stirred with a little water and the filtered solution submitted to dialysis; the clear solutions of invertase so obtained were used for a detailed comparison of the mode of action of this invertase with that from yeast. The relative velocities of inversion at different periods of the reaction are not the same with the two enzymes; the optimum  $p_H$  for honey invertase is 5.5—6.3 as against 4.4—5.0 for yeast invertase; moreover, for honey invertase the optimum  $p_H$  varies with different stages of the reaction, whereas with yeast it is constant throughout. The honey invertase is the less stable towards acid, being partly inactivated at  $p_H$  5.8. The effect of variations in sucrose concentration is similar with both enzymes, the optimum concentration being 4%. C. R. H.

**Decomposition of Invertase by Enzymes. I and II.** H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **138**, 11—20, 38—48).—Although the physical properties of invertase recall those of proteins (this vol., i, 466, 693, 799; cf., however, Willstätter and Schneider, this vol., i, 692), neither the separate nor successive actions of pepsin and trypsin produced a decrease in the viscosity of a solution of an invertase preparation of high activity ( $\eta_f=225$ ) approaching in magnitude that produced in a gelatin solution. Pepsin diminished the activity of the invertase only slightly (14%) in 38 hours; trypsin, however, caused a considerable diminution in 2 days, and after 5 days only 28% of the original activity remained. The authors conclude that invertase is only decomposed with difficulty by proteolytic enzymes, but that when such decomposition does occur the activity of the invertase is simultaneously destroyed; the activity of the invertase complex is thus closely connected with its protein portion. E. S.

**Invertase of *Aspergillus flavus*.** K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **138**, 144—147).—The hydrolysis of sucrose by this

mould follows the course of a unimolecular reaction; the curve expressing relationship of rate of hydrolysis to  $p_H$  lies between those obtained with the invertases of yeast and of *Penicillium glaucum*. C. R. H.

**Lichenin and Lichenase.** H. PRINGSHEIM and W. KUSENACK (*Z. physiol. Chem.*, 1924, **137**, 265—271).—The swelling of lichenin is due to the fact that it forms an ester with silicic acid. A lichenin preparation purified by repeated solution and precipitation contained 2.64% of ash which consisted of silica only. The presence of silica as an adventitious impurity in lichenin thus purified is scarcely conceivable. In order to ascertain whether lichenin is entirely composed of cellobiose residues, it was hydrolysed with the lichenase recently found in malt extract (this vol., i, 233), which also contains cellobiase. Further observations now show that cellobiase disappears completely after keeping the malt extract for 6 months, and it then contains lichenase only. When lichenin is hydrolysed with such an extract at 37° and  $p_H$  5, it is quantitatively converted into cellobiose in about 4 days. Cellobiose on acetylation in pyridine solution does not give  $\beta$ -octa-acetylcellobiose, m. p. 228°, but the  $\alpha$ -form, m. p. 195°. D. R. N.

**Laccase.** P. FLEURY (*Bull. Soc. Chim. biol.*, 1924, **6**, 436—448; 449—463).—The oxidation of guaiacol by laccase was studied quantitatively by determining colorimetrically the guaiacoquinone formed. The latter is proportional to the time or the quantity of the enzyme so long as the action is carried out at a moderate temperature and not too far. When the "initial velocity" (or activity) of the enzyme is plotted against the concentration of guaiacol, keeping the quantity of enzyme constant, a curve is obtained which may be divided into two parts, the first in which the velocity is proportional to the quantity of guaiacol, and the second in which it is independent of its concentration. When the amount of laccase is varied, the point of inflexion of the curve is displaced towards lower concentrations with diminishing amounts of laccase. The influence of the oxygen concentration is very similar to that of guaiacol. The results may be explained by assuming a combination between the enzyme and the substrate, or by the influence of the rate of diffusion of oxygen into the medium. D. R. N.

**Comparison of Liver Esterase with Pancreatic Lipase. Stereochemical Specificity of Lipases.** R. WILLSTÄTTER and F. MEMMEN (*Z. physiol. Chem.*, 1924, **138**, 216—253).—The hydrolytic activity of liver esterase, whether purified or not, towards glycerides is reduced by the addition of such substances as calcium chloride and sodium oleate which favour the action of pancreatic lipase; in the hydrolysis of simple esters the addition of these substances is without effect. A comparison of the rate of hydrolysis of different substances by the enzymes from liver and pancreas of the same animal shows that in the case of olive oil the pancreatic enzyme is enormously more active, whilst in that of methyl butyrate the liver enzyme is the more active. The best purification of the

hepatic enzyme was effected by extracting the liver with dilute ammonia, redissolving the crude product, obtained by evaporating this extract, in a solution of acetic acid and ammonium acetate of  $p_H$  4.2, and adsorbing the enzyme on kieselguhr or aluminium hydroxide, from which it was subsequently recovered with dilute ammonia; such preparations are about twenty times as active as the crude desiccated liver; on keeping they lose about one-fifth of their activity in the first few days and thereafter remain almost constant. The activity of the enzyme, especially of the purified preparations, is strongly inhibited by atoxyl, and slightly by quinine.

A series of experiments was made to determine the stereochemical specificity of the two enzymes (cf. Dakin, A., 1904, i, 1071; 1905, i, 556). Pancreatic lipase hydrolysed the laevorotatory component more rapidly in the case of the racemic esters of mandelic, phenylmethoxyacetic, phenylchloroacetic, and phenylbromoacetic acids and the dextrorotatory component of the esters of phenylaminoacetic and tropaic acids and of leucine; with hepatic esterase, on the other hand, the dextrorotatory component was the more rapidly hydrolysed in all the above cases except for the esters of phenylchloroacetic, phenylbromoacetic, and tropaic acids. The degree of specificity of the pancreatic enzyme was the greater throughout. The authors conclude, on the whole, that the two enzymes are distinct from one another.

C. R. H.

**Enzymic Activity of Lactic Acid Bacteria. II.** A. I. VIRTANEN (*Z. physiol. Chem.*, 1924, **138**, 136—143; cf. this vol., i, 915).—Dried preparations of *Bacillus casei*  $\epsilon$  possess the power of synthesising hexosephosphate from solutions containing dextrose and inorganic phosphate, which suggests a similarity between the process of lactic acid fermentation and the formation of lactic acid in muscle.

C. R. H.

**Activity of Urease in High Concentrations of Alcohol.** N. N. IVANOV (*Biochem. Z.*, 1924, **150**, 108—114).—Urea is decomposed, to some extent, by urease in concentrations of alcohol as high as 92.5% and of acetone up to 85%. It is suggested that such solutions, in which the decomposition proceeds much more slowly than in water, may afford suitable media for the study of the intermediate products of the reaction.

C. R. H.

**Enzymic Hydrolysis of Phenaceturic Acid.** C. NEUBERG and J. NOGUCHI (*Biochem. Z.*, 1924, **147**, 370—371).—Taka-diastase contains an enzyme capable of hydrolysing sodium phenaceturate with the liberation of phenylacetic acid.

J. P.

**Phenolases in the Blood.** K. HIZUME (*Biochem. Z.*, 1924, **147**, 216—220).—There is present in human serum a phenolase capable of oxidising dihydroxybenzene derivatives, which is affected neither by heating at 56° for 30 minutes nor by dialysis. The phenolase is also found in the sera of sheep, rabbits, dogs, and guinea-pigs in amounts diminishing in the order cited.

J. P.

**Enzymes of the Skin.** Y. YAMASAKI (*Biochem. Z.*, 1924, **147**, 203—215).—Diastase and lipase are present in human skin

in the superficial and deeper layers. The latter enzyme is stable to both quinine and atoxyl and therefore differs from the other lipases of the body. Peptolytic and autolytic enzymes are also present, together with a catalase and an oxidase, the latter being capable of oxidising dihydroxybenzene derivatives but not the monohydroxy compounds. J. P.

**Formation of *l*-Leucic Acid in Acetone-Butyl Alcohol Fermentation.** E. G. SCHMIDT, W. H. PETERSON, and E. B. FRED (*J. Biol. Chem.*, 1924, **61**, 163—175).—From the solution obtained by the fermentation of maize mash by *Bacillus granulobacter pectinovorum* there were isolated the calcium and zinc salts of an acid,  $C_6H_{13}O_3$ . On distillation with permanganate this acid gave an aldehyde, which was identified by its *p*-nitrophenyl-hydrazone and its aldomecon as isovaleraldehyde. The acid was therefore  $\alpha$ -hydroxyisohexoic acid; it gives all the qualitative reactions for lactic acid, and it is suggested that it may have been this acid, and not lactic acid, which was obtained by Speakman (this vol., i, 371) under similar conditions. C. R. H.

**Activation of Papain by Hydrocyanic Acid.** R. WILLSTÄTTER and W. GRASSMANN (*Z. physiol. Chem.*, 1924, **138**, 184—215).—The activating effect of hydrocyanic acid on papain first observed by Mendel and Blood (*A.*, 1910, i, 796) has been studied in a series of experiments on the hydrolysis of gelatin by this enzyme. The rate of hydrolysis is approximately trebled by the addition of cyanide; the optimum temperature for the enzyme is 65—70°, the rate of reaction being nearly doubled by every rise of 10° from 30° to 70°; the optimum reaction, with or without the addition of cyanide, is  $p_H$  5, and it is suggested that the closeness of this optimum reaction to the isoelectric point of gelatin ( $p_H$  4.7) may indicate that this enzyme attacks the undissociated protein molecule. The maximum activation is obtained by allowing the cyanide to act on the enzyme for an hour, before mixing with the gelatin solution; this is true of both crude and purified preparations and of those which, having been once activated with cyanide, have been inactivated again by removal of the hydrocyanic acid; it therefore shows that the activation consists in the formation of a dissociable compound between enzyme and cyanide. The sensitivity of the enzyme to the presence of cyanide is so great that it can be used as a test for the presence of amounts of cyanide of the order of 0.001 mg. Commercial peptone and peptide mixtures prepared by the partial digestion of gelatin are scarcely attacked by papain unless activated by cyanide; pure dipeptides are not hydrolysed even by the activated enzyme. The best purification of the enzyme was effected by adsorption on aluminium hydroxide from an aqueous-alcoholic solution containing ammonia, and subsequent recovery from the precipitate by means of dilute acetic acid. C. R. H.

**Asymmetric Enzymic Hydrolysis of Benzoylated Amino-acids.** C. NEUBERG and K. LINHARDT (*Biochem. Z.*, 1924, **147**, 372—376).—Benzoyl-*dl*-glycine and benzoyl-*dl*-alanine are hydrolysed by preparations of takadiastase, the *d*-stereoisomerides

being preferentially attacked whilst the *l*-isomerides remain unchanged. Thus it is possible to obtain both antipodes of a racemic amino-acid, since the free *d*-amino-acid may be separated from the benzoyl-*l*-amino-acid and the latter may then be hydrolysed.  
J. P.

### Biochemical Method of Resolving Racemic Amino-acids.

C. HOPPERT (*Biochem. Z.*, 1924, **149**, 510—512).—Takadiastase contains an enzyme capable of hydrolysing hippuric acid and its homologues into benzoic acid and the amino-acid. This *amino-acidase* was found by the author to hydrolyse benzoyl-*d*-alanine, but not its stereoisomeride, and he adopted this method for resolving the inactive amino-acid.  
S. S. Z.

### Enzymes of *Utricularia vulgaris*. I. A. N. ADOWA (*Biochem.*

*Z.*, 1924, **150**, 101—107).—Extracts of this insectivorous plant possess a slight power of hydrolysing gelatin and casein. In the case of gelatin, the hydrolysis proceeds best in an alkaline medium; in such a medium the process is inhibited by the addition of calcium chloride and of animal charcoal, but in a neutral medium it is slightly accelerated by these substances.  
C. R. H.

### Occurrence of Catalase in Micro-organisms. A. J. KLUYVER

(*Z. physiol. Chem.*, 1924, **138**, 100—101).—It is provisionally concluded that catalase occurs only in those bacteria which use free oxygen in their metabolic processes.  
E. S.

**Destruction of Rennin by Agitation: A Case of Catalysis at an Air-Liquid Interface.** E. K. RIDEAL and C. G. L. WOLF (*Proc. Roy. Soc.*, 1924, **A**, **106**, 97—116).—Agitation of rennin solutions reduces their power of clotting milk. This is traced to the presence of some substance, probably a fatty acid, which reacts chemically with the rennin, mainly at the air-liquid surface where they are both adsorbed and the molecules are orientated favourably for reaction. This substance can be removed by dialysis, and by selective adsorption by fuller's earth or starch, or it can be displaced from the surface by some capillary active substance such as saponin. It can also be rendered innocuous by conversion into a salt. Its effect can be imitated by the capillary-active organic acids or by phenol, but sulphuric acid (not capillary-active) is ineffective. As a result of the reaction the surface tension is increased and the  $p_H$  lowered. Dialysed solutions of rennin are less active owing to partial coagulation but may be peptised by small quantities of acid without the  $p_H$  being significantly increased. [Cf. *B.*, 1924, 726.]  
L. J. H.

### Mechanism of the Anti-peptic Action of Blood Serum.

L. LORBER (*Biochem. Z.*, 1924, **148**, 49—52).—The anti-peptic action of blood-serum is ascribed to the sodium hydrogen carbonate present.  
J. P.

### Efficiency of some Organic Dyes as Anti-ferments. E. H.

HARVEY (*Amer. J. Pharm.*, 1924, **96**, 585—589).—The efficiency of a number of organic dyes as anti-ferments has been measured by

observing the retardation of the change in rotation produced by their addition to yeast-sucrose solution. The following dyes are arranged in the order of decreasing efficiency: safranin, *p*-nitrophenol, methylene-blue, eosin Y, methyl-violet, cyanine, acid-fuchsin, alizarin-blue S. Mercuric chloride is the most effective anti-ferment, as it kills the yeast cells almost immediately; safranin shows 57.3% efficiency as compared with mercuric chloride, whilst that of alizarin-blue S is practically nil. Ultra-violet light shows an efficiency of 91.8%. R. B.

**Action of Uranyl Acetate. II. Action on Various Enzymes.** Y. MIKAWA (*Biochem. Z.*, 1924, **149**, 540—549).—Uranyl acetate reduces the action of takadiastase, serum diastase, liver diastase, blood catalase, liver catalase, serum lipase, and liver lipase. S. S. Z.

**Action of Poisons on Enzymic Processes. IX. Action of Poisons on Metallic Catalysts and Catalase Processes.** C. G. SANTESSON (*Skand. Arch. Physiol.*, 1923, **44**, 262—305; from *Chem. Zentr.*, 1924, i, 1964—1965; cf. A., 1922, i, 1077—1078).—From a consideration of the properties of catalases and metallic catalysts the action of catalases is held to be enzymic and not due to metals present in them. Electrolytes exert a stronger inhibitory effect on colloidal metallic catalysts than on catalases. This may be related to the protective effect of emulsoids, associated with or identical with the catalases. G. W. R.

**Action of Simple Narcotics on Succinodehydrogenase.** H. GRÖNVALL (*Skand. Arch. Physiol.*, 1923, **44**, 200—214; from *Chem. Zentr.*, 1924, i, 1961).—Methyl alcohol, ethyl alcohol, propyl alcohol, and the butyl alcohols inhibit the activity of succinodehydrogenase (Ohlsson, A., 1922, i, 785). The inhibitory effect increases with the number of carbon atoms. G. W. R.

**Action of Urethanes on Succinodehydrogenase.** D. SVENSSON (*Skand. Arch. Physiol.*, 1923, **44**, 306—314; from *Chem. Zentr.*, 1924, i, 1961; cf. preceding abstract).—Methyl-, ethyl-, propyl-, isobutyl-, and isoamyl-urethanes exert an inhibitory effect, which increases with the molecular weight of the urethane, on succinodehydrogenase. Chloral hydrate is as effective as isobutylurethane, whilst phenol and potassium fluoride have a still greater inhibitory power. G. W. R.

**Effect of Antipyretics on Succinodehydrogenase and on the Respiration of Tissues. I.** I. NITZESCU and J. COSMA (*Compt. rend. Soc. Biol.*, 1923, **89**, 1401—1402, 1406—1407; from *Chem. Zentr.*, 1924, i, 2163).—Sodium salicylate, pyramidone, and antipyrin exert an inhibitory effect on the succinodehydrogenase action of ox muscle on potassium succinate. A similar effect on the respiration of tissues is observed. Urethanes display a similar but weaker effect. G. W. R.

**Mechanism of the Action of Amino Promoters on Enzymes.** E. W. ROCKWOOD (*J. Amer. Chem. Soc.*, 1924, **46**, 1641—1645; cf. this vol., i, 351).—The rate of decay of urease

and ptyalin in solution, alone, and in the presence of three typical  $\alpha$ -amino-acids, glycine, aspartic and hippuric acids, has been measured. The results confirm the view that the promoter effect is only partly due to the prevention of decay of the enzyme, and prove that the promoter acts chiefly through a specific stimulating influence on the enzyme (cf. Sherman and Walker, A., 1923, i, 1033). R. B.

**Autolysis. XI. Relation of the Isoelectric Point to Digestibility.** A. B. HERTZMAN and H. C. BRADLEY (*J. Biol. Chem.*, 1924, **61**, 275—287).—Addition of proteins to autolysing liver increases the amino-acid production at and above a certain hydrogen-ion concentration which is specific to each protein and almost coincident with its isoelectric point. This is taken to be evidence that in order to be digested by liver proteases, proteins must be in the form of acid salts, and it explains the previous observation (A., 1916, i, 582) that addition of acid stimulates autolysis. C. R. H.

**Autolysis. II. Effect of Iodine on the Autolysis of Organs.** O. STEPPUHN and L. UTKIN-LJUBOVZOV (*Biochem. Z.*, 1924, **150**, 165—172; cf. A., 1923, i, 1158).—Autolysis of serum, liver, lungs, and kidneys is accelerated by small amounts of iodine and delayed by large amounts; tryptic digestion of casein is delayed by iodine in all concentrations. C. R. H.

**Oligodynamic Properties of Insoluble Mercury Compounds.** S. REBELLO (*Compt. rend. Soc. Biol.*, 1923, **88**, 1333—1335; from *Chem. Zentr.*, 1924, i, 924—925).—Mercury and insoluble mercury compounds (with the exception of mercuric sulphide) exert an inhibitory effect on bacterial growth by diffusion in gel cultures. G. W. R.

**Properties of Diphtheria Anatoxin.** G. RAMON (*Compt. rend.*, 1924, **179**, 422—425).—Diphtheria anatoxin differs from the original toxin in having lost toxicity (cf. this vol., i, 463) and possessing a greater resistance to heat. Preparations of the anatoxin retained their strength, as measured by the amount of antitoxin required to cause flocculation, without sensible variation when kept at 3° to 4° for a year. The rate of flocculation is slightly diminished, and this effect is a little more pronounced when the anatoxin is kept at laboratory temperature (20°). The length of time for which the preparations were kept was without appreciable effect on their immunising or hyperimmunising power, *in vivo*, and in no case was any return of toxicity observed, even after the lapse of a year. Anatoxin preparations warmed at 65° or 70° for 1 hour retained their full flocculating and immunising powers, the appearance of the flocculation being more or less retarded, and these properties begin to decrease only when the preparation is heated at 72—75°. R. B.

**Effect of Oxidising Agents on Diphtheria Toxin.** F. DE POTTER (*Compt. rend. Soc. Biol.*, 1923, **89**, 422—425; from *Chem. Zentr.*, 1924, i, 930).—Diphtheria toxin is oxidised only with difficulty even by ozone and potassium permanganate. G. W. R.

**Yeast Protein as Antigen.** H. LÜERS and F. OTTENSOOSER (*Biochem. Z.*, 1924, **148**, 130—146).—From dried yeast, the proteins cerevisin and zymocasein were isolated in yields of 10% and 3%, respectively. They can be differentiated by crossed precipitin reactions, from which it is concluded that their specificity as antigens has primarily a chemical basis. Anaphylaxis experiments reveal the presence of yeast proteins as well as those of barley in the precipitate formed during the pasteurisation of beer. J. P.

**Products of the Catalytic Degradation of the Feathers of the Goose.** Remarks on W. S. SSADIKOV and N. D. ZELINSKY'S Work. E. ABDERHALDEN (*Biochem. Z.*, 1924, **149**, 572—574).—Polemical. S. S. Z.

**Preparation of Insulin.** H. PÉNAU (*J. Pharm. Chim.*, 1924, **30**, 145—153).—Impure insulin is obtained from the pancreas by extraction with alcoholic hydrogen chloride, removing fatty impurities and a portion of the salts and proteins, and precipitation with absolute alcohol. It is purified by saturating its solution with sodium chloride, centrifuging, and dialysing the solution of the solid so obtained. The insulin so obtained does not cause harmful secondary reactions. [Cf. *B.*, Oct. 31.] W. T. K. B.

**Preparation of Insulin and its Physiological Action.** C. SERONO, E. TROCELLO, and A. CRUTO (*Rassegna Clin. Terap. Sci. aff.*, 1923, **22**, 243—247; from *Chem. Zentr.*, 1924, i, 1409).—Directions are given for the preparation of insulin free from diastase. It is stated that methæmoglobin occurs in the blood of rabbits under the influence of insulin. G. W. R.

**Preparation of Insulin.** A. SORDELLI and V. DEULOFEU (*Compt. rend. Soc. Biol.*, 1923, **89**, 743—744; from *Chem. Zentr.*, 1924, i, 1234).—The precipitate in 0.1—0.2*N* picric acid is purified by washing with acetone. The picric acid may also be removed by adsorption on silk. G. W. R.

**Metabolin and the Internal Secretion of the Pancreas.** E. VAHLEN (*Münch. med. Woch.*, 1924, **71**, 101—102; from *Chem. Zentr.*, 1924, i, 2178).—"Irreversible" metabolin (Gehe's "irrebolin") is effective against adrenaline glycosuria in rabbits when administered per os, and still more effective per rectum. Insulin is held to inhibit the formation of sugar in the liver, whilst "irrebolin" increases the oxidation of sugar. The complete function of the inner secretion of the pancreas is due to a combination of the actions of these two hormones. G. W. R.

**Yeast Growth Promoting Vitamin Tested on Animals.** J. DEAS (*J. Biol. Chem.*, 1924, **61**, 5—8).—An infusion of malt combings, which has been shown to contain the "bios" described by Wildiers (*La Cellule*, 1901, **18**, 313) and which is apparently identical with the vitamin-*D* of Funk and Dubin (*A.*, 1922, i, 203), when administered to rats in combination with a diet free from vitamin-*B*, does not promote their growth. The "bios" and vitamin-*B* are therefore not identical. C. R. H.



**Comparative Physiological Importance of Iron and Zinc.**

G. BERTRAND and H. NAKAMURA (*Compt. rend.*, 1924, **179**, 129—133; cf. A., 1922, i, 893).—It has already been shown that when a litter of young mice was divided into two groups, one of which was fed on a diet free from vitamins and also completely free from zinc, the other on a diet free from these vitamins but containing small quantities of zinc, the life of the latter group was prolonged 25—50% beyond that of the former. The experiments have now been repeated with both groups receiving zinc but only one group receiving iron. In only one experiment in a series of six did the iron-fed mice survive the others, and the presence of iron in the diet has not therefore the marked effect of that of zinc. F. G. M.

**Colloidal Properties of Phloridzin.** R. SCHAEFER and F.

SCHMIDT (*Biochem. Z.*, 1924, **149**, 585—591).—Phloridzin diffuses very slowly through gelatin gels. Solutions of widely differing concentrations do not produce any perceptible lowering of the freezing point and display a strikingly low conductivity. The addition of alkali or acid does not alter its degree of dissociation. A Tyndall cone is observed in phloridzin solutions of considerable dilutions and colloidal particles can be seen with the immersion ultramicroscope. By means of the ultra-filter the dimensions of these particles are found to be probably smaller than 10  $\mu\mu$ .

S. S. Z.

**Characters and Composition of Mustard Oil.** J. C. DELAGE

(*Ann. Falsif.*, 1924, **17**, 336—343).—Specimens of mustard oil examined had  $d$  1.0186 to 1.0237 and contained from 96 to 97.7% of allylthiocarbimide. On fractional distillation from a few drops to 7% distils at 148.5° to 149.9°; the greater part distils at 150—150.5° (pure allylthiocarbimide) and the residue amounts to 1 to 2%. The composition of mustard oil varies with its age; the maximum amount of allylthiocarbimide is present a few months after its preparation, and then decreases.

W. P. S.

**Insecticidal Principle in *Chrysanthemum cinerariaefolium*.****IV. Insecticidal Principle Produced on Dry Distillation of *Chrysanthemum cinerariaefolium*.** R. YAMAMOTO and M. SUMI

(*J. Chem. Soc. Japan*, 1923, **44**, 1070—1085).—By distilling powdered flowers of *Chrysanthemum cinerariaefolium* at 260—280°, an acidic distillate was obtained, in which the following compounds were found: Acetic and propionic aldehydes and acids, methyl-, trimethyl-, butyl-, and amyl-amines, pyridine and a homologue of pyridine (picrate, m. p. 84°; chloromercurate, m. p. 125°). For determining the insecticidal power of these compounds, the effects of homologous acids, esters, and bases were compared on flies and other insects. When naturally evaporated, formic acid is more potent than any other fatty acid; butylamine and *tert.*-amylamine have the strongest action amongst amines. In the case of aliphatic amines boiling below 80°, the insecticidal power is proportional to the molecular weight. When evaporated by heating or eaten by

insects, nicotine is the most toxic of the substances investigated. Generally cyclic compounds have greater power than aliphatic substances.

K. K.

**Chemistry of Grape Pigments. II. Anthocyanins in Clinton Grapes.** R. J. ANDERSON and F. P. NABENHAUER (*J. Biol. Chem.*, 1924, **61**, 97—107; cf. this vol., i, 251).—The anthocyanin of Clinton grapes has been isolated and appears to be identical with that obtained by Willstätter and Zollinger from *Vitis riparia* (A., 1917, i, 47). It was isolated as the *picrate* which was converted into an amorphous *chloride*,  $C_{23}H_{35}O_{12}Cl \cdot 2H_2O$ . On boiling with hydrochloric acid it gives dextrose and crystalline *anthocyanidin chloride*,  $C_{17}H_{15}O_7Cl \cdot 1.5H_2O$ . On boiling with hydriodic acid this yields delphinidin iodide; the methoxyl content is intermediate between those required by a mono- and a di-methyl ether of delphinidin. Phloroglucinol was isolated from the products of alkali fusion of the anthocyanidin chloride; the latter, on boiling with acetic anhydride, gave an acetyl derivative (m. p. 205—210°); this, on oxidation with permanganate, gave an ether-soluble substance from which, by hydrolysis with hydriodic acid, gallic acid was obtained.

C. R. H.

**Presence of Valine in Zein.** H. D. DAKIN (*J. Biol. Chem.*, 1924, **61**, 137—138).—The presence of valine in zein, recorded by Osborne and co-workers (A., 1908, i, 115; 1910, i, 598), is confirmed by the isolation of about 1% of pure crystalline valine after hydrolysis of zein by boiling with dilute sulphuric acid. The author suggests that his own previous failure to detect valine in this protein (A., 1923, i, 1243) may have been due to racemisation owing to the high temperature at which the hydrolysis was carried out.

C. R. H.

**Optically Active Asparagine in Seedling Lupins.** A. PIUTTI (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 384—386; from *Chem. Zentr.*, 1924, i, 1941).—*d*-Asparagine was obtained together with small quantities of *s*-asparagine from lupin seedlings.

G. W. R.

**Henna.** O. A. OESTERLE (*Schweiz. Apoth.-Ztg.*, 1923, **61**, 541—543; from *Chem. Zentr.*, 1924, i, 1388).—From a hot alcoholic extract of henna, mannitol and tribenzacetal were isolated. It is possible that mannitol is not a normal constituent of henna.

G. W. R.

**Ternary Materials of Green and Etiolated Leaves.** H. COLIN and H. GRANDSIRE (*Compt. rend.*, 1924, **179**, 288—291).—The green leaves of the variegated chestnut always contain starch, which is absent from the etiolated leaves, and a larger proportion of both sucrose and reducing sugars than the latter. The sugars of etiolated leaves contain a larger proportion of dextrose. At midsummer a dextrorotatory, non-reducing sugar, which is oxidised

by nitric acid to mucic acid and which, after the action of invertase, is slowly hydrolysed by emulsin, appears in the green leaves and increases in quantity up to 0.5% as the season advances. No such product is found in etiolated leaves. Both green and etiolated leaves contain at least two glucosides, æsculin and fraxin, and the quantity of fatty materials is practically the same in both. The green leaves, however, contain a larger quantity of pectins which are precipitated by alcohol, baryta, and basic lead acetate and on hydrolysis yield arabinose.

J. W. B.

**Essence of Iris.** P. LANGLAIS and J. GOBY (*Compt. rend.*, 1924, **179**, 173—175).—The acidic constituents of iris essence have been separated by fractional distillation into octoic acid, b. p. 110—111°/4 mm., *anilide*, m. p. 51°; nonoic acid, b. p. 124—125°/4 mm., *anilide*, m. p. 57°; decoic acid, b. p. 138—139°/4 mm., *anilide*, m. p. 65.5°, ethyl ester, b. p. 104°/4 mm.,  $d^{28}_{20}$  0.859; undecoic acid, b. p. 145—146°/4 mm., *anilide*, m. p. 71°; dodecoic acid, b. p. 153—154°/4 mm., *anilide*, m. p. 75.5°; tridecoic acid, *anilide*, m. p. 81.5°. This is claimed to be the first occasion on which nonoic, undecoic, and tridecoic acids have been found in natural products.

F. G. M.

**Phytosterols of Wheat Endosperm.** R. J. ANDERSON and F. P. NABENHAUER (*J. Amer. Chem. Soc.*, 1924, **46**, 1717—1721; cf. this vol., i, 924).—The unsaponifiable matter from the fat extracted from wheat endosperm has been separated into an unsaturated sterol, identical with sitosterol, a saturated sterol, dihydrositosterol,  $C_{27}H_{47}OH$ , m. p. 144—145°,  $[\alpha]^{20}_D +25.82^\circ$  (in chloroform), and a non-crystallisable oil which has not been examined. The two sterols cannot be separated by crystallisation of their bromination products from alcohol, but are readily separated by treatment with acetic anhydride and sulphuric acid. The dihydrositosterol gives an acetyl derivative, m. p. 140°, and appears to be identical with the saturated sterol occurring in maize endosperm. The sterol is present throughout the wheat endosperm, but especially in the bran.

R. B.

**Effect of Germination on the Aleurone Layer.** E. B. BENNION (*Cereal Chem.*, 1924, **1**, 179—183).—A section of the aleurone layer from an ungerminated wheat grain placed on purified starch and kept moist showed no diastatic action in 8 days. From this and other experiments, it is concluded that the aleurone cells of the wheat grain are not glandular in the same sense as the epithelial cells of the scutellum; they provide a reserve food supply but do not function until 6 days after germination.

Analyses of barley and wheat after definite periods of germination showed a gradual decrease in nitrogen content after 30 hrs. Subsequently, in the case of wheat, after about 220 hrs. there is a rapid increase in percentage of nitrogen due to the complete utilisation of the starch in the endosperm. During the early stages of germination, amides formed by the degradation of proteins are further broken down and ammonia is evolved.

C. I. G.

**Zinc and Copper Compounds of Phæophytin.** R. WILL-STÄTTER and K. SJÖBERG (*Z. physiol. Chem.*, 1924, **138**, 171—176).—By the action of zinc acetate in glacial acetic acid solution a compound was obtained containing 1 mol. of zinc to 2 mols. of phæophytin; in pyridine solution 1 mol. of zinc combined with 1 mol. of phæophytin. Two copper compounds were prepared in similar ways, both of which contained 1 mol. of copper to 1 mol. of phæophytin. On hydrolysis with methyl-alcoholic potassium hydroxide, both zinc compounds gave zinc compounds of phytochlorin E and phytorhodin G which were easily decomposed by hydrochloric acid; the copper compound prepared in glacial acetic acid behaved similarly, but that prepared in pyridine solution gave copper derivatives of the hydrolysis products which were very stable towards hydrochloric acid. C. R. H.

**Wine Yeasts.** E. KAYSER and H. DELAVAL (*Compt. rend.*, 1924, **179**, 295—297).—The authors have isolated and described several strains of red yeasts from the vine "Breton," two of which are bottom yeasts, producing red colonies, and a third a top yeast forming pigments most intensely in the presence of slightly fermentable or non-fermentable sugars. These yeasts liquefy gelatin, and ferment lævulose, dextrose, and sucrose, but neither lactose nor raffinose. They ferment lævulose more readily than dextrose, the reverse being the case with a colourless yeast of the same origin. They are equally sensitive to the presence of nitrogenous substances (cf. Kayser, A., 1912, ii, 861) and produce a relatively larger proportion of volatile esters than does the colourless yeast. The ratio of valeric acid to acetic acid in the case of the red yeasts is also twice that obtained with the colourless variety.

J. W. B.

**Formation of Starch from Sugar by the Leaves of Higher Plants.** A. W. REINHARD (*Compt. rend. Soc. Biol.*, 1923, **89**, 1274—1275; from *Chem. Zentr.*, 1924, i, 1548).—The leaves of beans, peas, and white acacia produce starch when immersed in 10% sugar solution and exposed to light.

G. W. R.

**Transformation of Hydrocyanic Acid by Plant Sap.** S. DEZANI (*Biochim. terap. speriment.*, 1923, **10**, 85—96; from *Chem. Zentr.*, 1924, i, 2159).—Plant sap produces substances which on treatment with alkalis yield ammonia from hydrocyanic acid. This property is not shown by fermented plant juices or after addition of dextrose on account of the high acidity produced.

G. W. R.

**Reactions of the Alga *Chondrus crispus*, particularly with certain Dyes used in Therapy.** E. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1924, **30**, 154—161).—The action of various acids, bases, salts, and dyestuffs on an aqueous extract of the alga is described. Flocculation is caused by azines (e.g., safranin) and thiazines (e.g., methylene-blue), but not by oxazines (e.g. Meldola's-blue) nor by methyl violet or magenta. W. T. K. B.

**Detection of Acids in Plants. II.** H. SCHMALFUSS and K. KEITEL (*Z. physiol. Chem.*, 1924, **138**, 156—163).—A detailed description is given of a method of qualitative separation of the acids which may be obtained from plants, and also of micro tests for certain individual acids. C. R. H.

**Method for Preparing Large Quantities of Yeast Nucleic Acid as a Magnesium Compound.** E. J. BAUMANN (*J. Biol. Chem.*, 1924, **61**, 1—4).—Yeast is extracted with water, the solution made alkaline with sodium hydroxide, then partly neutralised with hydrochloric acid, and finally acidified with acetic acid; to the filtered solution is added magnesium sulphate to make 5% concentration and hydrochloric acid until precipitation is complete. The preparations so obtained are protein-free, but contain somewhat less than the theoretical nitrogen and phosphorus; the yield is 0.6 to 1.2% of the fresh yeast. C. R. H.

**Feeding of Plants with Aldehydes. V. Influence of Formaldehyde on the Function of Plant Enzymes.** T. SABALITSCHKA (*Biochem. Z.*, 1924, **148**, 370—382).—Germination of seeds is inhibited more or less completely by 0.13% formaldehyde solution, whilst the growth of young twigs is somewhat affected by 4% solutions, and the fermentation of dextrose by living yeast is stopped by 0.3% formaldehyde and slowed by concentrations between 0.3 and 0.005%. In the cell sap of plants grown in atmospheres containing formaldehyde less than 0.055% of the aldehyde was found. In general, no evidence was forthcoming in support of the view that in such concentrations the aldehyde acts as a stimulant of plant metabolism. J. P.

**Composition and Digestibility of Lupins and Lupin Offals, before and after the Removal of the Bitter Principle; and the Loss of Crude and Digestible Foodstuff resulting from Different Processes of Removal of the Bitter Substances.** F. HONCAMP, E. MÜLLER, F. POMMER, and R. SOIKA (*Landw. Versuchs-Stat.*, 1924, **102**, 261—307).—Lupins, after removal of the bitter contents, have a high food value and the milling offals (excepting the “bran”) are characterised by a high content of digestible protein. Losses in food value occasioned by the elimination of the bitter flavour, fall mostly on the nitrogen-free extractives, mineral matter, and to a less extent on easily soluble amides. The proteins are but little affected. A. G. P.

**Lime Requirement of Soils, and a New Method of Mechanical Analysis.** A. N. SOKOLOWSKI (*Arb. Wiss. Inst. Düngemittel*, 1923, **13**, 1—22; from *Chem. Zentr.*, 1924, **i**, 1584).—Adsorbed calcium is removed from soils by leaching with alkali salts. The soil thereby becomes deflocculated and water extracts from it an “active sediment” which is considered to be its most important constituent. Directions are given for the determination of this material in soils. From the content of a soil in adsorbed calcium

and its saturation capacity for calcium and ammonium respectively, a formula for the lime requirement is developed. G. W. R.

**Effect of Manganese on Vegetation.** G. D'IPPOLITO (*Staz. Sperim. agrar. ital.*, 1923, **56**, 386—400; from *Chem. Zentr.*, 1924, i, 952).—Marked increases in yield were obtained in pot and field experiments when manganese compounds were used as fertilisers. Manganese dioxide was more effective than manganic sulphate.

G. W. R.

**Determination of the Availability of Fertilisers.** C. LUMIA (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 370—371; from *Chem. Zentr.*, 1924, i, 2003).—A method is proposed for determining the availability of fertilisers by comparing their effect with that of water-soluble fertilisers on the activity of brewer's yeast.

G. W. R.

**Dependence of Denitrification on the Reaction of the Medium.** T. M. SSACHAROWA (*Arb. Wiss. Inst. Düngemittel.*, 1923, **15**, 1—22; from *Chem. Zentr.*, 1924, i, 2000).—In culture media the optimum reaction for denitrification lies between  $p_H$  7.0 and  $p_H$  8.2. This process does not occur below  $p_H$  5.5 or above  $p_H$  9.8. The optimum for the decomposition of nitrites lies between  $p_H$  5.5 and  $p_H$  7.0.

G. W. R.

**Chemical and Biological Studies with [Calcium] Cyanamide and some of its Transformation Products.** K. D. JACOB, F. E. ALLISON, and J. M. BRAHAM (*J. Agric. Res.*, 1924, **28**, 37—69).—Under laboratory conditions, ammonification of calcium cyanamide in soil is rapid, but nitrification follows only slowly, probably owing to the formation of small quantities of dicyanodiamide which, when added to soil, inhibits the process of nitrification. Guanyl carbamide and guanidine salts also tend to inhibit nitrification. [Cf. *B.*, 1924, 842.]

C. T. G.

**Critical Note on Method of Correcting Protein Digestion Coefficients.** H. E. WOODMAN (*J. Agric. Sci.*, 1924, **14**, 428—434).—The method of Pfeiffer for correcting "apparent" protein digestion coefficients for the undigested protein in the faeces is adversely criticised. Figures are recorded illustrating anomalous results which may be obtained by the adoption of this correction.

A. G. P.

## Organic Chemistry.

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**Superheating of Uniform Organic Compounds. I. Aryl-paraffins and Aliphatic Esters.** S. SKRAUP and F. NIETEN.—(See i, 1185.)

**Condensation of Acetylene with Hydrogen Sulphide in Presence of Aluminium Oxide.** A. E. TSCHITSCHIBABIN and O. S. BAGDASSARJANZ (*J. pr. Chem.*, 1924, [ii], **108**, 200—208).—When acetylene (2 vols.) and hydrogen sulphide (1 vol.) are passed over aluminium oxide at 425—450°, a liquid product is obtained, consisting of thiophen (40%), 2- and 3-ethylthiophen, mercaptans, unsaturated hydrocarbons, and products of b. p. above 186°. The catalyst loses its activity rapidly; the specific gravity of the crude condensation product decreases as the catalyst ages. (Cf. Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 709.)

F. G. W.

**Action of Alkali on Ethyl Alcohol and the "Nitric Oxide Reaction" of W. Traube.** M. STECHOW (*Ber.*, 1924, **57**, [B], 1611—1615).—Contrary to previous assumptions, the action of nitric oxide on an alcoholic solution of sodium ethoxide or hydroxide leads invariably to the production of considerable amounts of the compound,  $\text{CH}_2[\text{N}(\text{NO})\cdot\text{ONa}]_2$ , identical with the product isolated by Traube by the action of nitric oxide on a solution of acetone in alcohol in the presence of alkali. The production of the salt depends entirely on the quantity of alkali present and the duration of the experiment; it ceases with exhaustion of the alkali, but starts again after addition of further amounts of the latter. The source of the product is unknown, but it is significant that the protracted action of alkali ethoxide or hydroxide on ethyl alcohol in the absence of oxygen leads to the formation of resin acids, acetaldehyde, acetic acid, and condensation products of acetone such as mesityl oxide, phorone, and mesitylene. Traube's reaction is therefore unsuitable for the elucidation of constitutional problems.

H. W.

**Vapour-pressure Curves for Systems containing Alcohol, Ether, and Water.** E. A. LOUDER, T. R. BRIGGS, and A. W. BROWNE (*Ind. Eng. Chem.*, 1924, **16**, 932—935).—By the static method (the apparatus is described and figured), the vapour pressures of ethyl alcohol and of ethyl ether have been determined for the temperature range 0—50°. The values obtained are generally a little higher (about 0.5 mm. for ether, 0.5—1 mm. for alcohol) than those of Ramsay and Young or of Regnault. The vapour pressures of mixtures of (i) alcohol and ether, (ii) alcohol, ether, and water, and (iii) alcohol (95%), ether, and diphenylamine, were also measured over the same temperature range.

W. A. S.

**Pyrogenic Decomposition of Propyl Alcohol.** (MLLE.) E. PEYTRAL (*Bull. Soc. chim.*, 1924, [iv], **35**, 960—964; cf. A., 1920, i, 217).—By the methods previously employed (A., 1918, i, 1), it is shown that propyl alcohol when passed through a platinum tube at high temperatures undergoes the two primary decompositions:  $\text{CH}_2\text{Et}\cdot\text{OH}=\text{Et}\cdot\text{CHO}+\text{H}_2$  and  $\text{CH}_2\text{Et}\cdot\text{OH}=\text{CHMe}\cdot\text{CH}_2+\text{H}_2\text{O}$ , the former reaction, which requires the least deformation of the molecule, slightly preponderating. The propaldehyde undergoes further decomposition to give ethane and carbon monoxide, whilst the ethane is partly decomposed to ethylene and hydrogen. A small quantity of acetylene is also formed, probably by decomposition of ethylene, and traces of formaldehyde were detected, probably due to the primary decomposition:  $\text{CH}_2\text{Et}\cdot\text{OH}=\text{H}\cdot\text{CHO}+\text{C}_2\text{H}_6$ . R. B.

**Components of Wood Spirit Oil.** II. H. PRINGSHEIM and A. GORGAS (*Ber.*, 1924, **57**, [B], 1561—1566; cf. A., 1923, i, 1052).—The portion of the oil, b. p. 90—130°, which is not attacked by sodium hydrogen sulphite has been separated into four components: (1)  $\Delta^a$ -buten- $\gamma$ -ol, b. p. 97°, characterised by oxidation to pyruvic acid and by reduction to *sec.*-butyl alcohol; (2) diethyl ketone; (3) 2:5-dimethyltetrahydrofuran, b. p. 108°, characterised as the ferrocyanide, and (4) 2-methyl-5-ethyl-4:5-dihydrofuran, m. p. 125°, which is converted by warm water into ethyl  $\gamma$ -hydroxy-*n*-butyl ketone. A method is given for the determination of methyl propyl ketone and diethyl ketone in mixtures which depends on the difference between their velocities of oximation. H. W.

**Dilution of Ethylene Bromohydrin with Water.** J. READ and G. J. BURROWS (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 54—57; cf. T., 1920, **117**, 1214).—When water is added to ethylene bromohydrin, a negative thermal effect is produced up to a dilution of about 80% followed, at about 75%, by a positive thermal effect which persists to a dilution of about 10%. Conversely, on adding small amounts of ethylene bromohydrin to water the initial positive thermal effect is followed by a negative effect. The density-concentration curve is regular and of the same type as the refractive index-concentration curve (cf. *loc. cit.*). At 20°, a maximum contraction (1.07%) occurs at a concentration of about 50%, and at 25°, at a concentration of about 46% of ethylenebromohydrin. The viscosity of solutions increases regularly with an increasing proportion of the bromohydrin. W. T. K. B.

**Pyrogenic Decomposition of Ethyl Ether.** (MLLE.) E. PEYTRAL (*Bull. Soc. chim.*, 1924, [iv], **35**, 964—968).—When the vapour of ethyl ether is passed rapidly through a platinum tube at high temperatures, the only primary reaction is its decomposition into ethane and acetaldehyde. The latter substance undergoes secondary decomposition into carbon monoxide and methane as previously shown (A., 1920, i, 217), whilst the ethane partly decomposes into ethylene and hydrogen, a fraction of the ethylene undergoing a tertiary decomposition to acetylene and hydrogen when the

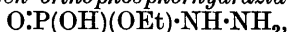


velocity of the gas through the tube is relatively low. Decomposition of the ether to give water and 2 mols. of ethylene or 1 mol. of cyclobutane either does not take place or occurs only to a negligible extent, the primary decomposition being thus that which involves the least deformation of the molecule. R. B.

**Decomposition of Ethers by Metallic Sodium. II. Relative Tenacity of Different Radicals to the Oxygen Atom.** P. SCHORIGIN.—(See i, 1185.)

**Glyceryl Tri-*m*-nitrobenzoate.** F. STATHER (*Ber.*, 1924, 57, [B], 1392—1393).—*Glyceryl tri-m-nitrobenzoate*, m. p. 130° (corr.), is prepared by the action of *m*-nitrobenzoyl chloride on glycerol in the presence of chloroform and quinoline. The substance, m. p. 161°, described under this name by Bauer (this vol., i, 825) is probably *m*-nitrobenzoic anhydride. The interchange of acyl radicals during the acylation of mono- or di-glycerides in the presence of quinoline has not yet been observed. H. W.

**Behaviour of Esters of Metaphosphoric Acid and of Phosphorous Acid towards Hydrazine, Hydroxylamine, and their Derivatives.** W. STRECKER and H. HEUSER (*Ber.*, 1924, 57, [B], 1364—1372).—The action of an excess of hydrazine hydrate causes hydrolysis of metaphosphoric esters. If, however, molar quantities of the reactants are brought together in chloroform solution, *ethyl hydrogen orthophosphorhydrazide*,



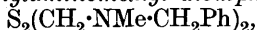
a viscous, multimolecular liquid, is produced. *Ethyl hydrogen orthophosphorphenylhydrazide*, m. p. 192°, and *ethyl hydrogen orthophosphor-p-tolylhydrazide*, m. p. 195°, are similarly produced. *p*-Bromophenylhydrazine forms the corresponding *p-bromophenylhydrazide*, m. p. 187°, with considerably greater difficulty, whereas *p*-nitrophenylhydrazine does not appear to react. Highly purified hydroxylamine and ethyl metaphosphate yield *ethyl hydrogen phosphorhydroxylamide*,  $\text{O}:\text{P}(\text{OH})(\text{OEt})\cdot\text{NH}\cdot\text{OH}$ , a syrupy liquid, but derivatives such as phenylhydroxylamine do not react.

Ammonia does not react with triphenyl or tri-*p*-tolyl phosphite at the atmospheric temperature, whereas hydrolysis takes place under more energetic conditions. Similarly, hydrazine hydrate is inactive in the cold, but when warmed yields a mixture of hydrazine phenoxide or *p*-tolyl oxide and *dihydrazine hydrogen phosphite*,  $\text{P}(\text{OH})_3\cdot 2\text{N}_2\text{H}_4\cdot \text{H}_2\text{O}$ , m. p. 105°. The use of halogenated phosphorous esters facilitates but does not alter the character of this reaction. Thus the monohalogenated ester,  $\text{PCl}(\text{OEt})_2$ , gives ammonium chloride, ammonium phosphite, and phenol with ammonia, whilst with hydrazine hydrate it yields dihydrazine hydrogen phosphite, hydrazine phenoxide, and hydrazine hydrochloride. The dichloride,  $\text{PCl}_2(\text{OEt})$ , gives the same products with greater readiness. Triethyl phosphite is not affected by hydrazine hydrate, possibly on account of its relatively low boiling point, whereas diethyl hydrogen phosphite gives dihydrazine hydrogen phosphite. The presence of a halogen atom attached to phosphorus facilitates the hydrolysis.

The normal esters of orthophosphoric or thiophosphoric acid do not react with hydrazine or ammonia. If, however, a halogen atom is present in place of an organic residue, it suffers replacement with production of the corresponding amide or hydrazide. The following new compounds are thus produced: *p*-Tolylthiophosphordiamide,  $\text{S}\cdot\text{P}(\text{NH}_2)_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{Me}$ , m. p.  $84^\circ$ ; phenylthiophosphordihydrazide,  $\text{S}\cdot\text{P}(\text{NH}\cdot\text{NH}_2)_2\cdot\text{O}\cdot\text{Ph}$ , m. p.  $95^\circ$ ; *p*-tolylthiophosphordihydrazide, m. p.  $106^\circ$ ; phenylorthophosphordihydrazide.

H. W.

**Sulphoxyl Compounds. XIII. Reduction of Aldehydesulphoxylates.** A. BINZ, C. RÁTH, and E. WALTER (*Ber.*, 1924, 57, [B], 1398—1403; cf. A., 1921, i, 30).—The oxidising action of aldehydesulphoxylates is illustrated by the production of the corresponding disulphides from formaldehydesulphoxylate and thiophenol or *o*-thiocresol, and from formaldehydesulphoxylate which has been condensed with *o*-anisidine or methylamine and thiophenol and ethyl mercaptan. Sodium formaldehydesulphoxylate is reduced by hypophosphorous acid or, in a more complex manner, by hydrogen sulphide to *bishydroxymethyl disulphide*,  $\text{OH}\cdot\text{CH}_2\cdot\text{S}\cdot\text{S}\cdot\text{CH}_2\cdot\text{OH}$ , m. p.  $155^\circ$ , the yields being poor. Better results are obtained when the sulphoxylate is previously condensed with a secondary amine; thus, formaldehydesulphoxylate, piperidine, and hypophosphorous acid or hydrogen sulphide give *dipiperidinomethyl disulphide*,  $\text{S}_2(\text{CH}_2\cdot\text{NC}_5\text{H}_{10})_2$ , m. p.  $42^\circ$  (*hydrochloride*, m. p.  $176^\circ$ ). *Diphenylhydroxymethyl disulphide*,  $\text{S}_2(\text{CHPh}\cdot\text{OH})_2$ , m. p.  $65^\circ$  (decomp.), from benzaldehyde sulphoxylate and hypophosphorous acid, is decomposed by cold sodium hydroxide into sodium disulphide and benzaldehyde and by boiling hydrochloric acid into benzaldehyde, hydrogen sulphide, and sulphur. *Dibenzylmethylaminomethyl disulphide*,



a yellow liquid (*hydrochloride*, m. p.  $135^\circ$ ), and *di-2-methylpiperidinomethyl disulphide*, a viscous liquid which gives a crystalline *hydrochloride*, are described.

The constitution,  $\text{HO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{S}\cdot\text{OH}$ , does not adequately explain the reduction of formaldehydesulphoxylate or the apparently dibasic nature of the substance (cf. Forke, *Diss.*, Berlin, 1923). Formaldehydesulphoxylic acid and diformaldehydesulphoxylic acid (Binz, A., 1918, i, 4) more probably have the constitutions I and II, respectively.



H. W.

**Complex Compounds of Lead Acetate [and Propionate] and the Corresponding Salts of the Metals of the Alkaline Earths.** R. WEINLAND and E. BAUER (*Ber.*, 1924, 57, [B], 1508—1514).—In a previous communication (Weinland and Stroh, A., 1922, i, 981), it has been shown that lead forms with acetic acid

residues polynuclear acetato cations. Salts are now described in which the lead atoms are partly replaced by other metallic atoms.

*Lead sodium acetate nitrate*,  $[\text{PbAc}_2\text{Na}]\text{NO}_3\cdot\text{H}_2\text{O}$ , is prepared by the spontaneous evaporation of an aqueous solution of lead acetate and sodium nitrate. The following *salts* are prepared in a similar manner: (1)  $[\text{Pb}_2(\text{CH}_3\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O})_4\text{Na}]\text{ClO}_4$ ; (2)  $[\text{Pb}(\text{OAc})_2\text{Sr}](\text{ClO}_4)(\text{OAc})\cdot 4\text{H}_2\text{O}$ ; (3)  $[\text{Pb}_2(\text{CH}_3\cdot\text{CH}_2\cdot\text{CO}_2)_2(\text{OH})_2\text{Na}](\text{ClO}_4)(\text{C}_3\text{H}_5\text{O}_2)$ , (4)  $\text{Pb}(\text{C}_3\text{H}_5\text{O}_2)_2, \text{Pb}(\text{OH})_2, \text{NaC}_3\text{H}_5\text{O}_2, \text{NaClO}_4$ ; (5)  $[\text{Na}_2(\text{OAc})_2\text{Ba}](\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$ ; (6)  $[\text{Ba}(\text{OAc})_2\text{Mg}](\text{ClO}_4)_2$ . These are all colourless, well-crystallised compounds of which (2) and (6) can be recrystallised unchanged from water.

Calcium and strontium resemble lead in their ability to yield acetato cations, which is established by the isolation of the *salts*:  $[\text{Ca}(\text{OAc})_2\text{Ca}](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ ;  $[\text{Sr}(\text{OAc})_2\text{Sr}](\text{ClO}_4)(\text{OAc})\cdot 4\text{H}_2\text{O}$ ;  $[\text{Sr}(\text{OAc})\text{Sr}](\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ .

Lead propionate has hitherto been described as non-crystalline. The isolation of a crystalline *salt* containing half a molecule of water of crystallisation causes it to be regarded as the propionate of a lead-propionato base,  $[\text{Pb}(\text{C}_3\text{H}_5\text{O}_2)_2\text{Pb}]\text{C}_3\text{H}_5\text{O}_2\cdot\text{H}_2\text{O}$ . This hypothesis is supported by the isolation of the salts:

$[\text{Pb}(\text{C}_3\text{H}_5\text{O}_2)_2\text{Pb}](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$  and  $[\text{Pb}(\text{C}_3\text{H}_5\text{O}_2)_2\text{Pb}](\text{BrO}_3)_2\cdot 4\text{H}_2\text{O}$ . Attempts to obtain similar propionato compounds from the crystalline barium propionate were unsuccessful. H. W.

**Pyrogenic Decomposition, at High Temperatures, of Acetic Anhydride.** (MILLER.) E. PEYTRAL (*Bull. Soc. chim.*, 1924, [iv], 35, 969—974; cf. A., 1922, i, 219).—The sudden decomposition of acetic anhydride when rapidly passed through a platinum tube at high temperatures yields as primary products keten and acetic acid, the decomposition involving the least deformation of the molecule. The keten undergoes secondary decomposition into ethylene and carbon monoxide, whilst the acetic acid by secondary decomposition gives methane and carbon dioxide. Small amounts of acetylene and hydrogen are formed, partly by decomposition of the ethylene, but also, especially as the velocity of flow of the acetic anhydride vapour diminishes, by primary decomposition. Hydrogen is also produced, when the velocity of flow is relatively low, by decomposition of the ethylene, giving free carbon or complex hydrocarbons. R. B.

**Composition of Soja Bean Oil.** E. S. WALLIS and G. H. BURROWS (*J. Amer. Chem. Soc.*, 1924, 46, 1949—1953).—The fatty acids contained in soja bean oil have been determined by the method of Twitchell (cf. A., 1914, ii, 685; 1917, ii, 428) and the results compared with those obtained in a detailed analysis by Jamieson and Baughmann (cf. A., 1923, i, 281). The percentages of the saturated acids were: palmitic 10, (6.8); stearic 2, (4.4); arachidic 1, (0.7); myristic 0, (—); lignoceric, —, (0.1); the figures in brackets being those of the analytical method. The

difference in the distribution between palmitic and stearic acids in the two sets has not been explained. A. C.

**Trichloroacrylic Acid and some of its Derivatives. III. Peroxide of Trichloroacrylic Acid.** J. BÖESEKEN and H. GELISSEN (*Rec. trav. chim.*, 1924, **43**, [v], 266—268).—The peroxide of trichloroacrylic acid,  $(\text{CCl}_2\text{CClCO})_2\text{O}_2$ , m. p.  $49^\circ$ , is prepared by the action of hydrogen peroxide and sodium hydroxide on trichloroacrylyl chloride. It is not hydrolysed by water, is sensitive to shock, is very volatile, and attacks the skin. J. K.

**Preparation of Dehydracetic Acid from Acetoacetic Ester.** F. ARNDT and P. NACHTWEG.—(See i, 1223.)

**Ferric Oxalate and its Application to the Separation of Iron and Calcium.** J. BARLOT (*Bull. Soc. chim.*, 1924, [iv], **35**, 1026—1030).—Ferric oxalate is obtained as an apparently amorphous, greenish-yellow substance,  $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$ , by the slow evaporation of a solution of ferric hydroxide in saturated oxalic acid solution. Its solution in water is more stable than that in oxalic acid, from which ferrous oxalate slowly separates. It forms stable double salts with other oxalates, and it is proposed to separate iron and calcium by taking advantage of the fact that in the presence of ammonium oxalate and acetic acid, the double calcium ferric oxalate is quantitatively decomposed into soluble ferric ammonium oxalate and insoluble calcium oxalate.

S. K. T.

**Action of Light on Solutions of Organic Compounds in Chloropicrin.** A. PIUTTI (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 437—438; from *Chem. Zentr.*, 1924, i, 2514; cf. A., 1921, i, 298).—Chloropicrin acts as an oxidising, chlorinating, or nitrating agent, respectively, according to the compound with which it is exposed to light. With acetic acid, oxalic and chloroacetic acids are formed together with chlorine, hydrochloric acid, and nitrous acid. Similarly, with ethyl succinate, succinic acid; with methyl salicylate, methyl chlorosalicylate, oxalic acid, and ammonium tetroxalate; with toluene, benzoic acid, *o*-nitrotoluene, and oxalic acid, and with naphthalene, benzoic and phthalic acids are produced. G. W. R.

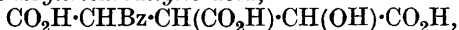
**Configuration of  $\alpha\alpha'$ -Dibromo-dibasic Acids. III. The  $\alpha\alpha'$ -Dibromosuccinic Acids.** H. R. ING and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1924, **125**, 1814—1830).—Methyl and ethyl esters of *dl*-dibromosuccinic acid described by Pictet and by Michael, but not definitely characterised, have now been obtained in a pure state. Bromination of ethyl maleate gave *ethyl dl-dibromosuccinate*, b. p.  $137$ — $138^\circ/11$  mm. *Methyl dl-dibromosuccinate* has m. p.  $43^\circ$ . *Ethyl mesodibromosuccinate*, m. p.  $58^\circ$ , and *methyl mesodibromosuccinate*, m. p.  $65^\circ$ , were obtained by bromination of the corresponding alkyl fumarates.

Condensation of methyl and ethyl *dl*-dibromosuccinates with the sodium derivative of the corresponding malonic esters gave a

yield of 80—90% of the respective *cyclopropane* esters, both of which on hydrolysis yielded *dl-cyclopropane-1 : 2 : 2 : 3-tetracarboxylic acid*, dihydrate, m. p. 100°; anhydrous, m. p. 198—200°. *d-cyclopropane-1 : 2 : 2 : 3-tetracarboxylic acid*, m. p. 195—196° (decomp.),  $[\alpha]_D^{25} +106.5^\circ$  in water, was obtained by resolving the *dl* isomeride by fractional crystallisation of the brucine salt. The brucine salt,  $C_7H_6O_8 \cdot 4C_{23}H_{26}O_4N_2 \cdot 2H_2O$ , has  $[\alpha]_D^{25} -43.01^\circ$ . When heated at 200°, the *d* acid is converted into inactive *trans-cyclopropane-1 : 2 : 3-tricarboxylic acid*, m. p. 220°.

Condensation of methyl *mesodibromosuccinate* with methyl sodiomalonate gives methyl- $\alpha$ -carbomethoxytricarballylate, methyl *cyclopropane-1 : 2 : 2 : 3-tetracarboxylate*, and methyl ethanetetra-carboxylate. By condensation of ethyl *dl*-dibromosuccinate and ethyl sodiocyanoacetate, a 90% yield of *ethyl 2-cyanocyclopropane-1 : 2 : 3-tricarboxylate*, b. p. 200—205°/8 mm., was obtained; this gave on hydrolysis *dl-cyclopropanetetra-carboxylic acid*. The main product from ethyl *mesodibromosuccinic acid* and ethyl sodio-cyanoacetate was methyl  $\alpha$ -cyanotricarballylate.

Ethyl *dl*-dibromosuccinate reacts in the cold with ethyl sodio-benzoylacetate to give ethyl 5-phenyl-2 : 3-dihydrofuran-2 : 3 : 4-tricarboxylate, b. p. 227—230°/12 mm., which on hydrolysis yields  $\alpha$ -hydroxy- $\gamma$ -benzoyltricarballic acid,



m. p. 142—143° (decomp.); this acid, when heated above its melting point, is converted into 5-phenyl-2 : 3-dihydrofuran-2 : 3-dicarboxylic acid, m. p. 182—183°, which by repeated crystallisation from boiling water is converted into  $\alpha$ -phenacyl- $\beta$ -hydroxysuccinic acid (phenacylmalic acid), m. p. 175—176°; the latter acid is reconverted into phenyldihydrofurandicarboxylic acid by repeated crystallisation from a mixture of methyl alcohol and chloroform.

Ethyl *meso*-dibromosuccinate and ethyl sodio-benzoylacetate condense to form as main products ethyl dibenzoylsuccinate and *ethyl  $\alpha$ -benzoyltricarballylate*, b. p. 220—225°/12 mm.; this when hydrolysed yields phenacylsuccinic acid, m. p. 162—163°. The oxime of phenacylsuccinic acid has m. p. 147—148°; the *phenyl-hydrazone*, m. p. 164—165°.

Condensation of ethyl *dl*-dibromosuccinate with ethyl sodio-acetoacetate gives a 95% yield of *ethyl 5-methyl-2 : 3-dihydrofuran-2 : 3 : 4-tricarboxylate*, b. p. 190—195°/18 mm., which yields on hydrolysis acetonilmalic acid, m. p. 150°, and, on treatment with ammonia, an amide, m. p. 195°. Ethyl diacetosuccinate and ethyl  $\alpha$ -acetyltricarballylate, m. p. 110°, result from the condensation of ethyl *meso*-dibromosuccinate and ethyl sodioacetoacetate.

C. J. S.

**Hydrated Active Tartaric Acid.** M. AMADORI (*Atti R. Accad. Lincei*, 1924, [v], 33, i, 507—510).—Crystallisation of aqueous tartaric acid solutions at temperatures below about 5° yields a monohydrated modification, blunt, rhombic prisms,  $n_{1.52}$ ,  $a : b : c = 0.4706 : 1 : 0.5294$ . The crystals are stable at temperatures below 5—10°, but at higher temperatures, after turning opaque,

they undergo gradual transformation into transparent crystals of ordinary tartaric acid.

T. H. P.

**Rotatory Dispersion of Derivatives of Tartaric Acid. I. Methylene Derivatives.** P. C. AUSTIN and V. A. CARPENTER (*J. Chem. Soc.*, 1924, 25, 1939—1946).—The results obtained for the specific rotation of methylene tartaric acid in aqueous solution at different concentrations and for various wave-lengths can be expressed in one term of Drude's equation. The hydrated and anhydrous acids have m. p. 140.5° and 165°, respectively, and the latter has  $[\alpha]_D^{20} - 81.3^\circ$ .

The rotatory dispersion of dimethylene tartrate can also be expressed in one term of Drude's equation, and the specific rotation appears to be independent of the concentration and the solvent. Dimethylene tartrate has m. p. 119°,  $[\alpha]_D^{20} + 107.9^\circ$  in ethyl acetate, and on hydrolysis yields a dibasic acid.

C. J. S.

**Glutaconic Acids. XVI. Three-carbon Tautomerism in the cycloPropane Series. III. Refractometric Evidence.** F. R. GOSS, C. K. INGOLD, and J. F. THORPE (*J. Chem. Soc.*, 1924, 125, 1927—1930).—The authors criticise the conclusions drawn by Auwers and Ottens (this vol., i, 513, 516) from their observations on the exaltations of refractivity exhibited by the esters of the isomeric glutaconic acids, disagree with the view that the isomerism is of geometric character, and consider that the esters belong to the "cis" rather than to the "trans" type.

Observations of the refractivities of isomeric forms of ethyl 2-methyl- $\Delta^1$ -cyclopropenedicarboxylate, in which ring formation excludes geometric isomerism, reveal marked exaltations of refractivity, a noteworthy feature being the smaller refractivity of the normal ester.

C. J. S.

**Behaviour of Formaldehyde.** A. FERRINI (*Boll. Chim. Farm.*, 1924, 63, 467—469).—Determination of the ammoniacal nitrogen in hexamethylenetetramine by simple distillation from a solution rendered alkaline by sodium hydroxide or magnesium, calcium, or barium oxide is not possible, only small proportions of ammonia being liberated in this way. Varying amounts of ammonia, always considerably less than the total amount present, are obtained when a mixture of ammonium chloride and the corresponding quantity of formaldehyde is similarly distilled from an alkaline solution, and still lower results are furnished when the ammonium chloride is replaced by ammonia. Addition of metals having a reducing action does not influence the yield of ammonia in any of the above cases.

T. H. P.

**Reaction between  $\alpha$ -Trioxymethylene and Sulphuryl Chloride.** K. FUCHS and E. KATSCHER (*Ber.*, 1924, 57, [B], 1256—1268).—The  $\alpha$ -modification of chloroacetic acid, m. p. 56°, is obtained in good yield by heating  $\alpha$ -trioxymethylene with sulphuryl chloride and a little zinc chloride at 150—170°. Methyl formate appears to be the primary product of the change, since it is formed in good yield by the action of zinc chloride on  $\alpha$ -trioxymethylene.

methylene at 125°; it is converted by sulphuryl chloride into chloroacetic acid. Higher alkyl formates do not react similarly; thus ethyl formate yields chloral hydrate (cf. Dunlop, T., 1914, 105, 1155; Hammick and Boeree, T., 1923, 123, 2881). H. W.

**Relationship of Carboligatic Synthesis to Carboxylatic Degradation (Application of Acetaldehyde as Acceptor).** C. NEUBERG and O. ROSENTHAL (*Ber.*, 1924, 57, [B], 1436—1441).—The fermentation of pyruvic acid by zymase solution in the presence of dipotassium hydrogen phosphate leads to the formation of acetaldehyde which is partly transformed into acetyl-methylcarbinol, CHMeAc·OH. If, under otherwise identical conditions, acetaldehyde is initially added to the solution, the yield of acetylmethylcarbinol is at least doubled, the generated acetaldehyde being “accepted” by the added reagent and utilised in synthetic directions. H. W.

**Polymerisation of Halogenated Derivatives of Ethylene Oxide and of Halogenated Aldehydes.** B. HELFERICH and E. BESLER (*Ber.*, 1924, 57, [B], 1276—1280).—The tendency of aldehydes towards trimeric polymerisation is considerably increased by the entry of halogen into the molecule; this does not appear to be the case with derivatives of ethylene oxide.

$\alpha\beta$ -Dichlorobutaldehyde, b. p. 48—49°/13 mm. (*semicarbazone*, m. p. 96—97°), is converted by an ethereal solution of magnesium ethyl bromide into  $\beta\gamma$ -dichloro-*n*-hexan- $\delta$ -ol, b. p. 88—93°/12 mm.,  $d_4^{19}$  1.1685,  $n_D^{19}$  1.4709, which is transformed by concentrated potassium hydroxide solution into  $\beta$ -chloro- $\gamma\delta$ -oxido-*n*-hexane, CHMeCl·CH·CH<sub>2</sub>Et, b. p. 49—50°/13 mm.,  $d_4^{17}$  1.0083,  $n_D^{17}$  1.4310.

Similarly, dichlorobutaldehyde and magnesium phenyl bromide yield  $\beta\gamma$ -dichloro- $\alpha$ -phenylbutan- $\alpha$ -ol, b. p. 162—168°/14 mm.,  $d_4^{15}$  1.2355,  $n_D^{15}$  1.5500, which is transformed into  $\gamma$ -chloro- $\alpha\beta$ -oxido- $\alpha$ -phenylbutane, b. p. 129—131°/15 mm.,  $d_4^{17}$  1.1352,  $n_D^{17}$  1.5325.  $\beta$ -Chloro-*n*-hexan- $\delta$ -ol, b. p. 78—79°/13 mm.,  $d_4^{19}$  1.0012,  $n_D^{19}$  1.4433, prepared from  $\beta$ -chlorobutaldehyde and magnesium ethyl bromide, is unchanged by aqueous potassium hydroxide solution (50%) at 40—50°.  $\beta\beta\gamma$ -Trichloro- $\alpha$ -phenylbutan- $\alpha$ -ol, b. p. 172—173°/13 mm., m. p. 53°, from butylchloral and magnesium phenyl bromide, is decomposed when treated similarly into benzaldehyde and resin.

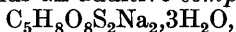
Halogenated butaldehydes (1 mol.) condense with acetaldehyde (2 mols.) in the presence of hydrogen chloride at 0° to yield hydroxyl-free products which are regarded as mixed paraldehydes. The following individuals are described: *diacet- $\beta$ -chlorobutparaldehyde*,  $O \begin{smallmatrix} \diagup \\ \text{CHMe}\cdot O \\ \diagdown \end{smallmatrix} \text{CH}\cdot\text{CH}_2\cdot\text{CHMeCl}$ , b. p. 83—85°/13 mm.,  $d_4^{19}$  1.0937,  $n_D^{19}$  1.4373; *diacet- $\alpha\beta$ -dichlorobutparaldehyde*, b. p. 110—112°/14 mm.,  $d_4^{17.5}$  1.2227,  $n_D^{17.5}$  1.4604; *diacet- $\alpha\alpha\beta$ -trichlorobutparaldehyde*, b. p. 118°/13 mm.,  $d_4^{18}$  1.3188,  $n_D^{18}$  1.4739; *diacetchloralparaldehyde*, b. p. 97°/13 mm.,  $d_4^{18}$  1.3915,  $n_D^{18}$  1.4708.

Monomeric  $\beta$ -chlorobutaldehyde, b. p. 28—33°/13 mm., prepared by the addition of the calculated quantity of hydrogen chloride

to crotonaldehyde in ethereal solution, passes rapidly into the trimeric form.

H. W.

**Degradation of Pyridine into Glutacondialdehyde and Re-conversion of the Latter into Pyridine.** I. P. BAUMGARTEN (*Ber.*, 1924, 57, [B], 1622—1627).—Pyridine is converted by ethyl chlorosulphonate into an additive compound, which is transformed by aqueous sodium hydroxide into sodium sulphamate and the *sodium* salt of the enolic form of glutacondialdehyde,  $\text{ONa}\cdot\text{CH}:\text{CH}:\text{CH}\cdot\text{CHO}$ . The isolation of the salt in two forms, brownish-red crystals and red leaflets, indicates the existence of the aldehyde also in the cyclic form,  $\text{CH}\langle\begin{smallmatrix}\text{CH}-\text{O} \\ \text{CH}:\text{CH}\end{smallmatrix}\rangle\text{CH}\cdot\text{OH}$ . The *barium* salt is described.  $\delta$ -Hydroxy- $\Delta^{\gamma}$ -butadienealdehyde can be preserved unchanged for a short time in ethereal solution, but is too unstable to permit its isolation in substance. The *acetyl* derivative, m. p.  $75^{\circ}$ , and the *benzoyl* compound, m. p.  $116-118^{\circ}$ , are described. The latter substance is converted by phenylhydrazine into a *compound*,  $\text{C}_{18}\text{H}_{14}\text{ON}_2$ , m. p.  $149-150^{\circ}$ , which has not been identified. As dialdehyde,  $\text{CHO}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{CHO}$ , glutacondialdehyde yields an additive *compound*,



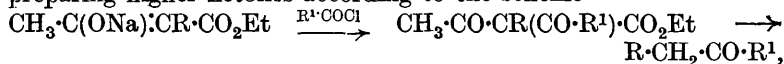
with sodium hydrogen sulphite (2 mols.). It reacts instantly with phenylhydrazine, but the product could not be crystallised; the *p*-bromophenylhydrazine,  $\text{C}_{17}\text{H}_{16}\text{N}_4\text{Br}_2$ , is an amorphous, reddish-brown powder. The sodium salt of the hydroxyaldehyde is converted by boiling aqueous ammonium acetate into pyridine.

H. W.

**Purification of Methyl Ethyl Ketone by Sodium Iodide.** H. L. LOCHTE (*Ind. Eng. Chem.*, 1924, 16, 956).—Methyl ethyl ketone, like acetone (cf. Shipsey and Werner, T., (1898) 103, 1255), combines with sodium iodide, forming the compound  $\text{C}_4\text{H}_8\text{O}\cdot\text{NaI}$ . This separates in the crystalline state only when the reagents are slightly moist. It has m. p.  $73-74^{\circ}$  (decomp., yielding the pure ketone). Commercial samples are best purified by this means.

W. A. S.

**Preparation of Higher Ketones.** B. HELFERICH and L. KEINER (*Ber.*, 1924, 57, [B], 1616—1620).—The possibility of preparing higher ketones according to the scheme



has been examined. The action of acyl chlorides on the sodium salts leads invariably to the production of a mixture of *O*- and *C*-acyl derivatives, the former of which yields the methyl ketone,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\text{R}$ , which is obtained also from the alkyl acetoacetate employed. A subsequent separation of the two ketones is therefore essential.

The following acylalkylacetoacetic esters are prepared by dissolving powdered sodium in a solution of the requisite alkylacetoacetic ester in ether and gradually adding the acyl chloride (pre-



pared by means of thionyl chloride) to the ice-cold product: *ethyl n-valerylallylacetate*, b. p.  $149^{\circ}/14$  mm.,  $d_4^{20}$  1.0028,  $n_D^{17}$  1.4545; *ethyl isovalerylallylacetate*, b. p.  $143\text{--}144^{\circ}/14$  mm.,  $d_4^{17.5}$  0.9998,  $n_D^{16.9}$  1.4546; *ethyl isovalerylbenzylacetate*, b. p.  $195\text{--}196^{\circ}/14$  mm.,  $d_4^{16.3}$  1.0524,  $n_D^{12}$  1.5014; *ethyl  $\Delta\gamma$ -pentenoyl- $\alpha$ -allylacetate*,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}(\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2)[\text{CO}\cdot\text{CH}(\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2)_2]\text{CO}_2\text{Et}$ , b. p.  $169\text{--}170^{\circ}/14$  mm.,  $d_4^{16.6}$  1.0000,  $n_D^{16}$  1.4739; *ethyl  $\alpha'$ -acetoxypropionylallylacetate*, b. p.  $167\text{--}168^{\circ}/14$  mm.,  $d_4^{21}$  1.0950,  $n_D^{19.5}$  1.4590; *ethyl p-acetoxybenzoylallylacetate*, b. p.  $235^{\circ}/14$  mm.; *ethyl o-acetoxybenzoylallylacetate*, b. p.  $216\text{--}218^{\circ}/14$  mm.; *ethyl o-anisoylallylacetate*, b. p.  $219^{\circ}/18$  mm.,  $d_4^{19.0}$  1.1376,  $n_D^{16.9}$  1.5300. *Ethyl  $\alpha'$ -benzoxypropionylallylacetate*, *ethyl trimethylgalloylallylacetate*, and *ethyl triacetylgalloylallylacetate* could not be distilled without decomposition. For the preparation of *ethyl  $\beta$ -chloropropionylallylacetate*, b. p.  $158^{\circ}/14$  mm.,  $d_4^{22}$  1.1282,  $n_D^{20}$  1.4710, it is necessary to add the alkylsodioacetate to a solution of  $\beta$ -chloropropionyl chloride in ether.

$\alpha$ -Benzoxypropionyl chloride, prepared from thionyl chloride and the corresponding acid, has m. p.  $23\text{--}24^{\circ}$  after softening at  $21^{\circ}$ .

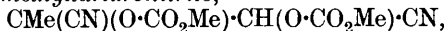
The acylalkylacetates are hydrolysed by potassium hydroxide to the following ketones: *n-butyl  $\Delta\gamma$ -butenyl ketone*, b. p.  $72^{\circ}/14$  mm.,  $d_4^{17}$  0.8435,  $n_D^{17}$  1.4320 (*semicarbazone*, m. p.  $88\text{--}89^{\circ}$ ); *isobutyl  $\Delta\gamma$ -butenyl ketone*, b. p.  $62\text{--}63^{\circ}/14$  mm.,  $d_4^{12}$  0.8362,  $n_D^{12.5}$  1.4288 (*semicarbazone*, m. p.  $101\text{--}102^{\circ}$  after previous softening); *p-hydroxyphenyl  $\Delta\gamma$ -butenyl ketone*, b. p.  $210\text{--}212^{\circ}/16$  mm., m. p.  $61.5^{\circ}$  after previous softening; *o-methoxyphenyl  $\Delta\gamma$ -butenyl ketone*, b. p.  $152^{\circ}/16$  mm.,  $d_4^{23}$  1.0466,  $n_D^{21}$  1.5244; *trimethoxyphenyl  $\Delta\gamma$ -butenyl ketone*, b. p.  $195\text{--}196^{\circ}/14$  mm., m. p.  $54\text{--}55^{\circ}$  (*semicarbazone*, m. p.  $151^{\circ}$  after previous softening); *trihydroxyphenyl  $\Delta\gamma$ -butenyl ketone*, m. p.  $130^{\circ}$  after softening at  $120^{\circ}$  or  $(+\text{H}_2\text{O})$  m. p.  $84\text{--}85^{\circ}$  (*semicarbazone*, m. p.  $174\text{--}175^{\circ}$ ). The hydrolysis of *ethyl isovalerylbenzylacetate*, *ethyl  $\Delta\gamma$ -pentenoylallylacetate*, *ethyl  $\alpha'$ -acetoxy(benzoxyp)propionylallylacetates*, and of *ethyl  $\beta'$ -chloropropionylallylacetates* did not lead to the desired ketone.

H. W.

**Dihydroxyacetone (II) and a New Method of Preparing Methylglyoxal.** H. O. L. FISCHER and C. TAUBE (*Ber.*, 1924, 57, [B], 1502—1507).—In continuation of previous work (Fischer and Mildbrand, this vol., i, 613) monomeric dihydroxyacetone has

been converted into its *methylcycloacetal*,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{O} \end{array} \text{C}(\text{OMe})\cdot\text{CH}_2\cdot\text{OH}$ , m. p.  $90\text{--}91^{\circ}$ . The *acetate* ( $\text{C}_7\text{H}_{12}\text{O}_4$ )<sub>2</sub>, m. p.  $109\text{--}110^{\circ}$ , and the *toluene-p-sulphonate*,  $\text{C}_{12}\text{H}_{16}\text{O}_5\text{S}$ , m. p.  $117\text{--}118^{\circ}$  (decomp.), of the corresponding *ethylcycloacetal* are described. *Dihydroxyacetonebenzoylhydrazone*,  $\text{CH}_2(\text{OH})\cdot\text{C}(\text{N}\cdot\text{NHBz})\cdot\text{CH}_2\cdot\text{OH}$ , m. p.  $133^{\circ}$ , *dihydroxyacetone-p-nitrophenylhydrazone*, m. p.  $156^{\circ}$ , and *diacetoxyacetone-p-nitrophenylhydrazone*, m. p.  $138^{\circ}$ , have been prepared. Dihydroxyacetone is fermented by certain varieties of bottom yeast, thus giving the first example of a triose which is fermentable without previous spontaneous conversion into a hexose.

Dihydroxyacetone is converted by distillation with phosphoric oxide into pyruvaldehyde,  $\text{CH}_3\cdot\text{CO}\cdot\text{CHO}$ , which is unimolecular in the vaporous state but termolecular in the freshly-prepared, dark green liquid form. When preserved during a few hours, the liquid aldehyde becomes converted into a brittle, resinous mass. It yields a *tetraethylacetal*,  $\text{CMe}(\text{OEt})_2\cdot\text{CH}(\text{OEt})_2$ , b. p.  $192^\circ/760$  mm., and a *dihydrazone*, m. p.  $93-94^\circ$ . It is converted by methyl chloroformate and potassium cyanide in aqueous solution into *dicarbomethoxymethyltartaronitrile*,



b. p.  $100^\circ/0.6$  mm., which is hydrolysed by saturated hydrochloric acid at  $-5^\circ$  to the corresponding *amide*, m. p.  $192^\circ$ . H. W.

**Saturation Relations in Mixtures of Sucrose, Dextrose, and Lævulose.** R. F. JACKSON and C. G. SILSBEE (*U.S. Bur. Standards, Tech. Paper* 259, 277—304).—Invert-sugar diminishes the solubility of sucrose in water, and the solubility of dextrose is decreased by the presence of sucrose or lævulose, although the total sugar content is increased. A mixture of sucrose and invert-sugar saturated with respect to both sucrose and dextrose at  $30^\circ$  contains 33.57% of sucrose and 45.44% of invert-sugar, whilst at  $50^\circ$  the proportions are 27.7% and 58%, such solutions possessing the maximum solubilities that can be attained by partly inverted sucrose solutions. Honey is a supersaturated solution of dextrose in presence of lævulose, and its degree of supersaturation can be calculated in terms of the percentages of dextrose, water, and lævulose. C. J. S.

**Acetone [*iso*Propylidene] Derivatives of Sugars and their Derivatives. II. Acetone Compounds of Lævulose.** H. OHLE and I. KOLLER (*Ber.*, 1924, 57, [B], 1566—1576).—Lævulose is converted by acetone in the presence of anhydrous copper sulphate into  $\alpha$ -diisopropylidene-fructose,  $\beta\gamma$ -isopropylidene-fructose, and apparently,  $\alpha$ -isopropylidene-fructose. If sulphuric acid is employed in place of copper sulphate,  $\alpha$ -diisopropylidene-fructose, m. p.  $118-119^\circ$ , is mainly produced with small concentrations of acid; with increasing concentration of the latter, the production of  $\beta$ -diisopropylidene-fructose becomes more pronounced and this substance becomes the main product when the proportion of acid is 4 c.c. per 100 c.c. of acetone. The preparation of  $\beta$ -diisopropylidene-fructose is effected more economically when lævulose is replaced by sucrose under otherwise identical conditions, whereby a mixture of  $\beta$ -diisopropylidene-fructose and diisopropylidene-glucose is formed which is separated into its components by fractional precipitation of its aqueous solution with 10*N*-sodium hydroxide solution.  $\beta$ -Diisopropylidene-fructose is readily obtained from inulin by means of sulphuric acid and acetone, whereas these reagents do not affect cellulose, starch, maltose, or lactose. It is similarly produced from  $\alpha$ -diisopropylidene-fructose. It has m. p.  $97^\circ$ , b. p.  $110-115^\circ/0.175-0.2$  mm.,  $[\alpha]_D^{25} -32.9^\circ$  in water ( $c=3.161$ )  $[\alpha]_D^{25} -28.98^\circ$  in benzene,  $[\alpha]_D^{25} -36.69^\circ$  in alcohol. It is very much more resistant than the corresponding  $\alpha$ -derivative to the hydro-

lysing action of acids (cf. Irvine and Garrett, T., 1910, **97**, 1277). Mainly for this reason, the authors reject the hypothesis of Irvine and his co-workers (*loc. cit.* and T., 1922, **121**, 2146) that the isomeric diisopropylidene-fructoses are related to one another in the relation of  $\alpha$ - to  $\beta$ -glucoside and consider the second isopropylidene residue of the  $\beta$ -derivative to be united to the oxygen atoms, 4 and 5; the position of the oxygen bridge is uncertain. *Methyl- $\beta$ -diisopropylidene-fructose* has b. p.  $90^{\circ}/0.12$  mm.,  $n_D^{25}$  1.4512,  $[\alpha]_D^{25} -35.24^{\circ}$  in alcohol. The following acyl derivatives of  $\beta$ -diisopropylidene-fructose are prepared in the presence of a large excess of pyridine: *acetate*, m. p.  $66^{\circ}$ ,  $[\alpha]_D^{25} -36.02^{\circ}$  in alcoholic solution; *benzoate*, long, thin prisms or coarse, poly-sided crystals, m. p.  $81^{\circ}$ ,  $[\alpha]_D^{25} -21.8^{\circ}$  in alcohol; *p-toluenesulphonate*, m. p.  $83^{\circ}$ ,  $[\alpha]_D^{19} -27.1^{\circ}$  in alcohol.

Since the same product is obtained from dextrose by the action of sulphuric acid in amount varying from 1 to 4 c.c. and acetone (100 c.c.) and its nature is independent of the use of  $\alpha$ - or  $\beta$ -glucose as initial material, it appears that diisopropylidene-glucose is a homogeneous product (contrast Irvine and Patterson, T., 1922, **121**, 2146). This view is confirmed by the observation that diisopropylidene-glucose under the action of sulphuric acid and acetone is, in part, unchanged and in part transformed into isopropylidene-glucose without any indication of the production of an isomeride.

H. W.

**Reversion Synthesis. I. Action of Yeast Maltase.** H. PRINGSHEIM and J. LEIBOWITZ (*Ber.*, 1924, **57**, [B], 1576—1579).—A solution of dextrose (40%) is subjected to the action of yeast maltase at  $37^{\circ}$  during four weeks, the optimal hydrogen-ion concentration,  $p_H = 6.4$ , being used. After fermentation of the residual dextrose by *Saccharomyces Marxianus*, maltose is isolated in the crystalline condition from the portion of the residue soluble in alcohol, whereas slightly impure revertose is obtained from the portion insoluble in alcohol (cf. Croft Hill, T., 1898, **73**, 634; 1903, **83**, 578). The quantity of revertose is much smaller than that of maltose, whereas the reverse is the case in Croft Hill's experiments.

H. W.

**Products of the Enzymic Fission of Starch.** K. SJÖBERG (*Ber.*, 1924, **57**, [B], 1251—1256).—The action of undialysed malt amylase solution on amylose followed by precipitation of the product with alcohol (80%) leads to the isolation of a dihexosan,  $[\alpha]_{H_2O}^{18}$  yellow  $+154.5$  to  $155.7^{\circ}$  in water, probably identical with the product described by Pringsheim and Wolfsohn (this vol., i, 714), which readily yields *dihexosan hexa-acetate*, m. p.  $150$ — $165^{\circ}$ ,  $[\alpha]_{H_2O}^{18}$  yellow  $+124.6^{\circ}$  in acetic anhydride,  $[\alpha]_{H_2O}^{18}$  yellow  $+123.5^{\circ}$  in pyridine, but is only converted by methyl iodide and silver oxide into *tetramethyldihexosan*,  $[\alpha]_{H_2O}^{18}$  yellow  $+144.9^{\circ}$ , from which  $\beta\gamma$ -dimethylglucose is obtained on hydrolysis. Amylopectin, when similarly treated, yields a trihexosan,  $[\alpha]_{H_2O}^{18}$  yellow  $+162.9$  to  $164.0^{\circ}$  in water, probably identical with the compound prepared by Pietet and Jahn (A., 1922, i 987) by heating potato starch in glycerol

at 200—210°; the corresponding nona-acetate has m. p. 156—165°,  $[\alpha]_{\text{H}_2\text{O}}^{18}$  yellow +131.4° in acetic anhydride,  $[\alpha]_{\text{H}_2\text{O}}^{18}$  yellow +132.9° in pyridine. H. W.

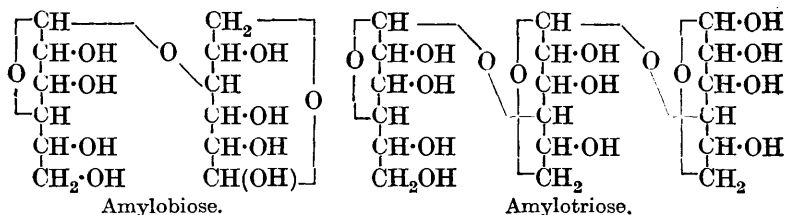
**Starch. XI. Halogen Compounds of the Polyamyloses.** H. PRINGSHEIM and A. STEINGROEVER (*Ber.*, 1924, 57, [B], 1579—1581).—Re-examination of the additive compounds of bromine with the polyamyloses (cf. Pringsheim and Eissler, A., 1913, i, 1156; 1915, i, 382) shows them to contain combined in addition to free bromine, so that in this respect they resemble the starch iodides (this vol., i, 618, 837). It does not, however, appear possible to establish a relationship between free and total halogen in the polyamyloses or to detect in their ash an amount of base corresponding with the amount of combined halogen. Bromo- $\alpha$ -hexa-amylose has approximately the composition  $(\text{C}_6\text{H}_{10}\text{O}_5)_6\text{Br}_2$ . Tri-amylose combines with about 2% more bromine than does hexa-amylose. H. W.

**Starch. XII. Constitution of Starch, Glycogen, and Lichen Starch.** H. PRINGSHEIM [with A. BEISER, K. WOLFSOHN, L. LEIBOWITZ, and W. KUSENACK] (*Ber.*, 1924, 57, [B], 1581—1598).—Further evidence of the difference in constitution of the content- and integument-substances of the starch granule (cf. this vol., i, 714) is afforded by the observation that the former is converted by cold, concentrated hydrochloric acid into *amylobiose*,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ,  $[\alpha]_{\text{D}}^{20}$  +110.9° in aqueous solution, whereas the latter yields *amylotriose*,  $\text{C}_{18}\text{H}_{32}\text{O}_{16}$ ,  $[\alpha]_{\text{D}}^{20}$  +124.5° in water (*osazone*, decomp. 142—145°). Under the influence of amylases, amylose is quantitatively converted into maltose, whereas reaction ceases when 65% of amylopectin has been transformed into this sugar; the unattacked residue is identified as trihexosan which, since it can be further fermented with undialysed malt extract, appears to be, not an essential component of the amylopectin molecule, but an accidental residue. The two components occur separately in nature, since amylose is shown to be identical with *isolichenin* (Pringsheim and Kusenack, this vol., i, 1144) obtained from Iceland moss, which is fermented quantitatively to maltose by fresh malt extract, transformed when heated in glycerol at 185—190° into dihexosan, and hydrolysed by cold, concentrated hydrochloric acid to amylobiose. Amylopectin is identified with glycogen, which is transformed by cold, concentrated hydrochloric acid into amylotriose. The identity of the disaccharide obtained from  $\alpha$ -tetra- and  $\beta$ -hexa-amylose and hydrochloric acid (Pringsheim and Leibowitz, this vol., i, 714) with amylobiose is also established.

The two-enzyme theory of the amylases (Pringsheim, "Die Polysaccharide," 1923, p. 141) renders account of the liquefaction, caused by fermentative fission of electrolyte, and of the saccharification which can be distinguished by the poisoning of malt amylase. A third type of action, consisting in the depolymerisation of the starch molecule to the non-reducing hexosans, appears to take place intermediately. Since the action consists in the rupture of the amylobiose linking, the enzyme complex is termed amylobiase.

Amylobiose, amylotriose, and di- and tri-hexosans are converted quantitatively by malt amylase into maltose; the experimental work is complicated by the unexpected observation that maltose in 1% solution at 37° is slowly converted into dextrose at the acidity ( $p_H$  4.5) which is optimal for malt amylase. They are not attacked by the  $\alpha$ -glucosidic maltase or the  $\beta$ -glucosidic enzyme of emulsin. The surprising fermentative production of a biose from a different biose or a triose, which has nothing in common with the reversible, synthetic action of enzymes, is most readily explained by the hypothesis that a glucose residue (1), probably as a consequence of the nature of its oxygen bridge, is eliminated as a radical which unites with another similar group to yield maltose.

The quantitative formation of maltose from amylobiose renders the formula proposed previously (Pringsheim and Leibowitz, *loc. cit.*) untenable. The following constitutions are proposed for amylobiose and amylotriose:



It is suggested that the formaldehyde formed during the assimilation of carbon dioxide by plants passes immediately into the author's radical, from which the content- and integument-substances of the starch granule are produced directly. H. W.

**Carbonic Esters of Cellulose.** E. HEUSER and F. SCHNEIDER (*Ber.*, 1924, 57, [B], 1389—1392).—The action of an excess of methyl chloroformate on a solution of hydrocellulose in cold aqueous sodium hydroxide (8%) gives *esters* which approximate very closely to the formula  $C_6H_8O_3(O\cdot CO_2Me)_2$ . They form a white, amorphous, granular material, soluble in pyridine, chloroform, and acetic acid. They are readily hydrolysed. Analysis of them is effected by determining carbon dioxide and methoxyl content. H. W.

**Mannan Content of Wood-cellulose and its Analytical Determination.** E. HEUSER and W. DAMMEL (*Cellulosechem.*, 1924, 5, 45—53).—The mannan in the cellulose from coniferous woods is determined by Schorger's method (*J. Ind. Eng. Chem.*, 1917, 9, 748) after hydrolysis with hydrochloric acid by precipitation in the form of mannose bromophenylhydrazone. Mannan is extracted by treating the pulp with 17% aqueous sodium hydroxide, but the exhaustion is not always complete even after two or three treatments. It is determined after hydrolysis of the extract, but Schorger's method by direct hydrolysis of the pulp is to be preferred.

On acidification of the alkaline extract and precipitation with alcohol, a portion of the mannan is found in the precipitated hemi-cellulose, but a further portion remains in the filtrate. The pentosans behave in a similar manner, being distributed in unequal proportions in the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cellulose fractions. There is no support for the suggestion that the mannose forms an integral component of the wood cellulose molecule. The statement of Lenze, Pleus, and Müller (*J. pr. Chem.*, 1922, **101**, 213) that when the  $\beta$ -cellulose from wood pulp is boiled with 4% nitric acid, the hemi-celluloses are completely hydrolysed, leaving a residue of oxycellulose, is not accepted as the basis of a valid method for the determination of oxycellulose in wood pulp. In the first place, the oxycellulose is not quantitatively present in the  $\beta$ -cellulose fraction, and, secondly, the hydrolysis is not quantitatively selective. The phenylhydrazone indicated by those authors as that of methylfurfuraldehyde is proved to be that of hydroxymethylfurfuraldehyde derived from dextrose.

J. F. B.

**Action of Liquid Ammonia and Sodamide on Halogen Derivatives of Ethane. Preparation of Pure Monoethylamine.** PICON (*Bull. Soc. chim.*, 1924, [iv], **35**, 979—981).—Liquid ammonia does not appreciably react with ethyl chloride even at the ordinary temperature. With ethyl bromide or iodide, reaction takes place at  $-40^\circ$ , more rapidly at the ordinary temperature, yielding a mixture of the primary and secondary amine in approximately equal amounts. The reaction between sodamide and potassium ethyl sulphate (Titherley, T., 1901, **79**, 391) gives very poor yields of ethylamine, owing to the large quantity of ethylene and ammonia produced. In the presence of liquid ammonia, at the ordinary temperature, sodamide yields a mixture of primary, secondary, and tertiary amine with ethyl bromide or iodide, some ethylene being also formed, but with ethyl chloride pure ethylamine is obtained. The yield amounts to only 30% of the theoretical, owing to the formation of a considerable quantity of ethylene.

R. B.

**Mechanism of Oxidation Processes. VIII. Scission by Oxidation of Amino-acids.** H. WIELAND and F. BERGEL (*Annalen*, 1924, **439**, 196—210; cf. this vol., i, 606).—Glycine, alanine, and phenylalanine are oxidised by gaseous oxygen in presence of active charcoal at  $38^\circ$  to carbon dioxide, ammonia (in equimolecular proportions), an aldehyde with one carbon atom less than the original acid, and a little of the corresponding acid. Aspartic acid gives 2 mols. of carbon dioxide to 1 mol. of ammonia.  $\alpha$ -Iminopropionic acid gives carbon dioxide, ammonia, and acetaldehyde;  $\alpha$ -aminoisobutyric acid is unaffected. The free oxygen may be replaced by alloxan, *m*-dinitrobenzene, dithioglycollic acid, or *p*-benzoquinone. Succinic acid is dehydrogenated by dithioglycollic acid in presence of freshly-minced liver. These experimental results provide new material for an exhaustive discussion of the mechanism involved in the disruption of  $\alpha$ -amino-acids.

W. A. S.

**Steric Series. IV. Configuration of Alanine.** K. FREUDENBERG and F. RHINO (*Ber.*, 1924, 57, [B], 1547—1557; cf. A., 1923, i, 215).—Basing the work on the hypothesis that analogous compounds of like configuration suffer corresponding changes in optical rotation under similar conditions (cf. Clough, T., 1918, 113, 526), an examination of lactic acid and alanine has been made. To obtain constants free from external influences it is necessary to avoid the presence of free hydroxy, carboxy, or amino groups and to determine the rotations of the liquid or molten substances. Where this is impossible, the rotation is obtained by extrapolation from a series of solutions of different and ultimately very high concentration. In cases of doubt, several solvents are employed, the choice falling on those in which the rotation of the dissolved substance is least dependent on the concentration. The elimination of the use of a solvent is the most important feature of the whole problem, since variations in rotation due to solvent are of very much greater magnitude than those due to temperature. The abnormalities due to rotatory dispersion also become less in evidence. The measurements are effected for light of four different wavelengths. Comparison of the different compounds with one another is based on the values of  $K_M$  deduced from the equation

$$(\lambda_u^2 - \lambda_0^2) \cdot [M]_u = K_M,$$

where  $M$  is the molecular rotation (cf. Rupe and Ackermann, A., 1920, ii, 652). It is thus established that *l*-lactic acid has the same configuration as natural *d*-alanine. From the point of view of the Walden inversion, the action of nitrous acid on alanine, serine, and aspartic acid occurs, therefore, without inversion, since these compounds yield hydroxy-acids belonging to the *l*-series.

The following compounds are incidentally described; the specific rotations are recorded for the wave-lengths 649, 578, 546, and 444  $\mu\mu$ : *ethyl d- $\alpha$ -acetoxypionate*, b. p. 170—172°/760 mm.; *ethyl r- $\alpha$ -hexahydrobenzoxypionate*, b. p. 132—135°/13 mm., and the corresponding *d*-ester; *methyl r- $\alpha$ -benzoxypionate*, b. p. 144—145°/13 mm., 275—280°/760 mm., and the corresponding *ethyl* ester, b. p. 150°/12 mm., 282°/760 mm., and the similar *d*-compounds. *r- $\alpha$ -Benzoxypropionamide*, m. p. 116—117°; *methyl r-p-toluenesulphoxypionate*, b. p. 170—173°/0.5 mm.; *ethyl d-p-toluenesulphoxypionate*, b. p. 175—177°/0.5 mm.; *ethyl r-p-toluenesulphoxypionate*, b. p. 175—177°/0.5 mm.; *r- $\alpha$ -p-toluenesulphoxypropionamide*, m. p. 87—88°, and the corresponding *d*-amide, m. p. 105°; *ethyl dl- $\alpha$ -acetamidopropionate*, m. p. 39°, and the corresponding *l*-ester, m. p. 34—35°; *ethyl r- $\alpha$ -hexahydrobenzamidopropionate*, from the components in the presence of pyridine, m. p. 77—78°; *ethyl l- $\alpha$ -hexahydrobenzamidopropionate*, m. p. 75°; *methyl l- $\alpha$ -benzoylamino-pionate*, m. p. 58°; *ethyl l- $\alpha$ -benzamidopropionate*, m. p. 97—98°; *l- $\alpha$ -benzamidopropionamide*, m. p. 228—229°; *l- $\alpha$ -p-toluenesulphonamidopropionamide*, m. p. 212—213°; *ethyl l- $\alpha$ -p-toluenesulphonamidopropionate*. H. W.

**Preparation of Melanins containing Sulphur.** O. ADLER (*Biochem. Z.*, 1924, 148, 541—547).—Using the method already

described (A., 1923, i, 591, 1218), *tyrosinesulphomelanin acid*, a dark grey, hygroscopic, amorphous powder, has been prepared from tyrosinesulphonic acid. The sodium and barium salts are described. By heating at  $270^{\circ}$  for 2 hours, the acid is converted into *tyrosinesulphomelanin*, a black, hygroscopic powder. Similarly, from thiophen, *thiophenmelanic acid*, a dark, amorphous powder, and *thiophenmelanin*, a black powder, were obtained.

J. P.

**Action of Triphenylmethyl Chloride on Ethyl  $\beta$ -Aminocrotonate and Analogous Compounds.** E. BENARY and P. LORTH.—(See i, 1192.)

**Complexes of Carbamide with Cadmium Salts.** L. BELLA-DEN and A. CIAMPA (*Gazzetta*, 1924, 54, 568—571).—The following complex compounds are described:  $\text{CdCl}_2 \cdot \text{CO}(\text{NH}_2)_2$ ;

$\text{CdCl}_2 \cdot 2\text{CO}(\text{NH}_2)_2$ ;  $\text{CdBr}_2 \cdot \text{CO}(\text{NH}_2)_2$  and  $\text{CdBr}_2 \cdot 2\text{CO}(\text{NH}_2)_2$ ;

$\text{CdI}_2 \cdot \text{CO}(\text{NH}_2)_2$  and  $\text{CdI}_2 \cdot 2\text{CO}(\text{NH}_2)_2$ ;  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{CO}(\text{NH}_2)_2$ ;

$\text{Cd}(\text{SCN})_2 \cdot 2\text{CO}(\text{NH}_2)_2$ . The results of cryoscopic and conductivity measurements show that, in aqueous solution, these complex compounds undergo complete dissociation into their components.

T. H. P.

**Electrolysis of Aqueous Solutions of Cyanamide.** N. KAMEYAMA (*J. Coll. Eng. Tokyo*, 1924, 13, 271—310).—The electrolytic oxidation and reduction of aqueous solutions of cyanamide, acidified with sulphuric acid, sodium acetate, and acetic acid, in the presence of potassium sulphate, and, in the case of oxidation, in alkaline solution, and of solutions of acid calcium cyanamide,  $\text{Ca}(\text{CN}_2\text{H})_2$ , using lead, mercury, cadmium, zinc, and platinum cathodes, was studied at the ordinary or a slightly elevated temperature. Electrolytic reduction follows the same course as that produced by nascent hydrogen, methylamine and ammonia being produced. The intermediate formation of hydrogen cyanide could not be detected. The highest current efficiencies obtained were 10—20% with the cadmium cathode in the cyanamide solution containing sodium acetate and acetic acid or in the acid calcium cyanamide solution. Electrolysis of cyanamide solution without the separation of anodic and cathodic compartments yielded a trace of cyanide in acidic or neutral solutions, and a larger quantity, together with some cyanate, in alkaline solutions. On anodic oxidation, using a Pukall diaphragm and a platinum anode, the cyanamide solution became first yellow, then reddish-orange, and at this stage, on standing over-night, the solution deposited an orange-red, crystalline compound containing nitrogen. On continued electrolysis, the solution became pale yellow again and finally colourless. Electrolysis of the cyanamide in alkaline solution without a diaphragm yielded cyanide. Preliminary experiments on the anodic oxidation of cyanamide in alkaline solution showed the production of cyanate in solution and the evolution of nitrogen.

J. W. B.



**Conversion of Calcium Cyanamide into Cyanides.** J. DODONOW (*Ann. Inst. agron. Saratow*, 1922, **1**, 1-13; from *Chem. Zentr.*, 1924, ii, 317-318).—When a mixture of calcium cyanamide (160 g.), sodium carbonate (125 g.), and wood charcoal (32 g.) was added gradually to 20 g. of sodium carbonate heated to bright redness, and the temperature maintained for 20 mins., 63.5 g. of sodium cyanide (78% yield on the nitrogen of the cyanamide) were obtained; with potassium carbonate the yield was 70%. By heating calcium cyanamide with excess of water at 60°, dicyanodiamide was produced in 82% yield, together with carbamide (7%); boiling with water gave a 60% yield.

**Hydrazidicarbonazide and its Formation as By-product of the Diazotisation of Carbohydrazide.** W. KESTING (*Ber.*, 1924, **57**, [B], 1321-1324).—The addition of hydrochloric acid to an aqueous solution of carbohydrazide and sodium nitrite in the presence of light petroleum, b. p. 98°, leads to the formation of carboazide,  $\text{CO}(\text{N}_3)_2$ , which passes into the light petroleum, and hydrazidicarbonazide,  $\text{N}_2\text{H}_2(\text{CO}\cdot\text{N}_3)_2$ , which remains in the aqueous layer (cf. Stollé and Krauch, A., 1914, i, 592). The latter substance, m. p. 150-152° (decomp.) when slowly heated, is highly explosive. With piperidine, *hydrazidicarbonpiperidide*,  $\text{N}_2\text{H}_2(\text{CO}\cdot\text{NC}_5\text{H}_{10})_2$ , m. p. 179°, is formed. H. W.

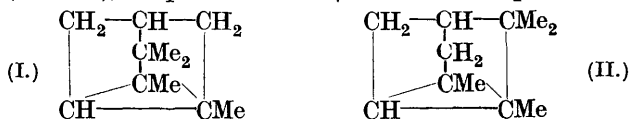
**Action of Ammonium Hydroxide on Copper Ferrocyanide.** E. D. CRITTENDEN (*J. Amer. Chem. Soc.*, 1924, **46**, 1210-1211).—Copper ferrocyanide does not dissolve in ammonia solution, but forms a silky, brown solid which probably has the formula  $\text{Cu}_2\text{Fe}(\text{CN})_6\cdot 4\text{NH}_3$ . The presence of a trace of ammonia seriously impairs the delicacy of the ferrocyanide test for small quantities of copper. M. S. B.

**Nitrogenous Condensation Products from Acetylene and Ammonia.** CHEM. FABR. RHENANIA (D.R.-P. 382091; from *Chem. Zentr.*, 1924, i, 2298-2399).—Acetylene and ammonia react in the presence of water vapour and a hydrated substance, such as aluminium hydroxide, forming under different conditions acetonitrile, picoline, aldehyde-ammonia, ethylamine, and nitrogenous bases of high molecular weight. The principal product is acetonitrile. G. W. R.

**Application of Zelinsky's Method of Catalytic Dehydrogenation to the Detection of Decahydronaphthalenes in Low-temperature Tar.** H. KAFFER (*Ber.*, 1924, **57**, [B], 1261-1265).—Suitable fractions of low-temperature tar are freed from aromatic hydrocarbons by treatment with sulphuric acid and dehydrogenated by repeated passage at 320-330° over platinised charcoal which has been activated by contact with oxygen at the atmospheric temperature. The products are treated with sulphuric acid and the sulphonic acids are decomposed into the corresponding hydrocarbons by means of superheated steam. Naphthalene, 1-methyl- and 1:6-dimethyl-naphthalene are thereby isolated,

thus establishing the presence of the corresponding decahydro compounds in the tar. Activated platinised charcoal is a more active catalyst than platinised asbestos. H. W.

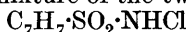
**Methylcyclene.** S. NAMETKIN and L. BRÜSSOFF (*Ber.*, 1924, 57, [B], 1258—1260).—6-Methylcamphor is converted by hydrazine hydrate at 180—190° into a mixture of the corresponding *hydrazone*, b. p. 153—154°/42 mm., m. p. 103—105°, and *azine*, m. p. 131—133°. The hydrazone is oxidised by mercuric oxide to *methylcyclene* (I or II), b. p. 168—168·5°/762 mm., m. p. 110·5—111°.



The new hydrocarbon is not identical with the product of the dehydration of *tert.*-methylfenchol or *tert.*-methylborneol (Bredt, A., 1919, i, 125). H. W.

#### Hydrolysis of the *p*-Toluenesulphonchloroamides in Water.

F. G. SOPER (*J. Chem. Soc.*, 1924, 125, 1899—1910).—In aqueous solution, *p*-toluenesulphonchloroamide is hydrolysed into hypochlorous acid (cf. Selivanov, A., 1893, i, 192) and the monochloroamide:  $\text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{NCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{NHCl} + \text{HOCl}$ , the existence of the latter, which could not be isolated, being indicated by the greater solubility of the dichloroamide in solutions of the sulphonamide than in water. The monochloroamide probably exists as an equilibrium mixture of the two isomerides,



and  $\text{C}_7\text{H}_7\cdot\text{SO}_2\text{H}\cdot\text{NCl}$ , hydrolysis of the monochloroamide from equimolecular quantities of the sulphonamide and hypochlorous acid and from acidification of "chloramine-T" (sodium salt of the monochloroamide), yielding identical results. From determinations of the solubility of the dichloroamide in solutions of the sulphonamide (cf. Löwenherz, A. 1898, ii, 326) and of the free chlorine in solutions of "chloramine-T" acidified with hydrochloric acid (cf. Orton and Jones, T., 1909, 95, 1456) the equilibrium constants of the hydrolysis of mono- and di-chloroamides of *p*-toluenesulphonamide in water at 25° have been calculated as  $4\cdot9 \times 10^{-8}$  and  $8\cdot0 \times 10^{-7}$ , respectively. The concentration of hypochlorous acid in solutions of acidified "chloramine-T" is independent of the concentration of the "chloramine-T." R. B.

**Nitro-*p*-*tert.*-butyltoluene.** M. BATTEGAY and P. HAEFFELY (*Bull. Soc. chim.*, 1924, [iv], 35, 981—988).—Nitration of *p*-*tert.*-butyltoluene with nitric and sulphuric acids at 5—10° gives 2-nitro-*p*-*tert.*-butyltoluene, a yellow oil, volatile in steam, b. p. 138—139°/13 mm., having a slight odour of musk. Its constitution is proved by the following series of reactions. On oxidation in pyridine with potassium permanganate it gives o-nitro-*p*-*tert.*-butylbenzoic acid, m. p. 145°, which on reduction in dilute ammonia with ferrous sul-

phate yields *o*-amino-*p*-tert.-butylbenzoic acid, m. p. 174°. The amino-acid, by treatment with potassium cyanide and formaldehyde in benzene suspension, followed by hydrolysis with sodium hydroxide, is converted into *p*-tert.-butylphenylglycine-*o*-carboxylic acid, m. p. 246°, and the sodium salt of the glycinecarboxylic acid on fusion with sodium and potassium hydroxides at 270° yields 6 : 6'-dibutylindigotin, violet needles, a reaction which proves the position of the nitro-group. On reduction, 2-nitro-*p*-tert.-butyltoluene yields *p*-tert.-butyl-*o*-toluidine, b. p. 128—129°/13 mm., volatile in steam (hydrochloride; acetyl derivative, m. p. 112°; benzoyl derivative, m. p. 143°; toluene-*p*-sulphonyl derivative, m. p. 158°), converted by the diazo reaction into *p*-tert.-butyl-*o*-cresol, a viscous oil, which on treatment with nitrous acid gives, besides traces of a nitrogenous substance, m. p. 172°, *p*-tert.-butyltoluquinone, golden-yellow spangles, m. p. 95°, volatile in steam and possessing a powerful quinone-like odour. On further nitration at 30° with fuming nitric and sulphuric acids, 2-nitro-*p*-tert.-butyltoluene gives, in 90% of the theoretical yield, the 2 : 6-dinitro-*p*-tert.-butyltoluene, m. p. 94—95°, obtained by Bialobrzewski (A., 1897, i, 514), the constitution of which follows from its reduction to *p*-tert.-butyl-2 : 6-tolylenediamine.

R. B.

**Artificial Musks.** M. BATTEGAY and M. KAPPELER (*Bull. Soc. chim.*, 1924, [iv], 35, 989—996).—With a view to obtain evidence as to whether the odour of artificial musk (trinitro-*tert*.-butyl-*m*-xylene) is due to the specific influence of the tertiary butyl group as such or merely to the tertiary carbon atom which it contains, a number of analogous derivatives of *m*-xylene have been prepared and the properties of their nitro derivatives examined. Replacement of the *tert*.-butyl group by cyclohexyl leads to an odourless trinitro compound; *tert*.-heptyl-*m*-xylene (*m*-xylyltriethylmethane) yields a nitration product with a strong but somewhat disagreeable odour of musk, whilst 5-triphenylmethyl-*m*-xylene yields only odourless nitration products, and it is concluded that both the tertiary carbon atom and the butyl radical as such exert an “osmophoric” influence.

*m*-Xylene and cyclohexyl bromide condense in the presence of ferric or aluminium chloride, yielding a dicyclohexyl-*m*-xylene, C<sub>20</sub>H<sub>30</sub>, m. p. 104°, and 5-cyclohexyl-*m*-xylene, b. p. 265—266°/748 mm., 142—143°/17 mm., with an odour of geranium, which on nitration with nitric and fuming sulphuric acids gives 2 : 4 : 6-trinitro-5-cyclohexyl-*m*-xylene, m. p. 117—118°, the constitution of which follows from its synthesis by nitrating the hydrocarbon obtained by deaminating the condensation product of cyclohexyl bromide and 2-*m*-xylidine hydrochloride. Similarly, *m*-xylene and methyldiethylethylene (Saytzeff, A., 1898, i, 289) in the presence of aluminium chloride readily yield 5- $\alpha$ -diethylpropyl-*m*-xylene, b. p. 257—259°/745 mm., which on nitration with nitric and sulphuric acids yields only trinitro-*m*-xylene, whilst with nitric acid and acetic anhydride an oily product of musk-like odour is obtained. Triphenylcarbinol and 2-*m*-xylidine hydrochloride in boiling acetic

acid yield 5-triphenylmethyl-2-m-xylidine hydrochloride, a red powder, m. p. 277—278°; the free base has m. p. 177°. On diazotisation of the sulphate in acetic acid solution with amyl nitrite and decomposition of the *diazonium* salt with absolute alcohol in the presence of copper, 5-triphenylmethyl-m-xylene, m. p. 154°, b. p. 450°, is obtained. No definite nitration product was obtained. R. B.

**Sulpho Derivatives of Acenaphthene.** K. DZIEWOŃSKI and T. STOLYHWO (*Ber.*, 1924, 57, [B], 1531—1540).—Acenaphthene-5-sulphonic acid (cf. Oliveri-Mandala, *Rend. Accad. Lincei*, 1912, 779) is conveniently prepared by the action of sulphuric acid (8 g.) on acenaphthene (10 g.) at 100°, and is readily separated as the sodium salt; the ethyl ester, m. p. 87—88°, and the *amide*, m. p. 196—199°, are described. The sodium salt is transformed when heated with potassium ferrocyanide, potassium cyanide, or potassium hydroxide into acenaphthylene and polyacenaphthylene. Acenaphthene-3-sulphonic acid (described erroneously in D.R.-P. 248994 as the 1-sulphonic acid because of its conversion by fused potassium hydroxide into acenaphthylene) is obtained by the addition of sulphuric acid (100%) or chlorosulphonic acid to a solution of acenaphthene in nitrobenzene at 0—20°. The *sodium* and *barium* salts are described. *Acenaphthene-3-sulphonyl chloride* is readily converted into *acenaphthene-3-sulphonamide*, m. p. 222—223°, and *ethyl acenaphthene-3-sulphonate*, m. p. 137—139°. Attempts to prepare the corresponding nitrile from the sulphonate yielded only acenaphthylene and its polymeride. The constitution of the acid is established by its oxidation with sodium dichromate in glacial acetic acid solution to 2-sulphonaphthalene-1:8-dicarboxylic acid (the *sodium hydrogen* salt and the *barium* salt are described); the acid is converted by fused potassium hydroxide into 2-naphthol-1:8-dicarboxylic acid (cf. Dziewonski and Stolyhwo, this vol., i, 1199).

Treatment of acenaphthene with an excess of concentrated or with fuming sulphuric acid leads to the formation of disulphonic acids of which two, termed provisionally  $\alpha$ - and  $\beta$ -acid, have been isolated. In contrast to the monosulphonic acids they yield barium salts which dissolve very freely in water and are adapted to their isolation. *Acenaphthene- $\alpha$ -disulphonic acid* is prepared from the hydrocarbon (10 g.) and concentrated sulphuric acid (20 g.) at 100°; the *sodium* and *barium* salts and the *disulphonyl chloride* are described. *Acenaphthene- $\alpha$ -disulphonamide* and *methyl acenaphthene- $\alpha$ -disulphonate* have m. p. 282° (decomp.) and 170—171°, respectively. The acid is readily nitrated to a nitroacenaphthene- $\alpha$ -disulphonic acid which is isolated as the *sodium* salt. Acenaphthene (10 g.) is converted by cold concentrated sulphuric acid (50 g.) into acenaphthene- $\beta$ -disulphonic acid [*barium* and *sodium* salts; *sulphonyl chloride*; *acenaphthene- $\beta$ -disulphonamide*, m. p. 301° (decomp.)]. Desulphonation of either acenaphthenedisulphonic acid gives primarily acenaphthene-5-monosulphonic acid and ultimately acenaphthene; in each case one of the two sulphonic groups must occupy position 5.

H. W.

**Complex Isomerism.** E. HERTEL (*Ber.*, 1924, 57, [B], 1559—1561).—*o*-Bromoaniline picrate exists in two forms, long, red needles, m. p. 128·5°, obtained by allowing a solution of the components in chlorobenzene to crystallise above 95°, and a yellow variety prepared in alcoholic solution. It therefore appears to fulfil the predictions of Pfeiffer ("Organische Molekülverbindungen," 1922, p. 226) with regard to the existence of two types of picrate, in one of which the hydroxylic hydrogen of picric acid is united by a subsidiary valency to the basic nitrogen atom ("true picrates"), whereas in the other the subsidiary valency of the nitro group of picric acid is saturated by the valency field produced by the residual affinities of the aromatic nucleus of the base,  $\text{OH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\ldots\text{RNH}_2$ . When picric acid is triturated with *o*-bromoaniline, a carmine-red mixture is obtained which becomes yellow slowly at the atmospheric temperature, instantaneously at 65°; a similar, irreversible effect is produced immediately by the vapours of ether, acetone, or ethyl acetate. Analogous observations are made with *o*-bromoaniline and trinitrobenzene. Picrates of the following bases are described incidentally: *m*-bromoaniline, m. p. 180°; *p*-bromoaniline, m. p. 180°; *o*-, *m*-, and *p*-chloroanilines, m. p. 134°, 177°, and 178°, respectively; 2:4-dichloroaniline, m. p. 106°; 2:4-dibromoaniline, m. p. 124°; 2:6-dibromoaniline, m. p. 123—124° (the molten product solidifies when quickly cooled to a red mass, m. p. 95°); 2:4:6-tribromoaniline.

H. W.

**Acetoacetanilide.** C. BÜLOW and E. KING (*Annalen*, 1924, 439, 211—220).— $\alpha$ -Chloroacetoacetanilide, m. p. 137·5°, is produced by the interaction of sulphuryl chloride and acetoacetanilide in cold ethereal suspension. With excess (3 mols.) of sulphuryl chloride,  $\alpha\alpha$ -dichloroacetoacetanilide, m. p. 46—47°, is formed, which tends to resinify on standing. By passing chlorine into an ethereal suspension of acetoacetanilide, a dark brown oil is produced which if dissolved in benzene slowly deposits crystals of  $\alpha\alpha$ -dichloroacetoacet-*p*-chloroanilide in very poor yield, m. p. 63—64°.  $\alpha$ -Chloroacetoacetanilide is more stable than acetoacetanilide, being hydrolysed only by dilute hydrochloric acid at 120—130° to chloroacetone, carbon dioxide, and aniline.

$\beta$ -*n*-Butylaminocrotonanilide, m. p. 98°, from *n*-butylamine and acetoacetanilide, is easily hydrolysed by water or dilute acids. By the interaction of  $\alpha$ -chloroacetoacetanilide and alcoholic ammonia,  $\alpha$ -chloro- $\beta$ -aminocrotonanilide, m. p. 143°, is produced; it is stable on boiling with water, but is hydrolysed by dilute acids;  $\alpha$ -chloro- $\beta$ -methylaminocrotonanilide, m. p. 96·5°, is similar.  $\alpha$ -Chloro- $\beta$ -*n*-butylaminocrotonanilide, m. p. 65°, is very unstable. The interaction of aniline and  $\alpha$ -chloroacetoacetanilide yields  $\alpha$ : $\beta$ -diphenylaminocrotonanilide, m. p. 201—202°.

$\beta$ -Chloro- $\alpha$ -hydroxylepidine, m. p. 276°, is formed by treatment of  $\alpha$ -chloroacetoacetanilide with concentrated sulphuric acid; the chlorine atom is very stable. On nitration it gives a mononitro

By coupling  $\alpha$ -chloroacetoacetanilide with diazotised aniline,  $\alpha$ -chloroglyoxyylanilide phenylhydrazone,  $\text{NHPh}\cdot\text{N}\cdot\text{CCl}\cdot\text{CO}\cdot\text{NHPh}$ , m. p.  $161^\circ$ , is produced. The chlorine is now easily replaceable, for with alcoholic ammonia,  $\alpha$ -aminoglyoxyylanilide phenylhydrazone is produced, m. p.  $152$ — $154^\circ$ , apt to gelatinise. The hydrochloride is unstable, decomp.  $150^\circ$ ; m. p.  $213^\circ$  in an atmosphere of dry hydrogen chloride. The corresponding  $\alpha$ -anilinoglyoxyylanilide phenylhydrazone has m. p.  $171^\circ$ . When chlorine is passed at  $0^\circ$  into an alcoholic suspension of  $\alpha$ -chloroglyoxyylanilide phenylhydrazone, the 2-chloroanilide 2 : 4-dichlorophenylhydrazone, m. p.  $199.5^\circ$ , is formed; this was also synthesised from acetoacet-2-chloroanilide and 2 : 4-dichlorobenzenediazonium chloride.

$\alpha$ -Chloroglyoxyylanilide o-tolylhydrazone, from the  $\alpha$ -chloroacetoacetanilide and diazotised o-toluidine, has m. p.  $115^\circ$ ; the p-tolylhydrazone has m. p.  $175^\circ$ ; the 1 : 3 : 5-xylylhydrazone, m. p.  $135.5^\circ$ ; the 1 : 3 : 4-xylylhydrazone, m. p.  $138^\circ$ .  $\alpha$ -Chloroglyoxyylanilide phenylhydrazone-o-carboxylic acid, from  $\alpha$ -chloroacetoacetanilide and diazotised anthranilic acid, has m. p.  $216$ — $217^\circ$  (decomp.). The  $\beta$ -naphthylhydrazone melts indistinctly at  $183^\circ$ , and the  $\alpha$ -naphthylhydrazone at  $189$ — $191^\circ$ .  
A. E. C.

**isoNitriles. VIII. Reaction with Aldehydes or Ketones in Presence of Organic Acids.** M. PASSERINI (*Gazzetta*, 1924, 54, 529—540).—The reaction of an aldehyde or ketone with an aromatic isonitrile in presence of an organic acid (cf. A., 1921, i, 895) is, with some exceptions, of general application and has now been extended to aliphatic aldehydes and to cases in which the aldehyde or ketone and the acid are derived from different organic radicals. Diketones also undergo this reaction, in which, however, only one of the two ketonic groups takes part. Neither camphor nor santonine reacts in this way. Halogenated ketones, which with water form hydrates, react with phenylcarbylamine in the same manner as the hydrates of halogenated aldehydes react in absence of organic acid (cf. A., 1922, i, 731).

$\alpha$ -Salicyloxyisobutyranilide,  $\text{NHPh}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , m. p.  $118$ — $119^\circ$ , obtained from phenylcarbylamine, acetone, and salicylic acid, yields  $\alpha$ -hydroxyisobutyranilide and salicylic acid on hydrolysis.  $\beta$ -Chloro- $\alpha$ -benzoyloxyisobutyranilide,  $\text{NHPh}\cdot\text{CO}\cdot\text{CMe}(\text{CH}_2\text{Cl})\cdot\text{OBz}$ , from phenylcarbylamine, chloroacetone, and benzoic acid, m. p.  $97$ — $99^\circ$ , yields  $\alpha$ -hydroxy- $\beta$ -chloroisobutyranilide and benzoic acid on hydrolysis.

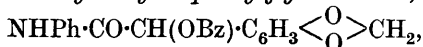
$\beta$ -Chloro- $\alpha$ -acetoxyisobutyranilide,  $\text{NHPh}\cdot\text{CO}\cdot\text{CMe}(\text{CH}_2\text{Cl})\cdot\text{OAc}$ , from phenylcarbylamine, chloroacetone, and acetic acid, forms a pale yellow syrup and undergoes normal hydrolysis.  $\alpha$ -Acetoxy- $\alpha$ -methylbutyranilide,  $\text{NHPh}\cdot\text{CO}\cdot\text{CMeEt}\cdot\text{OAc}$ , m. p.  $71^\circ$ , from phenylcarbylamine, methyl ethyl ketone, and acetic acid, on hydrolysis yields acetic acid and  $\alpha$ -hydroxy- $\alpha$ -methylbutyranilide, m. p.  $114^\circ$ , which undergoes further hydrolysis to aniline and  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid.  $\alpha$ -Acetyl-lactanilide,

$\text{NHPh}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{OAc}$ ,

m. p.  $122^\circ$ , from phenylcarbylamine, acetaldehyde, and acetic acid,

gives lactanilide on hydrolysis.  $\alpha$ -Benzoyl- $\alpha$ -benzoyloxy- $\alpha$ -phenylacetanilide,  $\text{NHPh}\cdot\text{CO}\cdot\text{CPhBz}\cdot\text{OBz}$ , from phenylcarbylamine, benzil, and acetic acid, m. p. 194—195° (decomp.), yields mandelanilide and benzoic acid on hydrolysis. *m*-Nitro- $\alpha$ -benzoylmandelanilide,  $\text{NHPh}\cdot\text{CO}\cdot\text{CH}(\text{OBz})\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , m. p. 155—157°, from phenylcarbylamine, *m*-nitrobenzaldehyde, and benzoic acid, yields aniline, benzoic acid, and *m*-nitromandelic acid on hydrolysis.

*o*-Benzoyl-4 : 5-dioxymethylenephénylglycollanilide,

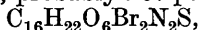


m. p. 160°, from phenylcarbylamine, piperonal, and benzoic acid, on hydrolysis, yields benzoic acid and 4 : 5-dioxymethylene-phenyl-1-glycollanilide, m. p. 114°.  $\beta\beta$ -Dichloro- $\alpha$ -hydroxyisobutyranilide,  $\text{NHPh}\cdot\text{CO}\cdot\text{CMe}(\text{OH})\cdot\text{CHCl}_2$ , m. p. 132—133°, from phenylcarbylamine and *as*-dichloroacetone hydrate, yields aniline and  $\beta\beta$ -dichloro- $\alpha$ -hydroxyisobutyric acid on hydrolysis. T. H. P.

**Preparation of Sulphinanilides by Means of Grignard's Reaction.** A. SONN and E. SCHMIDT (*Ber.*, 1924, **57**, [B], 1355—1356).—*Benzenesulphinanilide*,  $\text{Ph}\cdot\text{SO}\cdot\text{NHPh}$ , m. p. 112—113°, *phenylmethanesulphinanilide*, m. p. 144—145°, and *ethanesulphinanilide*, m. p. 72°, are prepared from thionylaniline,  $\text{PhN:S:O}$ , and the requisite Grignard reagent in ethereal solution. H. W.

**Amine Oxides derived from 4-Bromodimethylaniline and from 3- or 4-Nitrodimehtylaniline.** L. W. JONES and E. B. HARTSHORN (*J. Amer. Chem. Soc.*, 1924, **46**, 1840—1855).—The various interpretations offered to explain the isomerides of  $\text{NMe}_3(\text{OMe})\text{OH}$  discovered by Meisenheimer (cf. A., 1913, i, 595, 1048), especially those of Jones and of Michael, and the more recent explanations of Lewis and Langmuir, are discussed. An attempt to prepare isomerides of the same type from oxides of substituted dimethylaniline was not successful since such amine oxides do not react with alkyl halides as methyl iodide reacts with trimethylamine oxide. Permonosulphuric acid oxidises the tertiary amines to the oxides, which crystallise from solution as neutral or acid sulphate. The corresponding hydrochlorides are stable, crystalline salts, but the hydriodides decompose, yielding free iodine and the original amine. *p*-Bromodimethylaniline oxide hydriodide was isolated below 0°. The free bases do not liberate iodine from potassium iodide, unlike the alkylpiperidine oxides (cf. Wernick and Wolfenstein, A., 1898, i, 536). Solutions of the free amine oxides were obtained by shaking the hydrochlorides in methyl alcohol with moist silver oxide. The solid bases were difficult to isolate, but were obtained in fair purity by removing the methyl alcohol rapidly under diminished pressure. Sublimation, even in a vacuum, causes decomposition, traces of formaldehyde being given off. The chief point of differentiation from the aliphatic amine oxides is in their behaviour with methyl iodide (cf. A., 1899, i, 682). No additive products with the amine oxide are formed, but the oxide is reduced and iodine liberated without the production of formaldehyde. An excess of iodine yields

periodides of the quaternary salts of the amines in most cases, e.g.,  $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\cdot\text{I}\cdot\text{I}_2$ . The following compounds were prepared: 4-Bromodimethylaniline oxide, brown, very hygroscopic powder, m. p. 167—168°, probably not pure; sulphate,



darkens above 125° and explodes at 132—135°; hydrochloride, darkens above 160°, decomp. 165—166°; hydriodide, decomp. 92—94°; picrate, m. p. 126—127° (decomp.). 4-Bromophenyltrimethylammonium iodide, decomp. 187—187·5°, periodide, m. p. 165—166°. 4-Nitrodimethylaniline oxide, m. p. 110—111°, odour like coumarin; hydrogen sulphate, decomp. 147—149°; hydrochloride, decomp. 168—169°; picrate, m. p. 148—159°. Reduction of the hydrogen sulphate with sulphur dioxide gave mainly 4-nitrodimethylaniline, but also small amounts of what were assumed to be 5-nitro-2-dimethylaminobenzenesulphonic acid and 2-nitro-5-dimethylaminobenzenesulphonic acid. No quaternary salt was formed with methyl iodide; a small amount of a periodide, m. p. 162—163°, was separated from the main reduction product. 3-Nitrodimethylaniline oxide, m. p. 152—155°, has a slight odour of carbilamine; hydrochloride, decomp. 157—158°; picrate, m. p. 141—142°. *m*-Nitrophenyltrimethylammonium iodide, yellow prisms, decomp. about 200°; periodide, bronze plates, m. p. 144—145°.

A. C.

**Catalytic Alkylation of Aniline.** A. B. BROWN and E. E. REID (*J. Amer. Chem. Soc.*, 1924, **46**, 1836—1839).—Using silica gel as catalyst, a quantitative study of the alkylation of aniline by methyl, ethyl, *n*-propyl, and *n*-butyl alcohols has been made. The vapours of the mixture were passed over the catalyst at various temperatures (300—500°) until that at which the maximum conversion took place was found. The percentages of alkylanilines found and the ratios of monoalkyl to dialkyl at approximately optimum temperatures are as follows: series I for  $\text{NH}_2\text{Ph}:\text{ROH}=1:1\cdot05$ , and series II,  $1:2\cdot05$ . Methyl, I 37·8%, 5:2 at 365°; II 42%, 5:3 at 370°. Ethyl, I 41·5%, 5:1 at 385°; II 60·0%, 7:2 at 385°. *n*-Propyl, I 38·8%, 14:3 at 385°; II 54·8%, 3:1 at 385°. *n*-Butyl, I 32·0%, 31:10 at 385°; II 40·3%, 33:10 at 400°. The catalyst was found to have a dehydrating and also a dehydrogenating effect on the alcohols, especially at higher temperatures, gaseous hydrocarbons of the  $\text{C}_n\text{H}_{2n}$  type being evolved together with hydrogen. The activity of the catalyst fell off rapidly in the first hour and then more slowly. This falling-off was not so marked if the catalyst was not heated to a high temperature. Fouling of the catalyst is to be expected owing to the formation of condensation products from aniline and aldehydes, which easily polymerise.

A. C.

***n*-Amylaniline.** L. G. RADCLIFFE and R. GRINDLEY (*J. Soc. Dyers and Col.*, 1924, **40**, 290—292).—The preparation of *n*-butylaniline, *n*-amylaniline, and *n*-diamylaniline indicates that the reaction between aniline and an alkyl halide proceeds less smoothly and with much smaller yields as the molecular weight of the alkyl

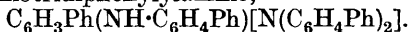


halide is increased. A good yield of *n*-amylaniline was obtained by heating equimolecular proportions of aniline and *n*-amyl bromide or chloride under pressure at 190° for 6 hrs. The crude product was purified by fractional distillation, conversion into phenyl-*n*-amylnitrosoamine, and subsequent reduction by means of zinc dust and glacial acetic acid. *n*-Amylaniline, colourless oil, b. p. 260—262° (uncorr.), darkens when exposed to light. Phenyl-*n*-amylnitrosoamine, a greenish-yellow oil, slightly volatile in steam, decomposes when heated above 100°, and yields *p*-nitroso-*n*-amylaniline when treated with alcoholic hydrogen chloride. *n*-Diamylaniline, b. p. 280—285°, is produced by heating equimolecular proportions of *n*-amylaniline and *n*-amyl chloride under pressure at 190—200° for 2 hrs. Attempts to prepare the acetyl and benzoyl derivatives of *n*-amylaniline were unsuccessful. A. J. H.

**Titanous Salts as Reducing Agents.** E. KNECHT (*J. Chem. Soc.*, 1924, 125, 1537—1546).—If an acceptor, such as a primary aromatic amine, is present in solution, and the reactants are present in the ratio  $2\text{TiCl}_3 : \text{HNO}_3$ , titanous chloride will reduce nitric acid to nitrous acid; a quantitative yield of the diazonium compound can be obtained in this manner. When 1-nitronaphthalene is reduced with titanous chloride in presence of a large excess of hydrochloric acid, the principal product (94%) is 4-chloro- $\alpha$ -naphthylamine.

[With (Miss) E. HIBBERT.]—Volumetric methods employing titanous chloride have been worked out for the determination of a number of organic compounds, including phenolphthalein, phenylhydrazine, tartrazine, tetramethyldiaminobenzhydrol, gallein, and isatin. S. B.

**Oxidation of Didiphenylamine.** W. BÜLOW (*Ber.*, 1924, 57, [B], 1431—1434).—Oxidation of didiphenylamine,  $\text{NH}(\text{C}_6\text{H}_5)_2$  (cf. Wieland and Süsser, A., 1911, i, 570), by sodium dichromate in the presence of glacial acetic acid and a little sulphuric acid, yields a dark green substance which is reduced by zinc dust to a substance,  $\text{C}_{48}\text{H}_{36}\text{N}_2$ , m. p. 276°, identical with the product obtained by Wieland and Süsser (*loc. cit.*) by the fission of tetradiphenylhydrazine with ethereal hydrogen chloride; it is regarded as *o*-diphenylaminotridiphenylamine,



In addition, diphenopiperazine,  $\text{C}_6\text{H}_3\text{Ph} \begin{smallmatrix} \text{N}(\text{C}_6\text{H}_4\text{Ph}) \\ \text{N}(\text{C}_6\text{H}_4\text{Ph}) \end{smallmatrix} \text{C}_6\text{H}_3\text{Ph}$ , m. p. above 345°, is produced [Wieland and Süsser (*loc. cit.*) give m. p. 325—330°].

*Tridiphenylamine*, m. p. 261—262°, is obtained together with the corresponding di-derivative from *p*-iododiphenyl and *p*-aminodiphenyl and copper powder (cf. Wieland and Süsser, *loc. cit.*). With antimony pentachloride, it yields a stable additive compound,  $\text{C}_{36}\text{H}_{27}\text{N}_3\text{SbCl}_5$ , m. p. 130—131° (decomp.). H. W.

**Steric Relations in the Acylation of Aromatic Amines and Aminophenols.** L. C. RAIFORD, R. TAFT, and H. P. LANKELMA (*J. Amer. Chem. Soc.*, 1924, 46, 2051—2057).—An

examination of the acetylation of thirteen substituted anilines by Sudborough's method (T., 1901, **79**, 533) indicates that the formation of a diacetyl derivative is favoured by the presence of one negative substituent (halogen or nitro) in the ortho-position to the amino group (cf. A., 1919, i, 12), and retarded by a similar substituent in the para-position. The accelerating effect is not in accordance with the relative weights of the substituents, and in the case of ortho-para substitution the two effects counterbalance. In the acylation of aminophenols with benzoyl chloride by the Schotten-Baumann process and with *p*-nitrobenzoyl chloride in pyridine or chloroform solution (cf. Fischer, A., 1920, i, 808), the presence of halogen atoms in the ortho-positions to the hydroxyl protects the hydroxyl group to a marked extent, but does not entirely prevent the formation of the *O*-acyl-*N*-acyl compound. With the symmetrical trihalogenated phenols steric hindrance is much more pronounced with benzoyl chloride than with *p*-nitrobenzoyl chloride, but only in the case of *s*-tribromoaniline was no acyl derivative obtained under these conditions. The following compounds were obtained: *o*-Chlorodiacetanilide, m. p. 86—87°; *o*-iododiacetanilide, m. p. 64—65°; 2:5-dichlorodiacetanilide, m. p. 91—92°; 2-chloro-4-benzamidophenol, m. p. 178°; 2-chloro-4-benzamidophenyl benzoate, m. p. 206°; 2-chloro-4-*p*-nitrobenzamidophenol, m. p. 242°; 2-chloro-4-*p*-nitrobenzamidophenyl *p*-nitrobenzoate, m. p. 253°; 2:6-dichloro-4-benzamidophenol, m. p. 198°; 2:6-dichloro-4-benzamidophenyl benzoate, m. p. 177°; 2:6-dichloro-4-*p*-nitrobenzamidophenol, m. p. 265°; 2:6-dichloro-4-*p*-nitrobenzamidophenyl *p*-nitrobenzoate, m. p. 246°; 2-bromo-4-benzamidophenol, m. p. 193° (cf. Meldola and Hollely, T., 1913, **103**, 182); 2-bromo-4-benzamidophenyl benzoate, m. p. 199°; 2-bromo-4-*p*-nitrobenzamidophenol, yellow needles, m. p. 237°; 2-bromo-4-*p*-nitrobenzamidophenyl *p*-nitrobenzoate, m. p. 255°; 2:6-dibromo-4-benzamidophenol, m. p. 208°; 2:6-dibromo-4-benzamidophenyl benzoate, m. p. 172°; 2:6-dibromo-4-*p*-nitrobenzamidophenol, m. p. 268°; 2:6-dibromo-4-*p*-nitrobenzamidophenyl *p*-nitrobenzoate, m. p. 237°; 2:6-di-iodo-4-nitrophenol, m. p. 155—156° (cf. Weselsky, *Annalen*, 1874, **174**, 108; Post, *ibid.*, 1880, **205**, 91); 2:6-di-iodo-4-amino-phenol, m. p. 169—171° (cf. Seifert, *J. pr. Chem.*, 1843, [ii], **28**, 437); 2:6-di-iodo-4-benzamidophenol, m. p. 222°; 2:6-di-iodo-4-benzamidophenyl benzoate, m. p. 210—211°; 2:6-di-iodo-4-*p*-nitrobenzamidophenyl *p*-nitrobenzoate, m. p. 277°; 2:4:6-trichlorophenyl benzoate, m. p. 74°; 2:4:6-trichlorophenyl *p*-nitrobenzoate, m. p. 105—106°; 2:4:6-tribromophenyl benzoate, m. p. 81°; 2:4:6-tribromophenyl *p*-nitrobenzoate, m. p. 153—154°; 2:4:6-tri-iodophenyl *p*-nitrobenzoate, m. p. 181°; phenyl *p*-nitrobenzoate, m. p. 129°, and 2-nitrobenzanilide, m. p. 212°. R. B.

**Mutual Solubility. III. Mutual Solubility of Glycerol and Amino and Hydroxy Compounds.** R. R. PARVATIKER and B. C. McEWEN.—(See ii, 659.)

**Aromatic Orthoformates.** J. E. DRIVER (*J. Amer. Chem. Soc.*, 1924, **46**, 2090—2093).—The method recently described for

the preparation of triphenyl orthoformate (this vol., i, 638) can be used for the preparation of the tolyl orthoformates. The action of chloroform vapour on potassium *p*-tolyl oxide at 108° gives tri-*p*-tolyl orthoformate, m. p. 112° (Auwers, A., 1907, i, 400), and traces of 1-methyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one, m. p. 53–55°, the formation of the latter compound suggesting that an unstable dichloromethoxytoluene is the first product of the reaction. Similarly, potassium *o*-tolyl oxide and boiling chloroform give tri-*o*-tolyl orthoformate, m. p. 96°, and potassium *m*-tolyl oxide at 110–120° yields tri-*m*-tolyl orthoformate, m. p. 50°. The tolyl orthoformates are not hydrolysed by boiling alkalis and are only slowly oxidised by boiling neutral permanganate. R. B.

### Decomposition of Ethers by Metallic Sodium. II. Relative Tenacity of Different Radicals to the Oxygen Atom.

P. SCHORIGIN (*Ber.*, 1924, 57, [B], 1627–1634; cf. A., 1923, i, 207).—The decomposition of mixed ethers, particularly those of the aromatic and fatty-aromatic series, by sodium occurs in accordance with the scheme:  $R\cdot O\cdot R^1 + 2Na \rightarrow RR^1O\cdots Na_2 \rightarrow R\cdot ONa + R^1Na$  or  $R\cdot Na + R^1\cdot ONa$ . The reaction has been applied to the determination of the relative firmness with which the radicals are attached to the oxygen atom. As is to be expected, the reaction takes place in both possible directions, but the more firmly bound of any two radicals is found to the greater extent as alkoxide or phenoxide in the products. The groups may be arranged in order of increasing tenacity to oxygen in the order: benzyl, ethyl, *iso*amyl,  $\beta$ -naphthyl,  $\alpha$ -naphthyl, phenyl. The relative positions of the naphthyl groups in the series is slightly uncertain.

Phenyl  $\alpha$ -naphthyl ether and sodium at 140° give a mixture of phenol and  $\alpha$ -naphthol (molecular ratio, 5 : 1) and benzene and naphthalene (1 : 10). The corresponding ratios for phenyl  $\beta$ -naphthyl ether are 7 : 1 and 1 : 8.  $\alpha\beta$ -Dinaphthyl ether did not give a definite result by reason of the difficulty of separating  $\alpha$ - from  $\beta$ -naphthol.  $\beta$ -Naphthyl ethyl ether yielded  $\beta$ -naphthol and ethyl alcohol (4 : 1) and naphthalene, ethane, and ethylene (1 : 3.3).  $\beta$ -Naphthyl benzyl ether gave only  $\beta$ -naphthol and toluene. Phenyl benzyl ether yielded only phenol and toluene with traces of benzene; it is isomerised to some extent to benzhydrol (cf. Schorigin, this vol., i, 1188). Phenetole gave almost exclusively phenol accompanied by a very little ethyl alcohol; ethane and ethylene are produced, but, apparently, no benzene. Benzyl ethyl ether gave an inseparable mixture of little benzyl alcohol and much phenylethylcarbinol, toluene, and ethylene. Diethyl ether is decomposed by sodium at 200–340° into ethylene, probably ethane and hydrogen, and a little ethyl alcohol. Diisoamyl ether is decomposed with greater difficulty than the diethyl compound, yielding  $\beta$ -methyl- $\Delta^a$ -butylene,  $\beta$ -methyl- $\Delta^b$ -butylene, and *iso*-pentane. H. W.

**Superheating of Uniform Organic Compounds. I. Aryl-paraffins and Aliphatic Esters.** S. SKRAUP and F. NIETEN (*Ber.*, 1924, 57, [B], 1294–1310).—The pyrogenic decomposition

of anisylparaffins in sealed tubes at as low a temperature as possible leads, in the case of compounds with an even number of carbon atoms in the aliphatic chain, to the loss of the terminal methyl group (as ethylene) and production of the next lower homologue with an odd number of carbon atoms. Under similar conditions, the compounds with an odd number of carbon atoms remain unchanged, but at a slightly higher temperature they lose the complete aliphatic chain, probably as olefine, and yield anisole. The phenyl esters of stearic and palmitic acids decompose at 300—320° in sealed tubes filled with nitrogen into pentadecane and tridecane, respectively, and phenyl acrylate; the latter is converted primarily into acetylene and phenyl formate, which then yields phenol and carbon monoxide. In an open vessel, on the other hand, phenyl stearate is decomposed at 320° into carbon monoxide, possibly hydrogen and phenol; acetylene, ethylene, or paraffin hydrocarbons are not produced, the chief product being a carbonised residue.

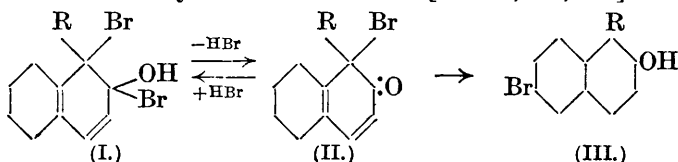
*p*-Anisyl *n*-propyl ketone, b. p. 162—163°/20 mm., m. p. —3° to —4° (*phenylhydrazone*, m. p. 77°), is prepared by the action of aluminium chloride on a solution of anisole and butyryl chloride in light petroleum or by the action of butyryl chloride on *p*-anisyl-chloromercurate at 135°. If light petroleum is replaced by carbon disulphide, the yield of the ketone is decreased and the product contaminated with  $\alpha$ -di-*p*-anisyl- $\Delta^a$ -butylene,  $\text{CHEt}:\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , m. p. 95—96°. The ketone is reduced by amalgamated zinc and hydrochloric acid to *p*-butylanisole (*sulphonamide*, m. p. 96°). *p*-Anisyl *n*-butyl ketone, b. p. 165—167°/14 mm., m. p. 26° (*phenylhydrazone*, m. p. 73°), is converted similarly into *p*-*n*-amylanisole, b. p. 124—125°/14 mm. (*sulphonamide*, m. p. 101°). *p*-Anisyl *n*-amyl ketone, m. p. 41° (*phenylhydrazone*, m. p. 28°), *p*-hexylanisole, b. p. 152—153°/15 mm., and its *sulphonic acid*, m. p. 75°, and *sulphonamide*, m. p. 87°, are described. *p*-Anisyl *n*-hexyl ketone, b. p. 192°/17 mm., m. p. 40° (*phenylhydrazone*, m. p. 35°), gives *p*-heptylanisole, b. p. 160—162°/17 mm. (*sulphonamide*, m. p. 108°). *p*-Anisyl *n*-octyl ketone, m. p. 43° (*phenylhydrazone*, m. p. 48°), yields *p*-nonylanisole, b. p. 178—180°/18 mm.

Phenyl  $\beta$ -chloropropionate, b. p. 141—143°/18 mm., is converted by boiling pyridine into *phenyl acrylate*, b. p. 202—203° (slight decomp.), 105°/20 mm., and, apparently, the quaternary compound,  $\text{C}_5\text{H}_5\text{NCl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , which, however, is not an intermediate product in the formation of the acrylate.

The action of propionyl chloride on dimethylaniline in the presence of zinc chloride gives a mixture of  $\alpha$ -bisdimethylamino-phenyl- $\Delta^a$ -propylene (the constitution of which is established by its oxidation to Michler's ketone) and *p*-dimethylaminopropiophenone, b. p. 270—272° (*phenylhydrazone*, m. p. 58°); the ketone is also prepared from propionyl chloride and dimethylaminophenylchloromercurate. Similarly, dimethylaniline, butyryl chloride, and zinc chloride yield *p*-dimethylaminophenyl *n*-propyl ketone, b. p. 180—185°/27 mm. (*phenylhydrazone*, m. p. 67—68°; *methiodide*, m. p. 163°), which does not appear to undergo reduction by Clem-

mensen's method, and  $\alpha\alpha$ -bisdimethylaminophenyl- $\Delta^a$ -butylene, m. p. 80—81°, which is oxidised to Michler's ketone. H. W.

**Reaction Processes Underlying Substitution.** K. FRIES and H. ENGEL (*Annalen*, 1924, **439**, 232—245).—By the bromination of derivatives of  $\beta$ -naphthol, under definite conditions, the intermediate products are ketobromides, derivatives of 1:2-dihydronaphthalene. The bromination is carried out in the cold in acetic acid in presence of sodium acetate; otherwise the products are insoluble resins. By the further action of hydrogen bromide or chloride in acetic acid, the product isomerises, giving the corresponding 6-bromo- $\beta$ -naphthol, the rate of isomerisation depending on the concentration of the halogen acid; the change takes place more rapidly with hydrogen bromide than with hydrogen chloride, and in the latter case no 6-chloro- $\beta$ -naphthol is formed. The first step in the bromination is supposed to consist in the addition of two atoms of bromine to the 1:2-double bond I followed by loss of hydrogen bromide to give the bromoketone II, which in its turn is more or less easily isomerised to III. [R=Br, Me, Et.]



1-Bromo- $\beta$ -naphthol on bromination under the above conditions yields 1:1-dibromo-2-keto-1:2-dihydronaphthalene, m. p. 70°, unstable in light or on warming. Reduction with zinc and acetic acid regenerates the bromonaphthol, and by treatment with hydrogen bromide or chloride in acetic acid, 1:6-dibromo- $\beta$ -naphthol is produced. By further bromination of the ketobromide, 1:1:6-tribromo-2-keto-1:2-dihydronaphthalene, m. p. 115°, is produced, which on reduction yields 1:6-dibromo- $\beta$ -naphthol. The tribromocompound is stable to hydrogen bromide in acetic acid at the ordinary temperature.

1-Bromo-2-keto-1-methyl-1:2-dihydronaphthalene, m. p. 80°, which is stable to dilute alkali, on reduction yields 1-methyl- $\beta$ -naphthol. With silver acetate in acetic acid, the ketobromide yields 1-acetoxy-2-keto-1-methyl-1:2-dihydronaphthalene, and by the action of halogen acids as above, it isomerises to 6-bromo-1-methyl- $\beta$ -naphthol, which forms a molecular compound with its acetyl derivative,  $C_{11}H_9OBr \cdot C_{13}H_{11}O_2Br$ , m. p. 119°. 6-Bromo-1-methyl- $\beta$ -naphthol on bromination yields 1:6-dibromo-2-keto-1-methyl-1:2-dihydronaphthalene, yellow prisms.

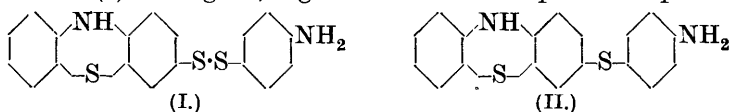
1-Ethyl- $\beta$ -naphthol, m. p. 105°, was obtained from 1-acetyl- $\beta$ -naphthol by Clemmensen's reduction method. It is unstable in the air. The acetyl derivative melts at 53°. On bromination in acetic acid in the absence of sodium acetate, 6-bromo-1-ethyl- $\beta$ -naphthol is formed, m. p. 109°; acetyl derivative, m. p. 138°. By bromination in presence of sodium acetate, the product is 1-bromo-2-keto-1-ethyl-1:2-dihydronaphthalene, m. p. 71°. By the

action of hydrogen bromide in acetic acid solution, a mixture of 6-bromo-1-ethyl- $\beta$ -naphthol and its acetyl derivative is formed, the proportions depending on the concentration of the halogen acid. 1 : 6-Dibromo-2-keto-1-ethyl-1 : 2-dihydronaphthalene, m. p. 103°, on reduction gives 6-bromo-1-ethyl- $\beta$ -naphthol. By the action of sodium nitrite and acetic acid on the ethereal solution of the last-named compound, 6-bromo-1-nitro-2-keto-1-ethyl-1 : 2-dihydronaphthalene is obtained, m. p. 112°, unstable on warming. A. E. C.

**Action of Oxalyl Chloride on Naphthols.** M. GIUA and V. DE FRANCISCIS.—(See i, 1092.)

**Ultra-violet Absorption Spectra of some Derivatives of Naphthols.** S. KOMATSU, B. MASUMOTO, and S. KUMAMOTO.—(See ii, 642.)

**Direct Sulphuration of Aniline.** H. H. HODGSON (*J. Chem. Soc.*, 1924, 125, 1855—1858).—The initial product of the action of sulphur on aniline at 170—180° is 2 : 2'-diaminodiphenyl disulphide, but increasing quantities of 4 : 4'-diaminodiphenyl disulphide are formed with rising temperature. On prolonged heating and with excess of aniline, the disulphides undergo transformation into 2 : 2'-diaminodiphenyl sulphide, 2 : 4'-diaminodiphenyl sulphide, and 4 : 4'-diaminodiphenyl sulphide. On heating with excess of sulphur, by diphenylamine condensation and further sulphuration a substance,  $C_{18}H_{14}N_2S_3$ , is produced to which the structure (I) is assigned, together with its desulphuration product,



$C_{18}H_{14}N_2S_2$  (II). The latter yields a brilliant red pigment when diazotised and coupled with  $\beta$ -naphthol. The azo- $\beta$ -naphthol derivative of 4 : 4'-diaminodiphenyl disulphide is described. Merz and Weith's thioaniline from sulphur and boiling aniline (*Ber.*, 1871, 4, 384) is 2 : 4'-diaminodiphenyl sulphide with a little 4 : 4'-diaminodiphenyl sulphide; their product in the presence of lead oxide is the latter sulphide (cf. Nietzki and Bothof, A., 1895, i, 132). Lead oxide thus promotes para-substitution (cf. Hodgson and Dix, T., 1914, 105, 952). R. B.

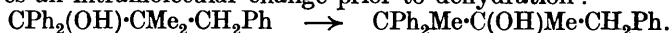
**Mechanism of Aniline Thionation [Sulphuration] with Observations on the Therapeutical Importance of the Dithioanilines.** H. H. HODGSON (*J. Soc. Dyers and Col.*, 1924, 40, 330—337).—A restatement of results already reported (preceding abstract). W. A. S.

**Transformation of Benzyl Ethers into Carbinols.** I. P. SCHORIGIN (*Ber.*, 1924, 57, [B], 1634—1637).—The action of sodium on phenyl benzyl ether at 100° (cf. Schorigin, i, 1185), leads to the production of benzhydrol in 30—35% yield. Benzyl ethyl ether and  $\beta$ -naphthyl benzyl ether similarly give phenylethylcarbinol and phenyl- $\beta$ -naphthylcarbinol. The presence of the

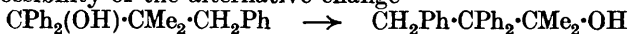
benzyl group in the ether appears to be essential for the transformation,  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{R} \rightarrow \text{CHPh}(\text{OH})\cdot\text{R}$ .  
H. W.

**Preparation of Alcohols from Aldehydes.** BADISCHE ANILIN-UND SODA-FABRIK (D.R.-P. 384351; from *Chem. Zentr.*, 1924, i, 2398).—Alcohols are prepared from aldehydes by reduction with hydrogen in the presence of activated magnesium. Examples are given of the preparation of cinnamyl alcohol, geraniol, b. p. 114—116°/13 mm., citronellol, b. p. 117—119°/17 mm.,  $\beta$ -phenylpropyl alcohol, b. p. 104—106°/10 mm., heptyl alcohol, b. p. 78—80°/12.5 mm., phenylethyl alcohol, and benzyl alcohol from the corresponding aldehydes.  
G. W. R.

**Intramolecular Change. Identification of the Products of Dehydration of  $\alpha\gamma$ -Triphenyl- $\beta\beta$ -dimethylpropan- $\alpha$ -ol.** (MME.) P. RAMART (*Compt. rend.*, 1924, 179, 400—402).—Magnesium benzyl chloride condenses readily with  $\alpha\alpha$ -diphenylethyl methyl ketone ( $\beta\beta$ -diphenylbutan- $\gamma$ -one) giving  $\alpha\gamma$ -triphenyl- $\beta$ -methylbutan- $\beta$ -ol,  $\text{CPh}_2\text{Me}\cdot\text{C}(\text{OH})\text{Me}\cdot\text{CH}_2\text{Ph}$ , m. p. 78—80°, b. p. 225—230°/3 mm., which on dehydration with a mixture of acetyl chloride and acetic anhydride, or by warming with infusorial earth, yields a mixture of two hydrocarbons, m. p. 110° and 90° respectively, which are identical with those previously obtained by the dehydration of  $\alpha\gamma$ -triphenyl- $\beta\beta$ -dimethylpropan- $\alpha$ -ol (this vol., i, 1062). The two hydrocarbons are regarded as stereoisomeric forms of  $\alpha\gamma$ -triphenyl- $\beta$ -methyl- $\Delta\gamma$ -butene,  $\text{CPh}_2\text{Me}\cdot\text{CMe}\cdot\text{CHPh}$ . Their formation from  $\alpha\gamma$ -triphenyl- $\beta\beta$ -dimethylpropan- $\alpha$ -ol involves an intramolecular change prior to dehydration:



The possibility of the alternative change

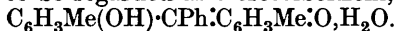


is excluded, since the  $\gamma\delta$ -triphenyl- $\beta$ -methylbutan- $\beta$ -ol, b. p. 205—210°/1 mm., obtained in 80—100% of the theoretical yield from magnesium methyl iodide and benzyl diphenylbenzylacetate, is dehydrated with difficulty, even by phosphoric anhydride, yielding a mixture of unchanged alcohol and a hydrocarbon,  $\text{C}_{23}\text{H}_{22}$ , b. p. 196—199°/3 mm., 235—236°/25 mm., which does not take up bromine.  
R. B.

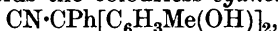
**Transformation of Cinnamaldehyde into Cinnamyl Alcohol, and the Constitution of Cubebin.** H. PAULY, H. SCHMIDT, and E. BÖHME (*Ber.*, 1924, 57, [B], 1327—1330).—The reduction of cinnamaldehyde diacetate by iron and acetic acid (Barbier and Léser, A., 1905, i, 653) depends essentially on the action of ferrous acetate on cinnamaldehyde whereby cinnamyl alcohol (diphenylurethane, m. p. 98°; phenylurethane, m. p. 91—91.5°) is produced.  $\gamma$ -Hydroxy- $\alpha\alpha$ -diphenylhexane, b. p. 130—136°/2 mm. (cf. von Braun and Kochendörfer, A., 1923, i, 1197), is formed as by-product together with resinous material. Piperonylacetaldehyde is reduced in a similar manner to  $\beta$ -piperonylallyl alcohol, m. p. 123°. This substance is not identical with cubebin, to which its structure has been assigned (cf. Mameli, A., 1922, i, 347). Cinnamaldehyde

cannot be converted into cinnamyl alcohol and cinnamic acid by Cannizzaro's reaction to an extent greater than 10%. H. W.

**Benzeins.** III. R. MEYER and E. FUNKE (*Ber.*, 1924, 57, [B], 1360—1363).—Schroeter's "dihydroxydimethyltriphenylcarbinol," prepared by the action of benzotrichloride on *o*-cresol, loses a molecular proportion of water when heated at 140—150°, and is therefore to be regarded as *o*-cresolbenzein,



It is conveniently purified through the *hydrochloride*. The *dibenzoate*, m. p. 134°, is described. Addition of hydrogen cyanide to *o*-cresolbenzein yields the colourless *cyanohydrin*,



m. p. 147°, which is converted by benzoyl chloride in the presence of sodium hydroxide into *dibenzoxydimethyltriphenylmethanecarboxylamide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{CPh}(\text{C}_6\text{H}_3\text{Me}\cdot\text{OBz})_2$ , m. p. 56°. *o*-Cresolbenzein is transformed by an excess of bromine in glacial acetic acid solution into *dibromo-o-cresolbenzein*,  $\text{C}_6\text{H}_2\text{BrMe}(\text{OH})\cdot\text{CPh}\cdot\text{C}_6\text{H}_2\text{BrMe}\cdot\text{O}\cdot\text{H}_2\text{O}$ , which loses a molecular proportion of water at 140°; it yields a blue *sodium salt*,  $\text{C}_{21}\text{H}_{15}\text{O}_2\text{Br}_2\text{Na}\cdot\text{H}_2\text{O}$ .

Dihydroxydimethyltriphenylmethane, m. p. 170°, is prepared by the condensation of benzaldehyde with *o*-cresol in the presence of sulphuric acid. H. W.

**Sulphonefluorescein and Dihydroxybenzoylbenzene-*o*-sulphonic Acid, and some of their Derivatives.** W. R. ORNDORFF and R. S. VOSE (*J. Amer. Chem. Soc.*, 1924, 46, 1896—1912).—Sulphonefluorescein has only been obtained previously in the amorphous condition and of doubtful purity. Five different methods of preparation are described. Heating resorcinol with "saccharin" and sulphuric acid at 135—140° gives a 52% yield, whilst *o*-sulphobenzoyl chloride with resorcinol at 100° gives 41% of the theoretical yield. Contrary to Fahlberg and Barge and to White (*A.*, 1896, i, 49; 1889, 709), it is obtained on heating *o*-sulphobenzoic anhydride with resorcinol at 135—140°, the reaction taking place in two stages with formation of *o*-2:4-dihydroxybenzoylbenzenesulphonic acid as intermediate product. Sulphonefluorescein separates in red needles with a blue surface colour which causes them to appear purple. When finely divided (rapid precipitation or grinding) it is bright yellow. Similarly prepared alkaline solutions of sulphonefluorescein and ordinary fluorescein are indistinguishable by the unaided eye, although the fluorescence of sulphonefluorescein is 10% more intense than that of fluorescein. In both cases the fluorescence spectrum consists of a single band extending approximately from  $\lambda$  5000 to  $\lambda$  5900, with a maximum at  $\lambda$  5249 for sulphonefluorescein and at  $\lambda$  5209 for fluorescein. Sulphonefluorescein gives rise to coloured quinonoid and colourless lactoid derivatives. Sulphonefluorescein itself does not occur in the lactoid form, but is probably a solid solution of the quinonoid form (as an oxonium or carbonium salt) and the quinonoid hydrate. It acts as a monobasic acid and forms highly coloured salts, soluble



in water with a green fluorescence: the *ammonium* salt is a dark red powder containing  $2\text{H}_2\text{O}$ ; *barium* salt, and *zinc* salt ( $7\text{H}_2\text{O}$ ), orange crystals. On reduction with zinc dust in water *sulphonefluorescein* is converted into the *zinc* salt of *sulphonefluorescein*, a nearly colourless solid which becomes yellow in air and on heating in air at  $120\text{--}125^\circ$  is changed to the orange-red salt of the *fluorescein*. *Sulphonefluorescein* forms straw-coloured crystals when isolated from the *zinc* salt. It is extremely soluble in water (in contrast to the unreduced substance). The solution in sodium hydroxide is colourless and almost non-fluorescent, but marked fluorescence appears on standing. *Sulphonefluorescein diacetate* has m. p.  $230^\circ$  (decomp.). Exposed to dry ammonia, *sulphonefluorescein* takes up 4 mols., 3 of which are lost on exposure to concentrated sulphuric acid. A *dianilino* compound, green crystals which do not melt at  $320^\circ$ , probably an inner *ammonium* salt, is formed on boiling *sulphonefluorescein* with aniline. *Sulphonefluorescein monoacetate*, dark green crystals, decomp. without melting above  $300^\circ$ , and the *monobenzoate*, yellow crystals, which dissolve in sodium hydroxide to deep purple solution, have the quinonoid structure; the *diacetate*, orange-yellow crystals, decomp.  $209^\circ$ , has the lactoid structure. *Sulphonefluorescein* reacts both with benzoyl chloride and phosphorus pentachloride to form the same *dichloride*, colourless, decomp.  $320^\circ$ , in which the chlorine atoms have replaced the hydroxyl groups. This forms a disodium (coloured) and a trisodium salt (colourless), and a *hydrate*,  $\text{C}_{19}\text{H}_{10}\text{O}_4\text{Cl}_2\text{S}\cdot\text{H}_2\text{O}$ , red, orange to greenish-orange by transmitted light. *Dibromosulphonefluorescein*, red needles with silky lustre, not melting at  $300^\circ$ , is soluble in dilute alkali forming solutions intensely green by reflected light and orange to red by transmitted light. The tetrabromo compound described by Sisley could not be made. The *diacetate*, which does not melt at  $300^\circ$ , is hydrolysed by water. It absorbs 4 mols. of ammonia and loses 3 of them over concentrated sulphuric acid. *Di-iodosulphonefluorescein*, red needles, forms a *diacetate*, short, yellow prisms, dark red at  $315^\circ$ . *o*-2 : 4-Dihydroxybenzoylbenzenesulphonic acid, prepared from the *ammonium* salt (containing  $3\text{H}_2\text{O}$ ), behaves as a monobasic acid towards methyl-red, but as dibasic to phenolphthalein. The 3 : 5-*dibromo* derivative, m. p.  $110\text{--}112^\circ$ , contains  $2\cdot5\text{H}_2\text{O}$ . It titrates as a dibasic acid with both of the above indicators.

A. C.

### Simple Synthesis of the Salts of N-Benzylideneamino-acids.

O. GERNGROSS and E. ZÜHLKE (*Ber.*, 1924, 57, [B], 1482—1489).—The sodium salts of arylideneamino-acids are obtained in almost quantitative yield by the action of an alcoholic solution of sodium ethoxide on an alcoholic solution of the ester of the amino-acid and the requisite aldehyde. Hydrolysis is ascribed to the action of sodium hydroxide formed from the ethoxide and water liberated by the partial condensation of the aldehyde and ester. The separation of the sodium salt disturbs the equilibrium established otherwise between amino ester, aldehyde, and arylideneamino ester and thus causes the completion of the reaction. The arylidene deriv-

atives are very stable towards alkali hydroxide, but are hydrolysed with great ease by acids.

*Ethyl p-nitrobenzylideneaminoacetate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , m. p.  $148^\circ$ , is readily prepared from ethyl aminoacetate and benzaldehyde in alcoholic solution. *Methyl l- $\alpha$ -p-nitrobenzylidene-amino- $\beta$ -hydroxyphenylpropionate*, m. p.  $125^\circ$ , is obtained similarly.

*Sodium benzylideneaminoacetate*, decomp.  $255\text{--}260^\circ$ , results from the action of sodium ethoxide on ethyl aminoacetate and benzaldehyde in alcoholic solution; the copper, calcium, and silver salts are described. *Sodium  $\alpha$ -benzylideneaminopropionate*, *sodium l- $\alpha$ -benzylideneamino- $\beta$ -hydroxyphenylpropionate*, decomp.  $275^\circ$  after darkening at  $240^\circ$ , and the hygroscopic sodium salt of benzylideneglycylglycine are similarly prepared.

[With J. ROTHE].—*Sodium piperonylideneaminoacetate*, m. p.  $232^\circ$ , is prepared from glycine ester hydrochloride, sodium ethoxide, and piperonal.

[With J. JODÉ].—Contrary to the observations of Puxeddu (A., 1909, i, 720), 5-o-nitrobenzylideneaminosalicylic acid is rather more resistant than the corresponding derivatives of aliphatic acids towards hydrochloric acid, but is smoothly hydrolysed by the mineral acid at varying concentrations into its components without giving indications of the formation of a hydrochloride. H. W.

**Action of Triphenylmethyl Chloride on Ethyl  $\beta$ -Aminocrotonate and Analogous Compounds.** E. BENARY and P. LORTH (*Ber.*, 1924, 57, [B], 1324—1327).—Triphenylmethyl chloride resembles acyl chlorides (A., 1923, i, 37, and previous abstracts) in its ability to react with  $\beta$ -aminocrotonic esters and related substances. It appears generally to yield only *N*-derivatives and to react only with compounds containing the unsubstituted amino group.

Ethyl  $\beta$ -aminocrotonate is converted by triphenylmethyl chloride in the presence of pyridine at  $100^\circ$  into *ethyl  $\beta$ -triphenylmethylaminocrotonate*,  $\text{CH}_3 \cdot \text{C}(\text{NH} \cdot \text{CPh}_3) : \text{CH} \cdot \text{CO}_2\text{Et}$ , m. p.  $137\text{--}138^\circ$ , which is inactive towards phenylhydrazine and is converted by alcoholic potassium hydroxide solution into *acetonetriphenylmethyl-imide*,  $\text{CMe}_2 \cdot \text{N} \cdot \text{CPh}_3$ , m. p.  $162^\circ$  (*tribromide*, m. p.  $235^\circ$  after darkening at  $230^\circ$ ).  *$\beta$ -Triphenylmethylaminocrotonanilide*, m. p.  $209^\circ$ ,  *$\beta$ -triphenylmethylaminocrotononitrile*, m. p.  $250\text{--}251^\circ$ , *N-triphenylmethylbenzoacetodinitrile*,  $\text{CPh}_3 \cdot \text{NH} \cdot \text{CPh} : \text{CH} \cdot \text{CN}$ , m. p.  $228\text{--}229^\circ$ , *N-triphenylmethylacetylacetoneamine*,  $\text{CHAc} \cdot \text{CMe} \cdot \text{NH} \cdot \text{CPh}_3$ , m. p.  $161^\circ$ , and *N-triphenylmethylbenzoylacetonamine*,  $\text{CHBz} \cdot \text{CMe} \cdot \text{NH} \cdot \text{CPh}_3$ ,

m. p.  $192\text{--}193^\circ$ , are prepared similarly. H. W.

**Preparation of Anilides and Esters.** E. DE B. BARNETT and I. G. NIXON (*Chem. News*, 1924, 129, 190—191).—Excellent yields of anilides and esters are obtained by slowly adding thionyl chloride (1 mol.) to a well-cooled equimolecular solution of the acid and phenol or primary amine in pyridine, the mixture being poured into water after 1 hour at the ordinary temperature. Phenylacetic acid gives very poor results, and the method fails with

diphenylamine and 1-aminoanthraquinone; with aliphatic alcohols, the results are uncertain. The following corrected m. p. are given: *isoeugenyl benzoate*, 106°;  $\beta$ -naphthyl *p*-nitrobenzoate, 169°; *o*-nitrophenyl *m*-nitrobenzoate, 129°; *m*-tolyl *p*-nitrobenzoate, 90°; *p*-nitrobenzanilide, 216°; *p*-nitrobenzo-*p*-nitroanilide, 274°; *p*-nitrobenzo-*o*-nitroanilide, 277°. The following compounds are new: *o*-nitrophenyl *o*-nitrobenzoate, m. p. 125°; *o*-nitrophenyl anisate, m. p. 96°; *p*-nitrophenyl *o*-nitrobenzoate, m. p. 111°; *p*-nitrophenyl *p*-nitrobenzoate, m. p. 159°; *p*-nitrophenyl anisate, m. p. 166°; *p*-nitrophenyl 3:5-dinitrobenzoate (+1 mol. acetic acid), m. p. 188°; *pyrocatechyl di-p*-nitrobenzoate, m. p. 169°; *quinyl di-p*-nitrobenzoate, m. p. 258°;  $\beta$ -naphthyl *o*-nitrobenzoate, m. p. 112°;  $\beta$ -naphthyl *m*-nitrobenzoate, m. p. 134°. R. B.

**Pressor Anæsthetics.** I. C. S. MARVEL and V. DU VIGNEAUD (*J. Amer. Chem. Soc.*, 1924, **46**, 2093—2099).—Three compounds have been prepared which contain both the grouping  $\text{Ph}\cdot\text{C}\cdot\text{C}\cdot\text{N}<$  characteristic of pressor activity (Barger and Dale, A., 1910, ii, 984) and  $\text{Ph}\cdot\text{CO}\cdot\text{O}\cdot\text{C}\cdot\text{C}\cdot\text{NR}_2$ , characteristic of local anæsthetic power (Pyman, T., 1908, **93**, 1796; 1917, **111**, 1121). Two of the compounds, 2-diethylamino-1-hydrindyl *p*-aminobenzoate hydrochloride and 2-di-*n*-butylamino-1-hydrindyl *p*-aminobenzoate hydrochloride, have only a very slight anæsthetic action, that of the diethylamino compound being the greater, whilst the third compound,  $\alpha$ -phenyl- $\beta$ -diethylaminoethyl *p*-aminobenzoate hydrochloride (phenylprocaine), has a strong anæsthetic action and a low toxicity. None of these three compounds showed any appreciable pressor action, and there is no record of the pressor activity of a similar compound containing both linkings,  $\text{CH}_3\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}(\text{CO}_2\text{Ph})\cdot\text{CH}_2\cdot\text{NMe}_2$  (Pyman, T., 1908, **93**, 1796), or of the benzoyl esters of ethyl- and diethyl-mydrinate.

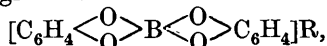
2-Bromo-1-hydroxyhydrindene (Pope and Read, T., 1912, **101**, 762) readily condenses with *p*-nitrobenzoyl chloride in benzene solution in the presence of pyridine, giving 2-bromo-1-hydrindyl *p*-nitrobenzoate, m. p. 131°, which could not be condensed with diethylamine. Diethylamine and 2-bromo-1-hydroxyhydrindene readily give 2-diethylamino-1-hydroxyhydrindene, b. p. 165—167°/15 mm.,  $d^{20}_D$  1.043,  $n^{20}_D$  1.5393, which readily turns red in the air, in 56—60% yield (hydrochloride, m. p. 175°); it condenses with *p*-nitrobenzoyl chloride in the presence of pyridine giving (yield 50—59%) 2-diethylamino-1-hydrindyl *p*-nitrobenzoate, yellow crystals, m. p. 85°. The hydrochloride, m. p. 210—212°, is obtained by condensing in the absence of pyridine, and on reduction with iron yields 2-diethylamino-1-hydrindyl *p*-aminobenzoate hydrochloride, m. p. 206° (yield 48%). Similarly, di-*n*-butylamine and 2-bromo-1-hydroxyhydrindene in benzene solution give in 63—65% yield, 2-di-*n*-butylamino-1-hydroxyhydrindene, rapidly turning red, b. p. 155—165°/7 mm.,  $n^{20}_D$  1.493, which with *p*-nitrobenzoyl chloride in benzene solution gives, in 60—67% yield, 2-di-*n*-butylamino-1-hydrindyl *p*-nitrobenzoate hydrochloride, m. p. 155—156°. Reduction of the hydrochloride with iron in neutral solution gives, in 72—

85% yield, 2-di-n-butylamino-1-hydrindyl *p*-aminobenzoate, m. p. 74° (*hydrochloride*, m. p. 229—230°, *hydrogen sulphate*, m. p. 200—201°).  $\omega$ -Chloroacetophenone and diethylamine in benzene solution yield  $\omega$ -diethylaminoacetophenone, b. p. 148—152°,  $n_D^{20}$  1.5180, which on reduction by Adams and Voorhees' method (A., 1922, ii, 558) yields  $\alpha$ -phenyl- $\beta$ -diethylaminoethyl alcohol,  $n_D^{20}$  1.507, and this with *p*-nitrobenzoyl chloride in benzene solution gives (yield 89—91%)  $\alpha$ -phenyl- $\beta$ -diethylaminoethyl *p*-nitrobenzoate *hydrochloride*, m. p. 155—156° (*nitrate*, m. p. 161.5°, insoluble in water) from which by reduction with iron at 45—50° is obtained  $\alpha$ -phenyl- $\beta$ -diethylaminoethyl *p*-aminobenzoate, m. p. 88—89° (*hydrochloride*, m. p. 210—212°). R. B.

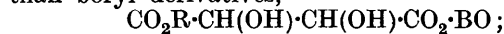
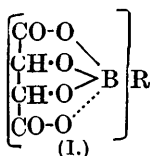
**Preparation of Acid Anhydrides.** E. DE B. BARNETT and J. W. COOK (*Chem. News*, 1924, 129, 191).—Acid anhydrides may be obtained in about 70% of the theoretical yield by treating the acid (2 mols.), in ice-cold pyridine, with thionyl chloride (1 mol.) and keeping the mixture at the ordinary temperature for 3 hrs. The anhydrides are isolated either by pouring into cold dilute hydrochloric acid, or by fractional distillation of the reaction mixture. Almost quantitative yields are obtained with *p*-toluic acid and anisic acid, but the method fails with palmitic, stearic, phenylacetic, *o*- and *p*-nitrobenzoic, and 3:5-dinitrobenzoic acids. R. B.

**Internally Complex Borates.** A. ROSENHEIM and H. VERMEHREN (*Ber.*, 1924, 57, [B], 1337—1342).—The constitution of a series of borates is most simply explained by regarding them as complex salts of tervalent boron in which the element, as in the anion  $\text{BF}_4^-$ , has the co-ordination number 4.

Analysis of the *sodium*, *potassium*, *lithium*, *calcium* (+6H<sub>2</sub>O), and *copper* salts of Jahn's "borodisalcyclic acid" are in agreement with the structure  $\text{R}[\text{C}_6\text{H}_4\langle\text{O}\rangle\text{B}\langle\text{O}\rangle\text{C}_6\text{H}_4]$ . Jahn's formulation does not explain the apparent impossibility of forming salts containing two equivalents of alkali. *o*-Hydroxytoluic acid forms well-crystallised compounds with borates of which the *calcium* salt,  $\text{C}_{32}\text{H}_{24}\text{O}_{12}\text{B}_2\text{Ca}\cdot 5\text{H}_2\text{O}$ , is described. Glycollic acid yields salts of the formula  $\left[\begin{array}{c} \text{CH}_2\text{O} \\ \text{CO-O} \end{array} \rangle \text{B} \langle \begin{array}{c} \text{O-CH}_2 \\ \text{O-CO} \end{array} \right] \text{R}$ , of which the *potassium*, *ammonium*, *sodium*, and *calcium* compounds are described. Analyses of the pyrocatechol-boric acid derivatives (*sodium*, *potassium*, and *ammonium* salts) agree with the formula

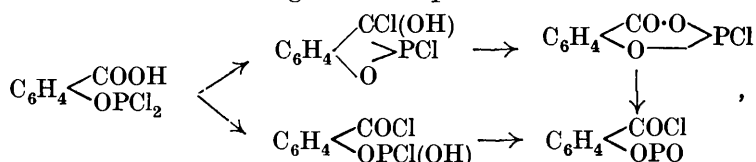


but not with the structure  $\text{R}_2\text{H}_2\text{B}_2\text{O}_4(\text{C}_6\text{H}_4\text{O}_2)_3$ , assigned by Böseken (A., 1918, i, 219). Similarly, the tartaric acid borates are considered to be internally complex salts (I) rather than boryl derivatives,



like considerations are extended to the antimonyl compounds. H. W.

**Reaction between the Chlorides of Phosphorus and *o*-, *m*-, and *p*-Hydroxybenzoic Acids.** L. ANSCHÜTZ (*Annalen*, 1924, 439, 265—275).—The constitution of the product of the interaction of phosphorus trichloride and salicylic acid (R. Anschütz and Emery, A., 1887, 947; 1890, 53) is *o*-phosphitobenzoyl chloride,  $\text{O:PO}\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ . With *p*-toluidine in absolute ether, followed by hydrolysis with hot water, salicyloyl-*p*-toluidide is formed. Traces of phosphine, phosphorous and phosphoric acids were also detected. To test the suggestion that the reaction between phosphorus pentachloride and salicylic acid (cf. R. Anschütz, A., 1906, i, 502) proceeds in two stages, the second being the interaction of phosphorus oxychloride and salicyloyl chloride, the two latter were heated together in equimolar proportions, but no evidence of combination was forthcoming. The alternate suggestion, that with either the trichloride or the pentachloride of phosphorus the phenolic hydroxyl group of the salicylic acid is first attacked, is supported by the ready interaction of phenol and phosphorus trichloride. The following scheme is put forward :



with the corresponding scheme for the interaction between the acid and phosphorus pentachloride.

By heating *m*- or *p*-hydroxybenzoic acid (1 mol.) with phosphorus trichloride (2 mols.) at  $120^\circ$ , no *m*- or *p*-phosphitobenzoyl chloride was obtained. The *o*-phosphitobenzoyl chloride exists in a comparatively stable state, probably owing to a saturation of the partial valency,  $\text{C}_6\text{H}_4\begin{array}{l} \text{<CCl}\cdot\text{O} \\ \text{>O}-\text{P}\cdot\text{O} \end{array}$ . Unsuccessful attempts were

made to synthesise phosphitobenzene,  $\text{PhOPO}$ , from phenoxyphosphorus dichloride and anhydrous oxalic acid at  $80$ – $90^\circ$ , and by the action of benzoic acid on the dichloride at  $90^\circ$ , whereby benzoyl chloride and phenyl benzoate were isolated on subsequent distillation under diminished pressure.

A. E. C.

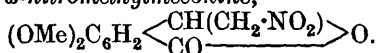
**Reduction Product of *o*-Nitromandelonitrile.** G. HELLER (*Ber.*, 1924, 57, [B], 1501—1502).—In reply to Reissert and Hessert (this vol., i, 853), the author slightly modifies his original conception (A., 1906, i, 585), but considers the reduction-product of *o*-nitromandelonitrile to be a double hydrochloride of hydroxylaminomandelamide and dihydroxylaminomandelonitrile instead of hydroxylaminomandelamide hydrochloride as proposed by these authors.

H. W.

[**Benzilic Acid Transformation.**] A. SCHÖNBERG (*Ber.*, 1924, 57, [B], 1396—1397; cf. Schönberg and Keller, A., 1923, i, 928).—A reply to the criticisms of Lachman (this vol., i, 653).

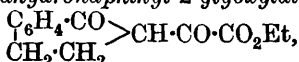
H. W.

**Nitromethylmeconine.** W. RODIONOW and S. KAGAN (*Ber.*, 1924, 57, [B], 1442—1443).—With the object of preparing 5 : 6-dimethoxy-2- $\omega$ -nitrovinylbenzoic acid, opianic acid has been condensed with nitromethane. The product, m. p. 166—167°, is, however, stable towards bromine or permanganate, and insoluble in cold but soluble in hot sodium carbonate solution. It is therefore regarded as  $\omega$ -nitromethylmeconine,



H. W.

**Preparation of  $\gamma$ -o-Carboxyphenyl-*n*-butyric Acid.** W. HÜCKEL and E. GOTH (*Ber.*, 1924, 57, [B], 1285—1290).—Ethyl 1-keto-1 : 2 : 3 : 4-tetrahydronaphthyl-2-glyoxylate,



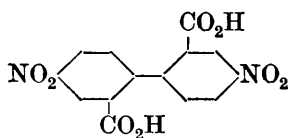
m. p. 48°, prepared in 90% yield by the condensation of 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene with ethyl oxalate in the presence of ethyl-alcoholic sodium ethoxide, loses carbon monoxide when heated and yields ethyl 1-hydroxy-3 : 4-dihydronaphthalene-2-carboxylate, m. p. 34° (the corresponding copper salt, m. p. 196°, and the free acid, m. p. 93° [decomp.] are described). The ester does not readily undergo fission under the influence of alkali but is transformed by a solution of sodium in boiling cyclohexanol into  $\gamma$ -o-carboxyphenyl-*n*-butyric acid, m. p. 139—140°, in 20% yield; 3 : 4-dihydronaphthalene-2-carboxylic acid, m. p. 120°, tetrahydro- $\beta$ -naphthoic acid, m. p. 94°, and 1-naphthol-2-carboxylic acid, m. p. 188°, are simultaneously formed.  $\gamma$ -o-Carboxyphenyl-*n*-butyric acid is smoothly hydrogenated in the presence of spongy platinum to  $\gamma$ -o-carboxycyclohexyl-*n*-butyric acid, m. p. 92—94°. 1-Naphthol-2-carboxylic acid is hydrogenated to 1-hydroxy-5 : 6 : 7 : 8-tetrahydronaphthalene-2-carboxylic acid, m. p. 164—165° (cf. Schroeter, A., 1922, i, 130), which is reduced further with difficulty to 1-hydroxy-decahydronaphthalene-2-carboxylic acid, m. p. 167—168°. Catalytic hydrogenation of ethyl 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate gives a mixture of ethyl decahydronaphthalene-2-carboxylate (cf. Borsche and Lange, this vol., i, 32) and ethyl 1-hydroxydecahydronaphthalene-2-carboxylate; hydrolysis of the latter ester yields 1-hydroxydecahydronaphthalene-2-carboxylic acid, m. p. 198°.

H. W.

**Phenylsuccinic Acid Series. VIII. Resolution of *r*-Diphenylsuccinanilic and *r*-Diphenylsuccino-*p*-toluidic Acids into their Optical Antipodes.** H. WREN and R. E. BURROWS (*J. Chem. Soc.*, 1924, 125, 1934—1937).—*r*-Diphenylsuccinanilic acid has been resolved with quinine, the quinine *l*-diphenylsuccinanilate separating first from alcoholic solutions. 1-Diphenylsuccinanilic acid, m. p. 193—194° (decomp.), resolidifying and melting again at 224—226°, has  $[\alpha]_D^{20} -338.2^\circ$  in acetone,  $[\alpha]_D^{25} -350.3^\circ$  in ethyl alcohol, and on treatment with alcoholic hydrogen chloride yields 1-diphenylsuccinanil, m. p. 196—196.5°,  $[\alpha]_D^{25} -117.6^\circ$  (in chloroform), slight racemisation taking place when the dehydration is

effected with acetyl chloride at  $40^{\circ}$ . On heating at  $195^{\circ}$ , *l*-diphenylsuccinanilic acid is converted quantitatively into *r*-diphenylsuccinanil (Wren and Williams, T., 1918, 113, 838). *d*-Diphenylsuccinanilic acid has  $[\alpha]_D^{25} +337.8^{\circ}$  in acetone; *d*-diphenylsuccinanil, m. p.  $196-196.5^{\circ}$ , has  $[\alpha]_D^{25} +121.0^{\circ}$  in chloroform. *r*-Diphenylsuccino-*p*-toluidic acid was similarly resolved, the quinine salt of the *d*-acid separating in the first fractions (along with racemate). *l*-Diphenylsuccino-*p*-toluidic acid, m. p.  $209-209.5^{\circ}$ ,  $[\alpha]_D^{25} -329.5^{\circ}$  (in acetone) with alcoholic hydrogen chloride yields *l*-diphenylsuccino-*p*-tolil, m. p.  $178^{\circ}$ ,  $[\alpha]_D^{25} -131.5^{\circ}$  (in acetone),  $[\alpha]_D^{25} -136.3^{\circ}$  (in chloroform), which shows a similar change of crystalline form to the *r*-tolil (Wren and Williams, *loc. cit.*). *d*-Diphenylsuccino-*p*-toluidic acid has  $[\alpha]_D^{25} +330.0^{\circ}$  in acetone. *d*-Diphenylsuccino-*p*-tolil,  $[\alpha]_D^{25} +131.3^{\circ}$ , is rapidly racemised by traces of alkali. As with the active diphenylsuccinic anhydrides (Wren and Still, T., 1915, 107, 1457), the specific rotations of the active anils and tolils are much lower than those of the acids from which they are derived. R. B.

**Diphenic Acid Series. II.** H. W. UNDERWOOD, jun., and E. L. KOCHMANN (*J. Amer. Chem. Soc.*, 1924, 46, 2069—2078; cf. this vol., i, 176).—The transformation of diphenic acid or its anhydride into fluorenone-4-carboxylic acid previously described is a general reaction for diphenic acid derivatives containing no substituents in the rings. On heating with sulphuric acid, the dichloride, diamide, diethyl ester, dimethyl ester, monoethyl ester, monomethyl ester, monoamide, and imide (obtained by heating the monoamide with glacial acetic acid and acetic anhydride at  $130-140^{\circ}$ ) of diphenic acid are converted into the corresponding fluorenone-4-carboxylic acid derivatives, but hydrolysis occurs in every case, and no conclusions could be drawn regarding the lability of the groups in the side-chains of the diphenic acid derivatives. Isomerisation of phenanthridone does not take place under these conditions, and *pp'*-dinitrophenic acid, which does not form an



anhydride, gives no ketone acid, facts which suggest a *trans*-structure for the dinitro-acid (annexed formula), and also that the meta-orientating nitro group loosens the hydroxyl in the carboxyl group (since *m*-nitrobenzoyl chloride is more reactive than benzoyl chloride) and strengthens the bond holding the hydrogen atom in the latter group as well as that holding the ring hydrogen meta to the nitro group.

Phenoldiphenic acid is not isomerised by heat or fuming stannous chloride, but carbon dioxide is evolved at  $260-270^{\circ}$ . Phenoldiphenic acid does not give an oxime under the conditions employed for phenolphthalein. In the oxidation of phenanthrene with sodium or potassium dichromate and sulphuric acid, the maximum yield (56%) of phenanthraquinone was obtained with a 350% excess of potassium dichromate. Oxidation of phenanthraquinone gave a maximum yield of diphenic acid (76%) with a 750% excess of potassium dichromate in glacial acetic acid.

R. B.

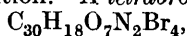
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**Diphenieins from Resorcinol and Substituted Diphenic Anhydrides. Structure of certain Diphenyl Derivatives.**

H. ADKINS, E. F. STEINBRING, and (MISS) E. PICKERING (*J. Amer. Chem. Soc.*, 1924, **46**, 1917—1924; cf. A., 1923, i, 578).—Anhydrides of substituted diphenic acids may be prepared when acetamido groups are present in the 4:4'- or 6:6'-positions, but not when the substituents are nitro or hydroxy groups. The views of various investigators as to the reason for this are discussed. The formation or non-formation of anhydrides is apparently dependent on whether the substituents cause the diphenyl rings to be superimposed or extended (cf. Kaufler, A., 1907, i, 307). The rings are apparently superimposed in the case of diphenic acid and of the amino derivatives of diphenyl but are extended in the case of the nitro or hydroxy derivatives. The 4:4'-diaminodiphenic acid, m. p. 250—251°, of Hummel, is shown to be impure. A method is described which furnishes the hydrochloride in fine, white needles, and the free acid as a white solid of m. p. 265°. 4:4'-Diacetamidodiphenic anhydride, white needles which do not melt, is prepared by refluxing the above hydrochloride with acetic anhydride. Heating with ammonia converts it into 4:4'-diacetamidodiphenamic acid,  $C_{18}H_{17}O_5N_3$ . Treatment with sodium hypobromite transforms the last into 2:7-diacetamidophenanthridone,

$$\begin{array}{c} \text{CO}-\text{NH} \\ \text{NHAc} \cdot \text{C}_6\text{H}_3 \cdot \text{C}_6\text{H}_3 \cdot \text{NHAc} \end{array}$$

which darkens but does not melt at 350°. 4:4'-Diaminodiphenic acid forms a *tetrazonium chloride*, which on hydrolysis gives 4:4'-dihydroxydiphenic acid, pure white crystals, m. p. 278° (Schmidt and Scholl describe it as yellow, m. p. 271—272°). 6:6'-Diaminodiphenic acid hydrochloride, prepared by reducing the corresponding dinitro derivative, forms white crystals; the free acid has m. p. 312—313° (decomp.). 6:6'-Diacetamidodiphenic anhydride is much less stable than the 4:4'-isomeride and readily forms the acid on exposure to moisture. Condensation of these substituted anhydrides with resorcinol in the presence of zinc chloride at 110° results in diphenieins. When higher temperatures are employed, the 4:4'-diacetamidodiphenic anhydride appears to change to the isomeric fluorenone-4-carboxylic acid, which condenses to form a fluorescein derivative having a free carboxyl group. This rearrangement is not possible in the case of the 6:6'-derivative. All these condensation products are fluorescent, although not so markedly as fluorescein. The condensation product of 4:4'-diacetamidodiphenic anhydride and resorcinol at 110° is a light red powder, which dissolves in dilute alkali to a reddish-brown solution with green fluorescence. On acetylation with boiling acetic anhydride, a dark red solid is obtained, insoluble in sodium carbonate solution. Similar acetylation of the condensation product made at 160—180° gives a substance,  $C_{40}H_{32}O_{12}N_2$ , soluble in sodium carbonate. Condensation of the 6:6'-derivative with resorcinol at 110° gives a similar fluorescent product which after acetylation is insoluble in sodium carbonate solution. A *tetrabromo* compound,



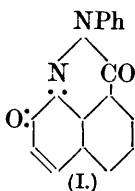


was prepared from a condensation product of the 4:4'-anhydride at 135–150°; it forms a red, amorphous powder. The results obtained by Underwood and Kochmann (this vol., i, 176) are criticised.

A. C.

**The Three Isomeric Naphthol-1:8-dicarboxylic Acids and their Azo Derivatives. Abnormal Coupling Reactions in the Naphthalene Series.** K. DZIEWOŃSKI and T. STOLYHWO (*Ber.*, 1924, 57, [B], 1540–1546).—4- and 2-Naphthol-1:8-dicarboxylic acids are distinguished from the 3-hydroxy compound by the marked mobility of the carboxyl group in the ortho or para position to the hydroxyl; this suffers replacement during coupling with diazonium chlorides.

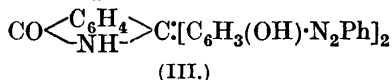
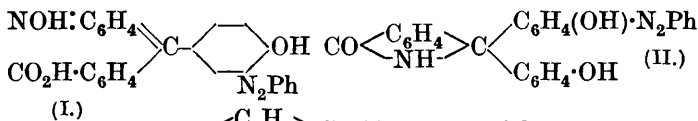
2-Naphthol-1:8-dicarboxylic anhydride, m. p. 350–351°, is prepared by fusing 2-sulphonaphthalene-1:8-dicarboxylic acid (cf. Dziewoński and Stolyhwo, this vol., i, 1178) with potassium hydroxide. Its constitution is established by its difference from the other two known naphtholdicarboxylic acids. It couples with benzenediazonium chloride in weakly alkaline solution to form 8-benzeneazo-7-naphthol-1-carboxylic acid, which is isomerised by warm acids into the quinonehydrazone form and thence into 1:8-phenylpyridazone-2-naphthaquinone (I), m. p. 201–202°; the latter substance is reconverted into 8-benzeneazo-7-naphtholcarboxylic acid by treatment with alkali hydroxide. 4-Naphthol-1:8-dicarboxylic acid and benzenediazonium chloride yield 8-benzeneazo-5-naphthol-1-carboxylic acid, which is transformed by acids into 1:8-phenylpyridazone-4-naphthaquinone, m. p. 238–240°.



3-Naphthol-1:8-dicarboxylic acid, on the other hand, couples normally with benzenediazonium chloride, yielding 4-benzeneazo-3-naphthol-1:8-dicarboxylic anhydride, m. p. 260–261°.

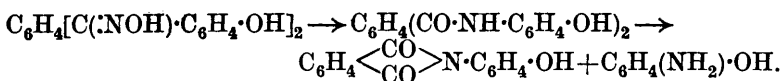
H. W.

**Phthaleins. V. Constitution of the Oximic and Iminic Compounds of Phenolphthalein.** B. ODDO and D. CURTI (*Gazzetta*, 1924, 54, 572–581).—Coupling with diazonium salts having proved of advantage in determining the structure of the phthaleins (A., 1913, i, 1110; 1916, i, 87), this method is now applied to the oxime and imide of phenolphthalein. Into the former it is found possible to introduce only one azo group, whereas the imide gives both mono- and bis-azo compounds. This difference in behaviour is regarded as due to the structure being respectively quinonoid and lactoid in the two cases, the azo compounds having the following formulæ:

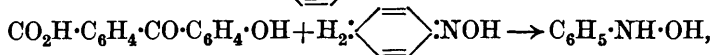
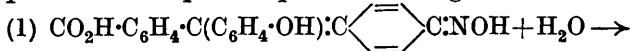


which are in agreement with the formation of a diacetyl compound by the first, and of a triacetyl compound by each of the last two.

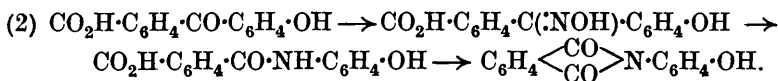
When prepared in the ordinary way, phenolphthaleinoxime is always accompanied by *p*-hydroxyphthalanil (cf. Piutti, A., 1886, 1026), which Meyer (A., 1899, i, 707) obtained by the action of excess of hydroxylamine hydrochloride on the oxime in aqueous alcoholic solution and regarded as formed by way of the dioxime, in accordance with the scheme :



Since this reaction does not take place when free hydroxylamine is used in place of its hydrochloride, the author considers that the hydrochloric acid first effects hydrolysis, the formation of *p*-hydroxyphthalanil and *p*-aminophenol resulting as follows :



which undergoes ready isomerisation into *p*-aminophenol.



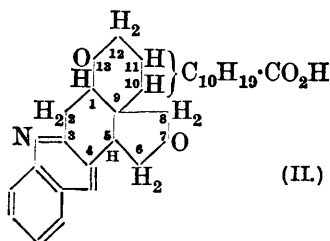
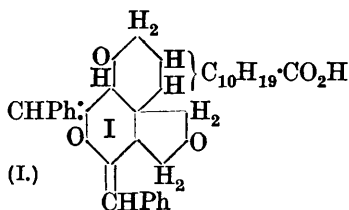
The fact that dichlorophenolphthalein yields, not a bisazo, but only a monoazo compound (cf. Consonno and Apostolo, A., 1921, i, 346), may be due to the presence of the two chlorine atoms; it cannot, therefore, be taken as a proof of the quinonoid constitution of phenolphthalein and its salts.

*Benzeneazophenolphthaleinoxime*, I, m. p. 202°, forms a *diacetyl* compound, m. p. 231—233°. Treatment of the oxime with excess of benzenediazonium chloride results in the formation of a yellow, crystalline compound, m. p. 230—231°. *Benzeneazophenolphthaleinimide*, II, pale yellow crystals, has m. p. 248—250°, and its *triacetyl* derivative, orange-yellow crystals, m. p. 183°. *Bisbenzeneazophenolphthaleinimide*, III, forms small, brownish-yellow crystals, m. p. 270—272°, and its *triacetyl* derivative, a brown, crystalline powder, m. p. 207—208°. T. H. P.

**Bile Acids. VI. Condensation of some Ketonic Acids of the Cholic Acid Group with Aromatic Aldehydes and with Isatin.** W. BORSCHKE and R. FRANK (*Ber.*, 1924, 57, [B], 1373—1380).—Condensation between aldehydes and certain acids of the cholic acid group occurs only when the carbonyl group is present in ring I (see formula) and the number of aldehyde residues entering the molecule does not exceed the number of methylene groups vicinal to the ketonic group. The failure of similar groups present in other rings to give a similar reaction is not explained. Analogously, condensation with *o*-aminobenzaldehyde or isatic acid to derivatives of quinoline occurs only when the group  $\cdot\text{CO}\cdot\text{CH}_2\cdot$

is present in ring I. Further examples are thus afforded of the failure of "typical" reactions when applied to complex compounds.

Dehydrocholic acid is converted by benzaldehyde in the presence of aqueous sodium hydroxide into *dibenzylidenedehydrocholic acid* (+H<sub>2</sub>O) (I), m. p. above 195°. *Dianisylidenedehydrocholic acid* is also described. With *o*-aminobenzaldehyde dehydrocholic acid yields 7:13-diketo-3:4(2':3')-quinocholanic acid (II), m. p. 296° (the corresponding *hydrochloride*, m. p. 264° after softening at 208°, *methyl ester*, m. p. 215°, and *dioxime*, m. p. 317°, are



described), whereas with isatin it gives 7:13-diketo-4-carboxy-3:4(2':3')-quinocholanic acid, m. p. 297° (decomp.) after previous darkening and softening [*dimethyl ester*; *monoxime*, m. p. 299° (decomp.); *monosemicarbazone*, m. p. 298° (decomp.)]. Dehydrodeoxycholic acid yields *dibenzylidenedehydrodeoxycholic acid*, C<sub>38</sub>H<sub>44</sub>O<sub>4</sub>·2H<sub>2</sub>O, m. p. (indefinite) above 95°, *di-p-chlorobenzylidenedehydrodeoxycholic acid*, 7-keto-3:4(2':3')-quinocholanic acid, m. p. 253°, and 7-keto-4'-carboxy-3:4(2':3')-quinocholanic acid, m. p. 298°. 7:13-Diketocholanic acid could not be caused to react with benzaldehyde, anisaldehyde, *p*-chlorobenzaldehyde, *o*-aminobenzaldehyde, or isatin, whilst bilianic or deoxybilianic acid did not condense with benzaldehyde, anisaldehyde, *o*-aminobenzaldehyde, or isatin. Pyrodeoxybilianic acid (cf. Wieland and Kulenkampff, A., 1921, i, 112) gives *benzylidenepyrodeoxybilianic acid*, C<sub>30</sub>H<sub>38</sub>O<sub>4</sub>, m. p. 244—245° (+CH<sub>3</sub>·CO<sub>2</sub>H, m. p. 238°), *anisylidene-pyrodeoxybilianic acid*, m. p. 270° after softening at 265°, *p-chlorobenzylidenepyrodeoxybilianic acid*, m. p. 282—284° after darkening at 260°, and *p-nitrobenzylidenepyrodeoxybilianic acid*, m. p. 296° (decomp.). *Pyroisodeoxybilianic acid* yields *anisylidenepyroisodeoxybilianic acid*, C<sub>31</sub>H<sub>40</sub>O<sub>5</sub>, m. p. 181°, and *p-nitrobenzylidenepyroisodeoxybilianic acid*, m. p. indefinite, 150—190°. H. W.

**Constitution of the Bile Acids. VII. A Ketone, C<sub>22</sub>H<sub>32</sub>O, from Deoxybilianic Acid.** W. BORSCHKE (*Ber.*, 1924, 57, [B], 1435—1436).—Distillation of deoxybilianic acid under 10—15 mm. pressure yields pyrodeoxybilianic acid (cf. Wieland and Kulenkampff, A., 1921, i, 112) and small quantities of a *ketone*, C<sub>22</sub>H<sub>32</sub>O, m. p. 143°. The latter substance combines with bromine, gives an *oxime*, m. p. 169—170°, and a 2-nitro-4-cyanophenylhydrazone, m. p. 258—259° (decomp.). The *anisylidene* derivative has m. p. 215—219°. H. W.

**Constitution of the Bile Acids. VIII. Acylation of Cholic Acid.** W. BORSCHÉ [with R. FRANCK, O. WEICKERT, and F. HALLWASS] (*Ber.*, 1924, **57**, [B], 1620—1622).—Triacetylcholic acid,  $C_{30}H_{46}O_8$ , m. p.  $257^\circ$  (cf. Wieland and Boersch, A., 1921, i, 178) is prepared in 30—35% yield by the action of acetyl chloride on a solution of cholic acid in glacial acetic acid; the *methyl* ester has m. p.  $180$ — $181^\circ$ . Acylation of cholic acid in the presence of pyridine gives mainly monoacyl derivatives even when an excess of the reagent is used. The following compounds are described: *methyl 3-carbethoxycholate*, m. p.  $147^\circ$ , which is oxidised by chromium trioxide in acetic acid solution to *methyl carbethoxyreductodehydrocholate*, m. p.  $125^\circ$ ; *methyl 3-anisoylcholate*, m. p.  $188^\circ$ ; *methyl 3-p-nitrobenzoylcholate*, m. p.  $217$ — $218^\circ$ , and thence *methyl p-nitrobenzoylreductodehydrocholate*, m. p.  $191$ — $192^\circ$ . H. W.

**Dioximes. XIX.** L. AVOGADRO (*Gazzetta*, 1924, **54**, 545—550).—Since the addition of ammonia or aniline to the oxides of the nitriles of  $\alpha$ -oximino-acids,  $NOH:CR:CNO$ , yields the labile forms of aminoglyoximes,  $NOH:CR:C(NH_2):NOH$ , or phenylaminoglyoximes,  $NOH:CR:C(NHPh):NOH$  (A., 1923, i, 472, 855), the action of magnesium methyl iodide on these nitrile oxides should give the analogous forms of the methylglyoximes. The existence of a labile form of phenylmethylglyoxime (cf. A., 1923, i, 1137; this vol., i, 294) may therefore be expected. Such a labile  $\alpha$ -phenylmethylglyoxime is formed by reducing phenylmethylglyoxime peroxide by means of zinc dust and acetic acid, but, owing to the readiness with which it undergoes isomerisation into the ordinary or  $\beta$ -form, it is best prepared as nickel compound by treating the reduced peroxide in alcoholic solution with nickel acetate and ammonia solutions, the nickel being eliminated by means of dilute hydrochloric acid in presence of ether.

Stable or  $\beta$ -phenylmethylglyoxime forms a *diacetyl* compound,  $NOAc:CMc:CPh:NOAc$ , m. p.  $88$ — $89^\circ$ , and a *dibenzoyl* compound, m. p.  $171^\circ$ .  $\alpha$ -Phenylmethylglyoxime, m. p.  $140$ — $141^\circ$ , is converted into the  $\beta$ -form by traces of extraneous substances or, more rapidly, by heating either alone above its melting point or with dilute acetic acid. It dissolves without coloration in dilute sodium hydroxide solution, and is reprecipitated unchanged by carbon dioxide. Concentrated sulphuric acid converts it into the anhydride, *phenylmethylfurazan*,  $O \begin{smallmatrix} \nearrow N:CMc \\ \searrow N:CPh \end{smallmatrix}$ , a colourless liquid

heavier than water and of characteristic odour. When treated either with nitrogen peroxide or with sodium hypochlorite in sodium hydroxide solution, it undergoes dehydrogenation to phenylmethylglyoxime peroxide. The *nickel* compound, probably  $C_9H_8O_2N_2Ni$ , forms a yellowish-green precipitate but was not obtained pure. The *diacetyl* derivative has m. p.  $100$ — $101^\circ$  with previous softening, and the *dibenzoyl* derivative, m. p.  $120^\circ$ .

T. H. P.

**Dioximes. XX.** G. RUGGERI and G. RIGOLI (*Gazzetta*, 1924, **54**, 550—556).—In view of the fact that the two forms of phenyl-

glyoxime behave differently towards nitrogen peroxide, concentrated sulphuric acid, diazonium salts, nickel, copper, and cobalt salts, etc., diversity in their behaviour towards reducing agents also is to be expected (cf. A., 1923, i, 471, 856); since only the  $\beta$ -modification is a true dioxime, this alone should yield phenylethylenediamine on reduction. Feist and Arnstein (A., 1895, i, 274) obtained this diamine by the action of sodium and alcohol on phenylglyoxime, but the latter probably consisted of a mixture of the  $\alpha$ - and  $\beta$ -forms, and the product obtained differs from Purgotti's so-called phenylethylenediamine, formed by the action of zinc and hydrochloric acid on  $\omega$ -cyanobenzylamine (A., 1895, i, 345). The authors find that this amine is not reducible under such conditions, so that the benzoyl compound and chloroplatinate described by Purgotti are not derivatives of phenylethylenediamine. When heated with either sodium and alcohol or hydriodic acid and red phosphorus,  $\omega$ -cyanobenzylamine yields ammonia, hydrocyanic acid, benzaldehyde, and other products not identified; with sodium amalgam in aqueous alcoholic solution kept neutral by means of acetic acid, traces of phenylethylenediamine are obtainable, but, in the cold, aluminium amalgam in ethereal solution, stannous chloride and hydrochloric acid, or red phosphorus and hydriodic acid are without sensible action.

Either modification of phenylglyoxime yields phenylethylenediamine when treated with sodium in alcoholic solution, but benzoyl cyanide oxime is probably formed as an intermediate product. By hydriodic acid and red phosphorus, both forms of the glyoxime are converted into  $\omega$ -aminoacetophenone, which is formed also from benzoyl cyanide oxime under the same conditions; the use of this reducing agent with oximino compounds is preferable to that of others as it furnishes directly hydriodides of amino derivatives, these being sparingly soluble and readily separable. Reduction of both  $\alpha$ - and  $\beta$ -phenylglyoxime in ethereal solution by means of aluminium amalgam gives diphenylpyrazine, which is a product of the condensation of  $\omega$ -aminoacetophenone; similar reduction of benzoyl cyanide oxime gives cyanobenzylamine.

$\omega$ -Aminoacetophenone phenylhydrazone,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{N}_2\text{HPh}$ , has m. p.  $153^\circ$  (slight decomp.), and benzoyl- $\omega$ -aminoacetophenone,  $\text{NHBz}\cdot\text{CH}_2\text{Bz}$ , m. p.  $125^\circ$ .

Cyanobenzylamine forms a *picrate*,  $\text{NH}_2\cdot\text{CHPh}\cdot\text{CN}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , m. p.  $160$ – $161^\circ$  (decomp.), and a benzoyl derivative, m. p.  $159$ – $160^\circ$ .  
T. H. P.

**s- and as-Dimethyl[cyclo]pentanones.** A. HALLER and R. CORNUBERT (*Compt. rend.*, 1924, 179, 315–320).—In continuation of previous work (cf. A., 1914, i, 291; also A., 1923, i, 92 for complete list of papers) it is confirmed that the dimethylcyclopentanone obtained by the alkylation of 1-methylcyclopentan-5-one is the unsymmetrical ketone by the preparation both of the symmetrical 1 : 4-dimethylcyclopentan-5-one from ethyl 1 : 4-dimethylcyclopentan-5-one-4-carboxylate, b. p.  $121^\circ/32$  mm.,  $d_4^{15}$  1.0157,  $n_D^{15}$  1.4431 (the preparation of which from ethyl cyclopentanonecarboxylate is

outlined), and of the unsymmetrical 1:1-dimethylcyclopentan-5-one obtained by Blanc (A., 1908, i, 654); and by the preparation of their oximes, semicarbazones, and benzylidene derivatives. The physical constants of the two dimethyl ketones have been redetermined; the 1:1- has b. p. 143—144° (corr.)/740 mm.,  $d_4^{18}$  0.8938,  $n_D$  1.4322; the 1:4-, b. p. 147°/744 mm.,  $d_4^{17}$  0.8918,  $n_D$  1.4312. Condensed with benzaldehyde in the presence of hydrochloric acid the symmetrical ketone yields a compound  $C_{21}H_{22}O_2$ , m. p. 129.5°, obtained by the loss of 1 mol. of water from 2 mols. of benzaldehyde and 1 mol. of ketone; it is the lower homologue of the corresponding cyclohexanone compound,  $C_{22}H_{24}O_2$  (cf. A., 1920, i, 390). The unsymmetrical ketone yields benzylidene-1:1-dimethylcyclopentan-5-one, m. p. 36°, together with a brown, viscous residue having a b. p. corresponding with that of the compound,  $C_{21}H_{22}O_2$ . The oxime of 1:4-dimethylcyclopentan-5-one is an uncrystallisable liquid, b. p. 11.5°/33 mm., and has a camphor-like odour when hot; that of the unsymmetrical ketone has m. p. 65.5° (Blanc, *loc. cit.*, gives 69°). A study of the semicarbazone of the product of alkylation of 1-methylcyclopentan-5-one shows that this consists mainly of the 1:1-dimethyl- together with a small quantity of the 1:4-dimethyl-cyclopentan-5-one. J. W. B.

### Conversion of Hydroaromatic into Aromatic Compounds.

**I. Action of Chlorine on 5-Chloro-1:1-dimethyl- $\Delta^4$ -cyclohexen-3-one.** L. E. HINKEL (*J. Chem. Soc.*, 1924, 125, 1847—1855).—The difference between the action of chlorine and bromine on the same hydroaromatic compound previously recorded (T., 1920, 117, 1296) has now been observed in the case of 5-chloro-1:1-dimethyl- $\Delta^4$ -cyclohexen-3-one (cf. Crossley and Renouf, T., 1914, 105, 169), which on treatment with chlorine in cold chloroform solution yields 4:5-dichloro-1:1-dimethyl- $\Delta^5$ -cyclohexen-3-one, a liquid with a camphoraceous odour, b. p. 120—121°/13 mm. The dichloroketone on heating loses hydrogen chloride and is converted into 5-chloro-o-3-xylenol (Hinkel and others, T., 1923, 123, 2968). Alcoholic potassium hydroxide converts it into the same compound, whilst on heating with sulphuric acid 6-chloro-o-4-xylenol, m. p. 98° (benzoate, m. p. 42°), is obtained. The structure of the last is established by its synthesis from 5-nitro-o-3-xylidine, which is converted by the diazo reaction into 6-chloro-4-nitro-o-xylene, m. p. 101°, giving on reduction 6-chloro-o-4-xylidine, m. p. 72°, from which 6-chloro-o-4-xylenol is obtained by diazotisation of the sulphate. On treatment of the dichlorohexenone with chlorine in chloroform solution there is obtained 3:4:5-trichloro-1:1-dimethyl- $\Delta^4$ -cyclohexen-3-one, m. p. 61°, the main product of the action of chlorine on 5-chloro-1:1-dimethyl- $\Delta^4$ -cyclohexen-3-one at the ordinary temperature. On treatment with alcoholic potassium hydroxide, the trichlorohexenone yields 4-chloro-3:5-dihydroxy-o-xylene, m. p. 123° (dibenzoate, m. p. 137°); sulphuric acid converts it into 5:6-dichloro-o-4-xylenol, m. p. 102° (benzoate, m. p. 94°), which with chlorine in light petroleum yields the trichloro-o-4-xylenol, m. p. 182.5° (benzoate, m. p. 120°), obtained by the action

of chlorine on 6-chloro-*o*-4-xylene; whilst on heating with quinoline at 170°, 4:5-dichloro-*o*-3-xylene, m. p. 95° (benzoate, m. p. 128°, tetrachloro derivative,  $C_8H_6OCl_4$ , m. p. 127.5°), is obtained.

The liquid from which the trichlorohexenone separates on distillation yielded a fraction, b. p. 145—155°/13 mm., from which 2:4:5:6-tetrachloro-1:1-dimethylcyclo- $\Delta^4$ -hexen-3-one, m. p. 91°, was obtained, probably formed from the dichloroketone by chlorination and loss of hydrogen chloride, since the trichloroketone is not further attacked by chlorine in boiling chloroform solution. On treatment with alcoholic potassium hydroxide, the tetrachloroketone yields a dichloroxylenol,  $C_8H_8OCl_2$ , m. p. 119—120° (benzoyl derivative, m. p. 129°), whilst with sulphuric acid a mixture of trichloro-*o*-3- and -*o*-4-xylenols is obtained.

R. B.

**Phenyl  $\gamma$ -Chloropropyl Ketone.** J. B. CONANT, J. B. SEGUE, and W. R. KIRNER (*J. Amer. Chem. Soc.*, 1924, **46**, 1882—1885).—The ketone was synthesised from trimethylene glycol in the following steps:  $OH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH \rightarrow CH_2Cl \cdot CH_2 \cdot CH_2 \cdot OH \rightarrow CH_2Cl \cdot CH_2 \cdot CH_2 \cdot Br \rightarrow CH_2Cl \cdot CH_2 \cdot CH_2 \cdot CN \rightarrow CH_2Cl \cdot CH_2 \cdot CH_2 \cdot COPh$ . The yields for successive steps were 65%, 70%, 42%, and 50%, giving an over-all yield on the glycol of about 9% of the theoretical. Phenyl  $\gamma$ -chloropropyl ketone, m. p. 19—20°, prepared by the interaction of ethereal solutions of  $\gamma$ -chlorobutyronitrile and magnesium phenyl bromide at 0°, has no lachrymatory properties, in contrast to the  $\alpha$ -chloroketones. The best method of identifying the ketone is through its condensation product with phenylhydrazine,

1:3-diphenyltetrahydropyridazine,  $NPh \cdot CH_2 \cdot CH_2 \cdot CH : CPh \cdot NH$ , m. p. 138—139°. Benzoylcyclopropane was obtained in good yield by the action of potassium hydroxide in methyl alcohol on the ketone at the ordinary temperature; the tendency to form this cyclopropane may account for the low yield in the last step of the synthesis.

A. C.

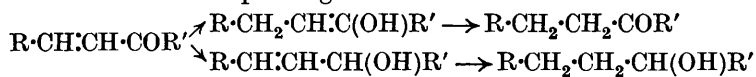
**CC-Phenylalkylmethane Dialkylsulphones.** CHEMISCHE FABRIK VON HEYDEN AKT.-GES. (D.R.-P. 376472; from *Chem. Zentr.*, 1924, i, 965).—The sulphones described are obtained by condensing ketones with alkylmercaptans and oxidising the resulting mercaptols. The following compounds are mentioned:  $\alpha\alpha$ -diethylthiol- $\alpha$ -phenylpropane,  $CPhEt(SET)_2$ , a light yellow oil, which on oxidation yields  $\alpha\alpha$ -diethylsulphone- $\alpha$ -phenylpropane,  $CPhEt(SO_2Et)_2$ , crystals, m. p. 115—116°;  $\alpha\alpha$ -diethylsulphone- $\alpha$ -phenyl- $\Delta^7$ -butylene, crystals, m. p. 136—138°.

G. W. R.

**Indene Series.** F. ISHIWARA (*J. pr. Chem.*, 1924, [ii], **108**, 194—199).—2-Bromo-1-hydroxyhydrindene is obtained by boiling indene dibromide with magnesium carbonate in aqueous acetone (cf. Krämer, A., 1891, 205). It is oxidised by dichromate and sulphuric acid to 2-bromo-1-hydrindone, which decomposes explosively at 152°. When boiled with sodium acetate in glacial acetic acid, the latter affords 2-acetoxy-1-hydrindone, b. p. 128°/0.1 mm., 137°/1.0 mm., 165°/17 mm., 172°/19 mm., which reduces cold Fehling's

solution, and is hydrolysed by potassium carbonate in aqueous methyl alcohol to 2-hydroxy-1-hydrindone, m. p. 40—40.5° (sinters at 38°), b. p. 95°/0.05 mm., 128—133°/1 mm., which also reduces Fehling's solution, and decomposes on keeping; the *phenylurethane* has m. p. 133—134° after sintering at 129°. It yields 1 : 2-diketohydrindene (cf. T., 1912, **101**, 232) on oxidation with chromic acid, and the *osazone* of this diketone, m. p. 222—223° (cf. Gabriel, A., 1897, i, 61), together with the substance  $C_{15}H_{14}ON_2$ , m. p. 123—124°, on treatment with phenylhydrazine. F. G. W.

**Formation of Alcohols and Hydrocarbons by the Catalytic Hydrogenation of Aromatic and Aliphatic-Aromatic Carbonyl Compounds.** F. STRAUS and H. GRINDEL (*Annalen*, 1924, **439**, 276—312).—The products of hydrogenation of several carbonyl compounds in acetone solution by means of palladium and hydrogen at the ordinary temperature and pressure, have been examined. Only those compounds in which the carbonyl group is in the  $\alpha$ -position to the benzene ring can be ultimately reduced to the saturated hydrocarbon, the other carbonyl compounds being reduced to the carbinol. The stages of the reduction may be followed graphically in some cases, by the different rates of absorption of hydrogen. This method of preparation of some of the intermediate reduction products is superior to other reduction methods, for example, the preparation of  $\alpha\gamma$ -diphenylpropyl alcohol. In some cases, mixtures are produced, especially where addition of hydrogen may take place at the 1 : 2- or 1 : 4-positions. Styryl methyl ketone and distyryl ketone, for instance, are only partly reduced to the corresponding carbinols :



and the methoxy derivatives behave similarly.

Phenyl styryl ketone on reduction yields progressively, phenyl  $\beta$ -phenylethyl ketone,  $\alpha\gamma$ -diphenylpropyl alcohol, and  $\alpha\gamma$ -diphenylpropane. *p*-Anisyl *p*-methoxystyryl ketone yields *p*-anisyl  $\beta$ -*p*-methoxyphenylethyl ketone, m. p. 42—43° (*oxime*, m. p. 116—118.5°, *semicarbazone*, m. p. 148—149°), and finally  $\alpha\gamma$ -di-*p*-methoxyphenylpropane, m. p. 45—46°. With 2 mols. of hydrogen a mixture of the saturated ketone, carbinol, and hydrocarbon are produced. Acetophenone yields phenylmethylcarbinol and, more slowly, ethylbenzene, whilst the *p*-methoxy derivative yields a mixture of acetylanisole, anisylmethylcarbinol, and ethylanisole. Benzophenone yields benzhydrol and, finally, diphenylmethane, whilst *pp*-dimethoxybenzophenone with 1 mol. of hydrogen yields a mixture of the ketone and dianisylmethane. Styryl methyl ketone yields phenylethyl methyl ketone, and the *p*-methoxy derivative yields a mixture of *p*-methoxyphenylethyl methyl ketone and  $\delta$ -*p*-methoxyphenylbutan- $\beta$ -ol. Phenyl propenyl ketone gives progressively, phenylpropylcarbinol, m. p. 14.5°, and *n*-butylbenzene. Distyryl ketone is partly reduced to the corresponding carbinol, and di-*p*-methoxystyryl ketone is more completely reduced to



di-*p*-methoxyphenylethyl ketone; the carbinol could not be isolated. Cinnamylideneacetophenone gave  $\alpha$ -diphenylpentane in good yield.

Cinnamaldehyde on exhaustive hydrogenation yielded a mixture of hydrocinnamaldehyde and propylbenzene; with 1 mol. of hydrogen, it gave a mixture of propylbenzene, hydrocinnamyl alcohol, and unchanged aldehyde. Cinnamyl alcohol gave the saturated alcohol and a small amount of the hydrocarbon. By exhaustive hydrogenation of cinnamaldehyde by Skita's method in alcoholic solution, the saturated alcohol was the chief product, with a little hydrocinnamaldehyde; with 1 mol. of hydrogen, some of the cinnamaldehyde was unchanged.

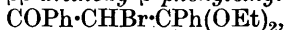
Benzaldehyde with 2 mols. of hydrogen yields toluene and with 1 mol. a mixture of benzyl alcohol, toluene, and benzaldehyde.

A. E. C.

**Use of Aliphatic Acid Anhydrides in the Preparation of Ketones by the Friedel and Crafts Reaction.** C. R. NOLLER and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, **46**, 1889—1896).—The poor results obtained by various workers on substituting acetic anhydride for acetyl chloride in the preparation of ketones by the Friedel and Crafts method is due to the fact that only 1 mol. or less of aluminium chloride was employed. Using 2 or more mols. of the latter, the condensations proceed regularly and smoothly and 80—90% of the theoretical yields (calculated on the results of the first distillation of the crude product) are readily obtainable. Some 19 ketones were prepared, and the only variation in conditions found necessary was an occasional change in the temperature or length of time of reaction. In the case of compounds containing alkoxy groups the splitting of the ether linking is less liable to occur than with acetyl chloride, and rarely amounts to more than 5% of the reaction mixture; using anhydrides other than acetic anhydride, it does not occur at all. In the case of *p*-methyl- $\omega$ -chloroacetophenone, the yield is comparatively low; it is better in this case to use chloroacetyl chloride than the chloroanhydride. Incidentally, the methoxyacetophenone prepared by Fries (A., 1921, i, 423) is shown to be 2-methoxy- $\alpha$ -naphthyl methyl ketone and the following compounds are described: 4-Methoxy-3-methylacetophenone, m. p. 26—26.5°, b. p. 116°/3 mm., 273.5°/744 mm.; 2-methoxy-5-methylbutyrophenone, b. p. 123°/3 mm., 276.5°/739 mm.,  $d_4^{20}$  1.0258,  $n_D^{20}$  1.5250; 4-methoxy-3-methylvalerophenone, m. p. 31—33°, b. p. 151.5°/4 mm., 308.7°/744 mm.

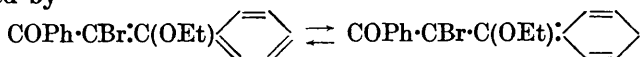
A. C.

**Multiple Forms (Pseudopolymorphism) of Derivatives of Phenylethylene, R'R''C:CR'''Ph.** A. GILLET (*Bull. Soc. chim. Belg.*, 1924, **33**, 377—388; cf. this vol., i, 651).—Phenyl  $\beta$ -ethoxystyryl ketone, CPhCH:CPh·OEt, when treated with 1 mol. of bromine in carbon disulphide solution at 0°, and then with a solution of anhydrous potassium acetate in absolute alcohol, gives phenyl  $\alpha$ -bromo- $\beta\beta$ -diethoxy- $\beta$ -phenylethyl ketone,



m. p. 72°, in 90% yield. The latter compound, when heated at

190—200°/3 mm., gives *phenyl α-bromo-β-ethoxystyryl ketone*,  $\text{COPh}\cdot\text{CBr}\cdot\text{C(OMe)}\cdot\text{C}_6\text{H}_5$  in 70% yield. This compound can be obtained in three isomeric and crystallographically distinct forms, all pale yellow crystals, m. p. (a) 64—65°, (b) 73°, (c) 75.5—76.5°, solubility in methyl alcohol at 18°, (a) 17.1, (b) 8.5, and (c) 6.4%. (a) and (b) are unstable and change, slowly on keeping and rapidly on seeding, into (c). The isomeride (a) is formed usually on spontaneous crystallisation of the molten compound, but each of the isomerides can be prepared by seeding the liquid with the required form. The author considers that the existence of two of these isomerides is due to "quinonoid transposition," probably represented by



One of the forms is almost certainly one of two *cis-trans* isomerides and the second geometrical isomeride is being sought. *Phenyl α-bromo-β-methoxystyryl ketone*, prepared similarly to the ethoxy compound, has been obtained in two crystallographically distinct forms, both pale yellow, m. p. (a) 63.5—64.5°, (b) 71—72°, solubility at 19° in petroleum of b. p. 80—85°, (a) 2.84, (b) 2.24%, in ethyl alcohol, (a) 9.9 at 19°, (b) 6.1% at 17°; (a) is obtained by spontaneous crystallisation, but is easily converted by seeding into the more stable (b); (a) can also be obtained by seeding the molten compound with the corresponding isomeride of phenyl dibromo- and di-iodo-styryl ketone. A third (*cis-trans*) isomeride, m. p. 101° (approx.), has been isolated. The isomerides (a) and (b) of the methoxy compound correspond with (b) and (c) of the ethoxy compound, respectively. *Phenyl α-bromo-β-propoxystyryl ketone* has been obtained in only one form, m. p. 49°, corresponding with the isomeride (a) of the ethoxy compound. Many examples of similar polymorphism already recorded are collected in the paper.

F. G. M.

**Correction of the Constitutional Formula of Benzylbenzoin.** A. GARCÍA BANUS and J. PASCUAL VILA (*Anal. Fis. Quím.*, 1924, 22, 262—263; cf. A., 1922, i, 734).—The product of the reaction of equimolecular portions of magnesium benzyl chloride and benzil, to which the formula  $\text{CH}_2\text{Ph}\cdot\text{CPh}\cdot\text{CH}_2\text{Ph}\cdot\text{OH}$  was originally assigned, is now shown to be identical with the benzyl ether of benzoin.

G. W. R.

**Action of Nitroxyl on α-Ketoaldehydes. IX. Preparation of α-Ketoformhydroxamic Acids.** C. GASTALDI (*Gazzetta*, 1924, 54, 589—592; cf. A., 1923, i, 1236; this vol., i, 733).—The addition of nitroxyl to the α-ketoaldehydes, phenylglyoxal,  $\text{Ph}\cdot\text{CO}\cdot\text{CH(OH)}_2$ , and *p*-tolylglyoxal,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH(OH)}_2$ , follows the normal course (cf. Angeli, A., 1902, i, 78, 765; 1904, i, 172; 1905, ii, 385). As a reagent for furnishing nitroxyl, benzenesulphonhydroxamic acid yields better results than nitrohydroxylaminic acid. Thus, addition of sodium hydroxide solution to a methyl-alcoholic solution of phenylglyoxal and benzenesulphon-

hydroxamic acid, cooled in ice, yields almost pure sodium benzoyl-formhydroxamate.

*p*-Methylbenzoylformhydroxamic acid,  $C_6H_4Me \cdot CO \cdot CO \cdot NH \cdot OH$  or  $C_6H_4Me \cdot CO \cdot C(OH) \cdot NOH$ , prepared from *p*-tolylglyoxal and benzene-sulphonhydroxamic acid, has m. p.  $112^\circ$  (decomp.); its sodium salt deflagrates when heated. Its  $\alpha$ -oxime,

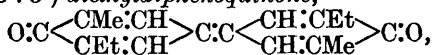
$C_6H_4Me \cdot C(:NOH) \cdot CO \cdot NH \cdot OH$  or  $C_6H_4Me \cdot C(:NOH) \cdot C(OH) \cdot N \cdot OH$ , pale red needles, m. p.  $186^\circ$  (decomp.), gives a deep red coloration with ferric chloride; the yellow nickel compound is soluble, and the olive-green copper compound insoluble, in dilute acetic acid. The  $\beta$ -oxime, obtained by heating the  $\alpha$ -modification with dilute acetic acid in presence of nickel acetate and decomposing the nickel compound formed by means of dilute sulphuric acid, m. p.  $183^\circ$  (decomp.), gives a violet-red coloration with aqueous ferric chloride; the nickel compound is a voluminous, brick-red precipitate, and the copper compound an olive-green precipitate.

T. H. P.

**Preparation of Higher Ketones.** B. HELFERICH and L. KEINER.—(See i, 1166.)

**Diphenoquinones.** K. VON AUWERS and G. WITTIG (*Ber.*, 1924, 57, [B], 1270—1275).—Monohydric phenols containing substituents in the two ortho positions to the hydroxy group resemble *vic*-*m*-xylenol (Auwers and Markovitz, A., 1905, i, 219; 1908, i, 629) in being oxidisable to diphenoquinones if the substituents are alkyl groups, but not if phenyl or chlorine is present. The oxidation is best effected by short, vigorous treatment of the phenols with chromium trioxide in boiling glacial acetic acid solution.

3-Ethyl-*o*-cresol, b. p.  $91\text{--}92^\circ/12$  mm. (*phenylurethane*, m. p.  $147\text{--}148^\circ$ ), prepared by the reduction of 3-acetyl-*o*-cresol with amalgamated zinc and hydrochloric acid, is oxidised to 3 : 3'(3 : 5')-dimethyl-5 : 5'(5 : 3')-diethyldiphenoquinone,



m. p.  $153^\circ$ , which is reduced by zinc dust and dilute acetic acid to 4 : 4'-dihydroxy-3 : 3'-dimethyl-5 : 5'-diethyldiphenyl, m. p.  $148^\circ$  (*di-benzoate*, m. p.  $171\text{--}172^\circ$ ). 3-Ethyl-*o*-cresol and nitrous acid yield 5-nitroso-3-ethyl-*o*-cresol, m. p.  $135\text{--}136^\circ$ , which is oxidised by potassium ferrieyanide to 5-nitro-3-ethyl-*o*-cresol, m. p.  $133\text{--}134^\circ$ .

3-Propenyl-*o*-cresol, b. p.  $113\text{--}115^\circ/12$  mm., m. p.  $41\text{--}42^\circ$ , obtained by the action of concentrated aqueous potassium hydroxide on 3-allyl-*o*-cresol at  $150^\circ$ , is reduced by sodium and boiling alcohol to 3-propyl-*o*-cresol, b. p.  $105\text{--}107^\circ/12$  mm. (*phenylurethane*, m. p.  $110\text{--}111^\circ$ ). The substance is also prepared by the reduction of 3-propionyl-*o*-cresol, b. p.  $127\text{--}129^\circ/15$  mm., m. p.  $22\text{--}23^\circ$  (*semicarbazone*, m. p.  $202^\circ$ ) by Clemmensen's method, the ketone being obtained together with 5-propionyl-*o*-cresol, m. p.  $83\cdot5\text{--}84^\circ$ , by the action of aluminium chloride at  $120^\circ$  on *o*-tolyl propionate, b. p.  $99^\circ/12$  mm. The cresol is transformed by

nitrous acid into 5-nitroso-3-propyl-o-cresol, m. p. 93—94°, and is oxidised by chromic acid to 3:3'(3:5')-dimethyl-5:5'(5:3')-dipropyl-diphenyl-quinone, bluish-green crystals, m. p. 136—137°; the latter is reduced to 4:4'-dihydroxy-3:3'-dimethyl-5:5'-dipropyl-diphenyl, m. p. 123.5—125° (diacetate, m. p. 95—96°).

4-Chloro-2-ethylphenol, b. p. 118—119°/12 mm., is converted into the corresponding acetate, b. p. 132°/12 mm., which is isomerised by aluminium chloride at 120° to 4-chloro-6-acetyl-2-ethylphenol, b. p. 145—146°/12 mm. (the sodium salt and the semicarbazone, m. p. 229—230°, are described). The ketone is reduced by zinc and hydrochloric acid to 1-chloro-2:6-diethylphenol, b. p. 128—132°/12 mm., m. p. 31—31.5°, which is converted by sodium and boiling alcohol into 2:6-diethylphenol, m. p. 37.5—38°. 3:5:3':5'-Tetraethyldiphenyl-quinone forms bluish-red needles, m. p. 142—143°. H. W.

**Naphthaquinone Derivatives.** SOCIÉTÉ ANONYME DES MATIÈRES COLORANTES ET PRODUITS CHIMIQUES DE SAINT-DENIS, A. WAHL and R. LANTZ (Brit. Pat. 206142).—A 4-arylamino-1-arylimino- $\beta$ -naphthaquinone is obtained, together with an equivalent of a 1-arylamino- $\beta$ -naphthol, by the action of a primary aromatic amine on a 1-arylimino- $\beta$ -naphthaquinone. By the further action of the same, or another, amine, the 1-arylimino group of the naphthaquinone produced may be replaced, when the aryl radical of the amine is different from that of the 1-arylimino group, by an arylimino group derived from the amine, the 4-arylamino group remaining unattacked. In this way, compounds containing the same or different aryl radicals attached to the 1-imino and 4-amino nitrogen atoms can be prepared. By carrying out the reaction in presence of air and a catalyst such as lime, baryta, or cupric oxide, the 1-arylimino- $\beta$ -naphthol is reoxidised to the 1-arylimino- $\beta$ -naphthaquinone, so that the latter under these conditions is completely converted into the 4-arylamino-1-arylimino derivative. The same result is obtained by treating a 1-arylamino- $\beta$ -naphthol with an amine in presence of air and one of the above catalysts. Under these conditions, the products are isolated as pure crystalline derivatives of the metal present. The 4-arylamino-1-arylimino- $\beta$ -naphthaquinones are hydrolysed by dilute acids to 4-arylimino-2-hydroxy- $\alpha$ -naphthaquinones and are isomerised when boiled in glacial acetic acid to 2-arylamino-4-arylimino- $\alpha$ -naphthaquinones. 4-Phenylamino-1-phenylimino- $\beta$ -naphthaquinone, brown-red crystals, 4-p-toluidino-1-p-tolylimino- $\beta$ -naphthaquinone, brown prisms, 4-phenylamino-1-p-tolylimino- $\beta$ -naphthaquinone, 4-o-methoxyphenylamino-1-o-methoxyphenylimino- $\beta$ -naphthaquinone, and the copper compounds of the first and last of these are described. F. G. W.

**Isomerism of Menthol and neoMenthol.** G. VAVON and A. COUDERC (*Compt. rend.*, 1924, 179, 405—408).—d-neoMenthol is readily prepared by the reduction of l-menthone with hydrogen in the presence of platinum black, using acetic acid, ether, or

alcohol as solvent. The velocity of reduction decreases with the solvents in the order named. The separation of the isomerides in the product, ( $[\alpha]_{578} +4^\circ$  to  $+10^\circ$ ) is effected by esterification with succinic anhydride and crystallisation of the *neomenthyl* succinate from aqueous alcohol and aqueous acetic acid to constant rotatory power. *d-neoMenthyl succinate*, m. p.  $68^\circ$ , has  $[\alpha]_{578} +34.70^\circ$  (in chloroform), and on hydrolysis yields a *d-neomenthol*, b. p.  $107-108^\circ/20$  mm.,  $d_4^{25}$  0.897,  $n_D^{25}$  1.4594,  $[\alpha]_{578} +21.95^\circ$  (cf. Pickard and Littlebury, T., 1912, **101**, 109). The velocity of esterification of *neomenthol* with acetic and butyric acids is much less than that of *menthol*, the difference being more pronounced at lower temperatures and in the presence of a catalyst (hydrochloric acid). Similarly, the hydrolysis of *neomenthyl* hydrogen succinate by alcoholic potassium hydroxide proceeds much more slowly than that of the corresponding *menthol* ester. These differences, and the preponderating formation of *neomenthol* in the reduction of *menthone*, are readily explained by the theory of steric hindrance, when *neomenthol* is regarded as the *cis*- and *menthol* as the *trans*-form of 1-methyl-4-*isopropyl*hexan-3-ol.

R. B.

**Dependence of Optical Rotatory Power on Chemical Constitution. V. Rotatory Dispersions of *d*-Camphorimide, *d*-Camphorbenzylimide, Benzyl-*d*-camphoramic Acid, and their Derivatives.** B. K. SINGH and A. C. BISWAS (*J. Chem. Soc.*, 1924, **125**, 1895—1898).—The rotatory powers of a number of benzyl and substituted benzyl derivatives of *d*-camphorimide and of *d*-camphoramic acid for the wave-lengths 5893, 5780, 5461, have been studied in benzene, ether, chloroform, acetone, ethyl alcohol, and methyl alcohol solution. Substitution of the benzyl group for the imido-hydrogen atom increases the rotatory power. In all cases except camphor-*o*-nitrobenzylimide, the rotatory power is lowest in benzene, which has the lowest dielectric constant, but no regular relation was disclosed between the rotatory powers and the dielectric constants of the other solvents. The rotatory dispersion of *d*-camphorimide and its benzyl derivative is highest in benzene where the rotatory power is lowest, whilst the converse is the case with camphor-*o*-nitrobenzylimide, and it appears that in this series the rotatory power and the rotatory dispersion are influenced in opposite directions by the change from an aliphatic solvent to benzene. The relative magnitude of the rotatory power of camphorbenzylimide and its three nitro derivatives varies with the nature of the solvent. Frankland's rule holds only in chloroform and in benzene, whilst Cohen's rule is valid except in chloroform and in methyl alcohol, the deviation in the latter solvent being very marked. The rotation is increased considerably when the ring structure is opened by hydrolysis, and the following values for  $[M]_D$  in ethyl alcohol are given: camphorimide,  $10.99^\circ$ ; camphoramic acid,  $89.45^\circ$  ( $\alpha$ );  $119.4^\circ$  ( $\beta$ ); camphorbenzylimide,  $30.19^\circ$ ; benzylcamphoramic acid,  $99.88^\circ$ ; camphor-*m*-nitrobenzylimide,  $31.92^\circ$ ; 3-nitrobenzylcamphoramic acid,  $106.70^\circ$ .

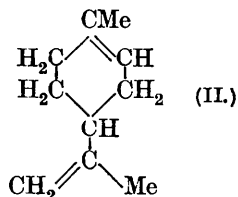
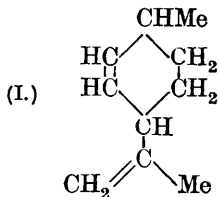
*d*-Camphor-*o*-nitrobenzylimide, m. p. 131°, from benzyl chloride and camphorimide in alcoholic potassium hydroxide solution, on hydrolysis with potassium hydroxide yields a dark greenish-brown and a brown *o*-nitrobenzyl-*d*-camphoramic acid. *d*-Camphor-*m*-nitrobenzylimide, m. p. 69°, similarly prepared, on hydrolysis yields two colourless *m*-nitrobenzylcamphoramic acids, m. p. 134° and 179°. *d*-Camphor-*p*-nitrobenzylimide similarly yields a brown-orange form, decomp. 250°, and a deep purple-brown form, m. p. above 325°, of *p*-nitrobenzoyl-*d*-camphoramic acid. *d*-Benzylcamphoramic acid has m. p. 149°. R. B.

**Valency. IV. Absorption Spectra of Camphor, Benzylicidenecamphor, and Camphorquinone. Optical Evidence of Two Types of Conjugation.** T. M. LOWRY and H. S. FRENCH (*J. Chem. Soc.*, 1924, 125, 1921—1927).—Quantitative observations of the absorption spectra of camphor and of camphorquinone in alcohol, benzene, and cyclohexane show that the position of the band is almost independent of the solvent and concentration. On passing from camphor to camphorquinone the band at 2880 Å. (alcoholic solution) is shifted to 4650 Å., whilst the molecular extinction coefficient remains practically constant at  $\log \epsilon = 1.5$ . The development of colour is thus not accompanied by any increase in absorptive power. In benzylicidenecamphor, the molecular extinction coefficient becomes  $\log \epsilon = 4.32$ , but the wave-length remains at 2900 Å., being practically unaltered by the extension of the conjugated system. It is concluded that benzylicidenecamphor and camphorquinone represent two different types of conjugation, and that some additional factor beyond a long conjugated chain is required to produce visible colour. In the quinones, this may be supplied by the presence of two doubly-linked oxygen atoms at the end of a conjugated chain. R. B.

**Carbylamines. IX. Reaction of Phenylcarbylamine with Pernitrosocamphor.** M. PASSERINI (*Gazzetta*, 1924, 54, 540—544).—Phenylcarbylamine and pernitrosocamphor interact slowly in the cold, giving nitrous oxide and *d*-bornylene-6-carboxylic anilide. The acid, formed when the anilide is hydrolysed, rapidly decolorises permanganate, readily unites with bromine, and is reduced to *d*-camphane-6-carboxylic acid by hydrogen in presence of platinum black. *d*-Bornylene-6-carboxylic acid (annexed formula), has m. p. 65—66°,  $[\alpha]_D^{25}$  (in ethyl acetate) +66.2°; anilide, m. p. 124—125°. *d*-Camphane-6-carboxylic acid has m. p. 72—74°,  $[\alpha]_D^{25}$  +11.2°, and yields a sparingly soluble silver salt. T. H. P.

**Diprene, a new Terpene.** O. ASCHAN (*Annalen*, 1924, 439, 221—232).—Isoprene (250 g.) was left in an atmosphere of carbon dioxide in a sealed vessel in the dark for 10 years, and then the residual isoprene (76%) was removed. The viscous, rubber-like residue possessed an odour resembling that of rancid olive oil and contained an oil (7.6 g.) volatile in steam. The non-volatile residue

on distillation under diminished pressure yielded an oil, b. p. below  $80^{\circ}/77$  mm. (7 g.). These two fractions were combined and distilled over sodium under normal pressures, whereby after two distillations, three main fractions were obtained: (1) b. p.  $171\text{--}172^{\circ}$ ,  $d_4^{20}$  0.8535 (4.2 g.); (2) b. p.  $173\text{--}173.5^{\circ}$ ,  $d_4^{20}$  0.8552 (1.6 g.); (3) b. p.  $175.5\text{--}178^{\circ}$ ,  $d_4^{20}$  0.8603 (1.2 g.). The first fraction is a new hydrocarbon,  $C_{10}H_{16}$ , which the author names *diprene*. It gives no reaction for sylvestrene, and no nitrosite, as does dipentene. It yields a *dihydrochloride*, m. p.  $51.5\text{--}52^{\circ}$ , which has an odour of juniper oil, and is not identical with that obtained from dipentene



(m. p.  $49\text{--}50^{\circ}$ ) or terpinene (m. p.  $51\text{--}52^{\circ}$ ).  $\beta$ -Terpinene, which closely resembles diprene in physical properties, yields a crystalline tetrabromide (Wallach, A., 1908, i, 813), but by the action of bromine on an alcoholic solution of diprene at  $-10^{\circ}$ , an oily tetrabromide is formed, stable towards permanganate, which will not crystallise, and may be a mixture of several stereoisomerides.

It is suggested that in the polymerisation of isoprene to form a dimeric compound, a dipentene would be more likely to be formed than a terpinene, at low temperatures, as the former would involve a smaller structural alteration than the latter. The new terpene probably possesses formula I, which isomerises to dipentene (II) on heating or further distillation. The higher boiling fraction (3) probably contains some dipentene, produced by isomerisation, which would account for the fact that the hydrochloride obtained from this fraction is difficult to crystallise. A. E. C.

### Heat of Combustion of Natural and "Sulphuric Acid"

**Caoutchouc.** F. KIRCHHOF and O. MATULKE (*Ber.*, 1924, 57, [B], 1266—1270).—The heat of combustion of plantation pale crêpe rubber is approximately 10,700 cal. per gram. Its empirical formula is  $(C_5H_8)_n$ , and is therefore identical with that of Congo and synthetic isoprene caoutchouc. The heat of combustion of "sulphuric acid caoutchouc" (cf. Kirchhof, A., 1921, i, 116; 1922, i, 562) is markedly lower than that of natural rubber and depends on the degree of internal polymerisation. The empirical formula of "sulphuric acid caoutchouc," calculated to ash- and sulphate-free material, corresponds very closely with the expression,  $(C_{100}H_{160})_nSO_2$ . The action of sulphuric acid on resin-free, natural caoutchouc in different media is accompanied by evolution of heat which is approximately proportional in amount to the content of undissolved caoutchouc; the latter is partly depolymerised and oxidised. The transformation (internal polymerisation) is, however, attended by absorption of heat. H. W.

**Caoutchouc. II. Hydrocaoutchouc and a Crystalline Form of Caoutchouc.** R. PUMMERER and A. KOCH (*Annalen*, 1924, 438, 294—313).—The following procedure affords samples of caoutchouc of progressively increasing purity, all operations being carried out in an inert atmosphere: (a) fractional precipitation from benzene by means of alcohol, the impurities containing oxygen being precipitated in the first fraction, and the solvent removed by extraction with acetone; (b) as in (a) followed by fractional precipitation from hexahydrotoluene by means of acetone; (c) treatment of the product from (b) in light petroleum solution with methyl-alcoholic potassium hydroxide, the ethereal solution of the product then being shaken with charcoal. The product from (a) gives a clear solution in benzene, turbid in hexahydrotoluene, ether, or light petroleum; that from (b) is clear in hexahydrotoluene; and that from (c) is clear in all four solvents, and sufficiently pure for direct cold catalytic hydrogenation. On cooling the product obtained as in (a) after extraction with acetone, crystals were formed in the rubber mass, the occurrence of three types of crystals in six modifications being ascribed to the presence of several chemical individuals in the purified product. The benzene-alcohol mother-liquors deposited, on keeping, further fractions of caoutchouc which gradually set to a mass of yellowish-white, spherical aggregates, non-crystalline material being removable by washing in ether, from which solvent recrystallisation could also be effected. The crystals became transparent and plastic at 60°, complete fusion taking place at 92°. The sample became partly isotropic at 44°, completely isotropic at 60—62°. The crystalline material is practically non-elastic. Molecular-weight determinations gave negative results.

Caoutchouc purified by method (c), above, absorbs hydrogen in cold hexahydrotoluene solution, in presence of spongy platinum, the reaction product, after removal of the platinum, being slightly opalescent and completely stable to air, bromine, or permanganate at the ordinary temperature. On evaporation of the ethereal solution, the hydrocaoutchouc is obtained as an opaque, viscous, non-elastic, partly crystalline mass,  $(C_5H_{10})_x$ , which does not depress the melting point of camphor. When heated for 3 hours at 200°, then for 20 mins. at 300°, in carbon dioxide at 12 mm. pressure, no visible change takes place, but the product shows a molecular weight of 1700. The crude hydrocaoutchouc was partly distilled at 350° (bath temperature) in hydrogen at 1 mm., slight decomposition taking place only at first. The distillate, comprising one-third of the whole, had a slight odour of limonene, and was unsaturated. It was purified by solution in acetone, followed by treatment with charcoal in ether, to a colourless, saturated hydrocarbon,  $C_{45}H_{92}$ . The composition of the undistilled residue, which was colourless and completely saturated, corresponded with the formula  $(C_5H_{10})_x$ , the molecular weight (in camphor) being 1500. It had b. p. 354°/1.5 mm., the purified distillate forming a viscous, colourless mass,  $C_{50}H_{102}$ .

When treated with hydrogen containing 5% of oxygen, in



presence of spongy platinum, purified caoutchouc afforded the unsaturated hydrocarbon,  $C_{50}H_{86}$ , which, however, did not react with bromine.

The bearing of the above results on the constitution is discussed, and a note on the *X*-ray examination of crystalline caoutchouc appended.

F. G. W.

**Ether-soluble Constituents of Lac-resin.** D. N. GUPTA (*J. Indian Inst. Sci.*, 1924, 7, 142—144).—Stick-lac produced by *Lakshadia mysorensis* grown on *Shorea talura*, Roxb., was finely ground and after removal of wax with light petroleum was percolated with ether. The ethereal extract yielded myricyl alcohol, a colouring matter apparently identical with Tschirch's erythrolaccin, and giving analytical values agreeing well with tetrahydroxyanthraquinone, palmitic acid, probably myristic acid, and an unsaturated hydroxy-acid, probably  $C_{15}H_{28}(OH) \cdot CO_2H$ . Neither mono- nor tri-hydroxypalmitic acid was isolated.

P. M.

**Amygdalin. III. Synthesis of Natural *l*-Amygdalin.** G. ZEMPLÉN and A. KUNZ (*Ber.*, 1924, 57, [B], 1357—1359).—The substance described previously (this vol., i, 975) as "stable hepta-acetyl-*l*-amygdalic acid" does not react with thionyl chloride or phosphorus pentachloride, whereas it is converted by dry methylalcoholic ammonia into *l*-amygdalamide which is isolated as *hepta-acetyl-l-amygdalamide*, m. p. 180—181°,  $[\alpha]_D^{25}$  —66.3° in chloroform. It is hence shown to be the lactone of hexa-acetyl-*l*-amygdalic acid. The hepta-acetyl amide is converted by phosphoryl chloride into hepta-acetyl-*l*-amygdalin,  $[\alpha]_D^{25}$  —38.1° in chloroform, which is identical with the product from natural amygdalin. The synthesis of the latter substance is rendered complete by the observation that hexa-acetyl-*l*-amygdalolactone is formed by the interaction of bromoacetogentiobiose and silver *l*-mandelate; the main product of the reaction, however, is *hepta-acetylgentiobiosidyl l-mandelate*,  $C_6H_5 \cdot CH(OH) \cdot CO \cdot C_{12}H_{14}O_{12}Ac_7$ , m. p. 177°,  $[\alpha]_D^{25}$  —51.76° in chloroform. (Cf. Campbell and Haworth, *J. Chem. Soc.*, 1924, 125, 1337.)

H. W.

**Digitalinum verum. II.** A. WINDAUS, A. BOHNE, and A. SCHWIEGER (*Ber.*, 1924, 57, [B], 1386—1388; cf. Windaus and Bandte, A., 1923, i, 1107; Kiliani, A., 1916, i, 493).—Analyses of digitalin, m. p. 229°, which is extracted from *Digitalinum verum* by a somewhat modified procedure, are in agreement with the formula  $C_{37}H_{58}O_{14}$ . The conception of the substance as a simply unsaturated trihydroxylactone in which one hydroxy group is free whilst the remaining two groups are united to dextrose and digitalose residues is confirmed by the observation that it absorbs only 1 mol. of hydrogen with formation of dihydrodigitalin. The hydrolysis of digitalin by dilute acids is accompanied by the loss of 2 mols. of water.

H. W.

**Saponins of *Polygala amara*.** E. GLASER and H. KRAUTER (*Ber.*, 1924, 57, [B], 1604—1610).—Two saponins are present in *Polygala amara* which can be separated from one another since one is acidic and precipitable with normal lead acetate whereas

the other is neutral and is precipitated with basic lead acetate. Both are dialysable, and neither is hydrolysed by emulsin nor precipitated by ammonium sulphate. The hygroscopic, neutral saponin,  $C_{34}H_{52}O_{20}$ , has  $[\alpha]_D +30^\circ$  in aqueous solution. It is hydrolysed by hydrochloric acid (2%) to 3 mols. of dextrose and the *sapogenin*,  $C_{14}H_{22}O_2$ , m. p.  $201-202^\circ$ , which is optically inactive; the latter substance contains one carboxyl group, since it readily yields a *methyl* ester,  $C_{15}H_{24}O_2$ , m. p.  $206^\circ$ , which combines with bromine in chloroform solution to give the *compound*  $C_{15}H_{24}O_2Br_4$ , thus establishing the presence of two double bonds. Since an acid,  $C_{13}H_{21}\cdot CO_2H$ , with a normal carbon chain must contain three double bonds in its molecule, the presence of a ring must also be assumed. The acid saponin,  $C_{22}H_{36}O_{10}$ , is a brown, amorphous powder which is hydrolysed by dilute acid to equimolecular quantities of dextrose and an amorphous, acidic *sapogenin*,  $C_8H_{14}O_3$ , m. p.  $198^\circ$ , which does not react with bromine.

The reactions, solubilities, and empirical formulæ of the acid and neutral saponins render it probable that they are respectively identical with polygalacic acid and senegin derived from *Polygala senega*.  
H. W.

**Saponin of the Primula Root.** L. KOFER and H. FRAUEN-DORFER (*Arch. Pharm.*, 1924, **262**, 318—328; compare Masson, A., 1912, ii, 979).—The author has attempted to determine the nature and amount of the saponin present in radix primulæ, using the hæmolytic index of the drug as a measure of its saponin content. The drug used for the investigation was derived from *Primula veris*, and had the hæmolytic index 1 : 16,000. The saponin, prepared from the drug by extraction with 70% alcohol, precipitation with water, and purification by animal charcoal and finally by electrodialysis (compare Kofler and Dafert, this vol., ii, 74), forms a white, microcrystalline powder, m. p.  $218-220^\circ$ , to which is given the name *primulinic acid* (cf. Masson, *loc. cit.*). It is insoluble in cold water, slightly soluble in hot, and readily soluble in alkaline media, from which it is precipitated by acids. It contains C 55.04%, H 8.03%, and no nitrogen. It has a bitter taste, and induces vomiting. The hæmolytic index of the pure saponin dissolved in physiological saline, with the aid of sodium hydroxide, to neutral solution, is 1 : 190,000. Its physiological reactions are typical of a saponin. The saponin content of the drug is 8.4%, the average content of the commercial drugs being slightly greater than 5%. The solution of the above crystalline saponin in alcohol, on precipitation with ether, yields the substance in the form of a jelly, which while fresh is more soluble in water than the original form, losing this property on standing. It is therefore suggested that there are two forms of *primulinic acid*, a crystalline form insoluble in water, and an amorphous, soluble form, and this assumption is used to explain various solubility properties of the substance. From an alcoholic extract of the original radix primulæ, after precipitation of the saponin with ether, another substance crystallised out, which the author regards as

the heptahydric alcohol volemitol, and is probably the substance which Hünefeld (*J. pr. Chem.*, 1836 and 1839) called primulin; some authors have regarded this as the saponin of the drug, although it is different from the latter in many ways. The tannin content of radix primulae is very low. B. F.

**Reduction of Sitosterol. Preparation of Dihydrositosterol or Sitostanol.** R. J. ANDERSON and F. P. NABENHAUER (*J. Amer. Chem. Soc.*, 1924, **46**, 1953—1956).—Sitosterol having  $[\alpha] -30.90^\circ$ , prepared from wheat bran, was reduced by hydrogen in ethereal solution in the presence of platinum black. The reduction product,  $C_{27}H_{47}OH$ , colourless, hexagonal plates, m. p. 141—142°,  $[\alpha]_D^{20} +24.16^\circ$  in chloroform, was dihydrositosterol. It did not absorb bromine, and gave negative Liebermann-Burchard and Whitby reactions. It is very similar to, if not identical with, the saturated sterol that occurs in the endosperm of maize and wheat. That the alcoholic hydroxyl has not been changed was shown by the preparation of an *acetyl* derivative,  $C_{27}H_{47}OAc$ , m. p. 138—139°. A. C.

**Separation of Unsaturated from Saturated Sterols.** R. J. ANDERSON and F. P. NABENHAUER (*J. Amer. Chem. Soc.*, 1924, **46**, 1957—1960).—A mixture of sitosterol and dihydrositosterol can be almost completely separated by fractional crystallisation from alcohol, in which the latter is less soluble, if sufficient material is available. It is, however, impossible to remove the last traces of sitosterol in this way. Only the sitosterol takes up bromine, but an attempt to separate a brominated mixture of the acetyl derivatives was equally ineffective. A modification of the Liebermann-Burchard reaction (cf. A., 1885, 1075) gave satisfactory results in one operation. The mixed sterols are dissolved in carbon tetrachloride and the solution is mixed with acetic anhydride; concentrated sulphuric acid is then added while the mixture is shaken and cooled. On adding a little water and keeping the mixture, the acids form a purple upper layer containing the unsaturated sterol in solution. The saturated sterol remains dissolved in the lower carbon tetrachloride layer, partly as acetyl compound and partly as an ethereal sulphate. After distilling off the solvent, the residue is hydrolysed by means of alcoholic potassium hydroxide and yields the dihydrositosterol in a pure condition. The intensely coloured acid mixture contains the unsaturated sterol in a very stable chemical combination. On dilution with water, the colour becomes grass-green, and on neutralisation with alkali, a clear yellow. This reaction product has not been isolated in the pure form. A. C.

**Is-[Kombe]-Strophanthidin.** H. THOMS and F. UNGER (*Z. angew. Chem.*, 1924, **37**, 721—723).—Chiefly a critical bibliographical survey (cf. Jacobs, this vol., i, 65, 67; Brauns and Closson, A., 1915, i, 435, etc.). The compound has the formula  $C_{23}H_{32}O_6 \cdot \frac{1}{2}H_2O$ . Its *methyl ether* has m. p. 229—230°, decomp. 232—234°. Its phenylhydrazone has a higher m. p., viz., 242—243°, than that

recorded by Jacobs and Heidelberg (A., 1923, i, 123). *Dibromostrophanthidin*,  $C_{23}H_{32}Br_2O_6$ , has m. p.  $154.5^\circ$ . Other observations are briefly described. W. A. S.

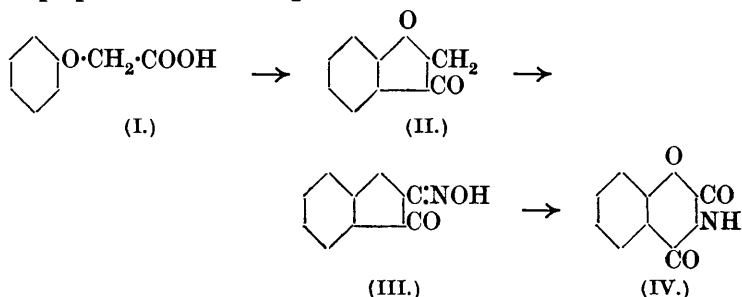
**Constitution of Catechin. VI. Production of Maclurin from Acacatechin.** E. O. HAZLETON and M. NIERENSTEIN (*J. Amer. Chem. Soc.*, 1924, **46**, 2100—2105).—By the action of *Penicillium solitum* on a 0.72% solution of acacatechin in water containing 5% of sucrose, a yield of 86% of the theoretical amount of maclurin is produced, an observation which is not consistent with formulæ proposed for catechin by Freudenberg, Ortner, and Fikentscher (this vol., i, 660). The phenol obtained by reduction of catechin tetramethyl ether with sodium and alcohol (cf. T., 1920, **117**, 1156) which Freudenberg and Cohn (A., 1923, i, 1219) regarded as 2-hydroxy-4 : 6 : 3' : 4'-tetramethoxy- $\alpha\gamma$ -diphenylpropane, on ethylation with ethyl iodide gives an *ethoxy* derivative, m. p.  $49-50^\circ$ , which on oxidation with alkaline potassium permanganate yields 4 : 6 : 3' : 4'-tetramethoxy-2-ethoxydiphenylacetic acid, m. p.  $137-138^\circ$  (*methyl* ester, obtained by methylation of the acid with diazomethane, m. p.  $64^\circ$ ). These results show that the fission of the chromane nucleus in acacatechin leads to the formation of an  $\alpha\alpha$ -diphenylpropane derivative in accordance with the structure assigned to acacatechin by Nierenstein, and not to the  $\alpha\gamma$ -derivative claimed by Freudenberg and Cohn. R. B.

**Oak-wood Tannin. Preparation and Purification of Tannins.** I. K. FEIST and H. BESTEHORN (*Arch. Pharm.*, 1924, **262**, 291—304).—Oak-wood tannin is best extracted by the method of Feist and Haun (A., 1914, i, 195), with the modification that a mixture of alcohol and acetone is used for the final extraction. The crude tannin thus obtained contains about 9% of inorganic matter, notably calcium, and 5 to 30% of ellagic acid. The latter cannot be removed by crystallisation or dialysis from pyridine; a solution of the crude tannin dissolves ellagic acid to the extent of about 26% of its tannin content. The inorganic matter, but not the ellagic acid, may be completely removed by an electro-osmotic method. The purified tannin yielded a methyl derivative of molecular weight 1343. Attempts to purify the crude tannin by ultra-filtration failed. B. F.

**Tetrahydrofurfuraldehyde.** H. SCHEIBLER, F. SOTSCHACK, and H. FRIESSE (*Ber.*, 1924, **57**, [B], 1443—1448).—Furfuraldehyde diacetate, b. p.  $129^\circ/17$  mm., m. p. (plates)  $52-53^\circ$ , m. p. (needles)  $49-51^\circ$  (cf. Law, A., 1908, i, 321), is hydrogenated in ethereal solution in the presence of palladised charcoal to *tetrahydrofurfuraldehyde diacetate*, b. p.  $133^\circ/29$  mm.,  $d_4^{20}$  1.1495,  $n_D^{20}$  1.44052. It is hydrolysed by *N*-sulphuric acid to *tetrahydrofurfuraldehyde*, a colourless, mobile liquid, b. p.  $45-47^\circ/29$  mm.,  $142-143^\circ/779$  mm.,  $d_4^{20}$  1.0501,  $n_D^{20}$  1.47036; the non-crystalline *phenylhydrazone* and *oxime* and the crystalline *as-phenylbenzylhydrazone*, m. p.  $67^\circ$ , are described. Furfuraldehydediethylacetal prepared by Claisen's method from furfuraldehyde and ethyl orthoformate (cf. A., 1907,

i, 940) is unsuitable for the preparation of tetrahydrofurfuraldehyde since it contains unchanged aldehyde. H. W.

**Transformation of Furan Rings into Oxazine Rings.** E. MAMELI (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 436; from *Chem. Zentr.*, 1924, i, 2517; cf. A., 1923, i, 61).—2:4-Diketobenzisooxazine (IV) has been prepared from phenol by way of the compounds I—III. The corresponding methyl derivatives have been prepared from *o*- and *p*-cresol.



G. W. R.

**Formation of Coumaranones, Chromanones, and Hydroxyhydrindones from Phenols.** K. VON AUWERS (*Annalen*, 1924, 439, 132—175; cf. A., 1920, i, 392, 866; 1921, i, 464; 1922, i, 1192). I. Dicyclic Ketones from *p*-Cresol and  $\alpha$ -Bromo- $\alpha$ -ethylbutyric Acid [with T. MEISSNER].— $\alpha$ -Bromo- $\alpha$ -ethylbutyryl bromide, b. p. 94°/20 mm., reacts with *p*-tolyl methyl ether in carbon disulphide solution in presence of aluminium chloride to yield *o*-[ $\alpha$ -bromo- $\alpha$ -ethylbutyryl]-*p*-cresol, b. p. 175°/14 mm.,  $d_4^{20}$  1.307,  $n_{\text{He}}^{20}$  1.5654. This is converted by cold sodium hydroxide into a mixture of about 2 parts of *o*-( $\alpha$ -hydroxy- $\alpha$ -ethylbutyryl)-*p*-cresol, m. p. 43—44°, b. p. 166—168°/18 mm.,  $d_4^{20}$  (supercooled) 1.081,  $n_{\text{He}}^{20}$  1.5409 (semicarbazone, m. p. 180—181°), and 1 part of 5-methyl-2:2-diethylcoumaranone, b. p. 145—146°/15 mm.,  $d_4^{20}$  1.034,  $n_{\text{He}}^{20}$  1.5326. The latter is the chief product of the reaction at 100°, and in behaving in this way the diethyl compound differs sharply from the dimethyl analogue (*loc. cit.*). When the bromobutyryl-*p*-cresol is heated with diethylaniline, 2:6-dimethyl-3-ethylchromanone, b. p. 151—153°,  $d_4^{21}$  1.0627,  $n_{\text{He}}^{21}$  1.53912 (semicarbazone, m. p. 210—211°; *p*-nitrophenylhydrazone, red prisms, m. p. 207—209°) is obtained; this yields a 2:3-dibromo derivative, m. p. 119—120°, and, by less prolonged treatment, a 3-bromo derivative, an oil, which when heated with diethylaniline gives 2:6-dimethyl-3-ethylchromanone, a yellow oil, b. p. 168—173°/13 mm.,  $d_4^{20}$  1.092,  $n_{\text{He}}^{20}$  1.5540; the latter is also obtained by treating a mixture of ethyl ethylacetoacetate and *p*-cresol with phosphorus pentoxide. Only a little dimethylethylchromanone is obtained from *p*-tolyl methyl ether,  $\alpha$ -ethylcrotonyl chloride, and aluminium chloride, the chief product being *o*-butyryl-*p*-cresol, m. p. 32—33°, b. p. 132—133°/15 mm.,  $d_4^{26.2}$  1.0191,  $n_{\text{He}}^{26.2}$  1.5240 (*p*-nitrophenylhydrazone, red prisms,

m. p. 184—186°; with semicarbazide two compounds, m. p. 190° and 159—162°, respectively, were obtained). A comparison sample was prepared by treating *p*-tolyl *n*-butyrate, b. p. 140—141°, with aluminium chloride. *p*-Tolyl  $\alpha$ -bromo- $\alpha$ -ethylbutyrate has b. p. 167—168° and when treated with aluminium chloride gives the above 2 : 6-dimethyl-3-ethylcoumaranone, together with 7-hydroxy-3 : 4-dimethyl-2-ethylhydrindone, b. p. 149·6—150·2°/8·5 mm.,  $d_4^{20}$  1·073,  $n_{\text{He}}^{20}$  1·5484 (semicarbazone, m. p. 186—188°; *p*-nitrophenylhydrazone, orange-red prisms, m. p. 218—219°). *p*-Tolyl  $\alpha$ -ethylcrotonate (from the cresol and the acid chloride) has b. p. 144—146°/12 mm.,  $d_4^{20}$  1·009,  $n_{\text{He}}^{20}$  1·5132, and is converted by treatment with aluminium chloride at 130—140° into the above hydroxyhydrindone. Anisole and crotonyl chloride in carbon disulphide solution react with aluminium chloride to give *p*-crotonylanisole, m. p. 22°, b. p. 165—167°/15 mm.,  $d_4^{17}$  1·0906,  $n_{\text{He}}^{17}$  1·58723, the dibromide of which has m. p. 104·5—105·5°. 7-Hydroxyhydrindone has b. p. 128—130·5°/9·5 mm.; 7-hydroxy-2 : 4-dimethylhydrindone has b. p. 136·5—137·5°/8 mm.,  $d_4^{23·8}$  1·0890,  $n_{\text{He}}^{23·8}$  1·54501; 7-hydroxy-3 : 4-dimethylhydrindone has b. p. 140·3°/8 mm.,  $d_4^{23·8}$  1·0999,  $n_{\text{He}}^{23·8}$  1·55156. The refractivities for the  $\alpha$ ,  $\beta$ , and  $\gamma$  lines are also recorded and the relations between the optical properties and the constitutions of the above compounds are discussed.

**II. Dicyclic Ketones from *m*-Cresol and  $\alpha$ -Bromoisobutyric Acid** [with J. KOCH.]-*o*-( $\alpha$ -Bromoisobutyryl)*p*-cresol does not yield a coumaranone, but the corresponding derivative of *s*-*m*-xlenol readily undergoes this conversion (*loc. cit.*). It is now shown that the reaction is governed by the position of the methyl group or groups in the phenyl nucleus. Thus, when *m*-tolyl methyl ether and  $\alpha$ -bromoisobutyryl bromide are treated in carbon disulphide with aluminium chloride a product is obtained from which may be separated 4-( $\alpha$ -chloro- or  $\alpha$ -bromo-isobutyryl)-*m*-cresol, 7-hydroxy-2 : 5-dimethylhydrindone, 5-hydroxy-2 : 7-dimethylhydrindone, and 2 : 2 : 4-trimethylcoumaranone; these substances were identified by comparing them with samples prepared in other ways (see below). When less aluminium chloride was used 4-( $\alpha$ -hydroxyisobutyryl)-*m*-cresol also was eventually obtained. *m*-Tolyl- $\alpha$ -bromoisobutyrate (from the cresol and the acid chloride), b. p. 132—135°/11 mm., when heated at 140° with aluminium chloride yields 7-hydroxy-2 : 5-dimethylhydrindone, a pale yellow, steam-volatile oil, b. p. 138—139°/11 mm.,  $d_4^{20}$  1·119 or 1·123,  $n_{\text{He}}^{20}$  1·5672 or 1·5647 (semicarbazone, needles, m. p. 232—233°; phenylhydrazone, m. p. 122—123°) and 5-hydroxy-2 : 7-dimethylhydrindone (not volatile in steam), m. p. 190—191°, b. p. 220°/10 mm. (semicarbazone, m. p. 228—229°; acetyl compound, m. p. 70—71°; 2 : 4 : 6-tribromo derivative, m. p. 169—170°). 2 : 2 : 4-Trimethylcoumaranone has m. p. 54—55°, b. p. 108°/10 mm., and yields the 5 : 7-dibromo derivative (m. p. 114°) when treated with an excess of bromine and a little aluminium. *m*-Tolyl isobutyrate, b. p. 104—106°/11 mm., when heated at 100° with aluminium chloride yields 4-isobutyryl-*m*-cresol, b. p. 120—121°/11 mm.,  $d_4^{20}$  1·042,  $n_{\text{He}}^{20}$  1·5401, which, brominated, affords 6-bromo-4-( $\alpha$ -bromoisobutyryl)-*m*-cresol, m. p. 98—99°, and 2 : 6-di-

*bromo-4-( $\alpha$ -bromoisobutyryl)m-cresol*, m. p. 90—92°. The latter is oxidised by hydrogen peroxide to 4:6-dibromo-*m*-hydroxytoluic acid. *m*-Tolyl methyl ether and  $\alpha$ -bromopropionyl bromide yield chiefly the steam-volatile 4-( $\alpha$ -chloropropionyl)*m*-cresol, b. p. 145—147°/13 mm., which, when heated with sodium acetate and alcohol, is converted into 2:6-dimethylcoumaranone, m. p. 60—61°, b. p. 118—120°/13 mm.; the *semicarbazone*, m. p. 204—205°, was produced normally at the ordinary temperature, but at 40—50° the product was the *disemicarbazone* of 4-pyruvyl-*m*-cresol, which crystallises with 1 mol. H<sub>2</sub>O and has m. p. 245°; with *p*-nitrophenylhydrazine the *dinitro-osazone* of this compound, m. p. 261°, or 275° when anhydrous, was obtained. When 2:6-dimethylcoumaranone is treated with sodamide and methyl iodide, 2:2:6-trimethylcoumaranone, m. p. 52°, b. p. 108°/12 mm. (*semicarbazone*, m. p. 250°; *p*-nitrophenylhydrazone, m. p. 196°), is obtained. When the crude steam-volatile product of the condensation of *m*-tolyl methyl ether and  $\alpha$ -bromoisobutyryl bromide is shaken with cold dilute sodium hydroxide, a mixture is obtained from which may be separated 7-hydroxy-2:5-dimethylhydrindone, 2:2:4-trimethylcoumaranone, and 4-( $\alpha$ -hydroxyisobutyryl)*m*-cresol, m. p. 54—55° (*semicarbazone*, m. p. 154—156°; *acetyl* derivative, m. p. 56—57°, b. p. 183—185°/13 mm.); but if the oil be heated with diethylaniline a chief product is 3:7-dimethylchromanone, m. p. 55—56° (*semicarbazone*, m. p. 221°). This compound is obtained also from *m*-tolyl methyl ether and  $\beta$ -chloroisobutyryl chloride; it yields a 3-bromo derivative, m. p. 97—98°, which, when heated with diethylaniline, affords 3:7-dimethylchromone, m. p. 78—79°, and the latter is disrupted by boiling sodium ethoxide, giving 4-propionyl-*m*-cresol, identified as *semicarbazone* (see below). *m*-Tolyl propionate, b. p. 108—110°/10 mm., when treated with aluminium chloride at 100°, yields the steam-volatile 4-propionyl-*m*-cresol, m. p. 41.5—42.5°, b. p. 115—120°/10 mm. (*semicarbazone*, m. p. 206—208°), and 6-propionyl-*m*-cresol, m. p. 114—115° (*semicarbazone*, m. p. 152.5—153.5°). 2:6-Dibromo-*m*-tolyl methyl ether has m. p. 73—74°.

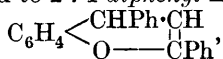
W. A. S.

**Transformation of *o*-Hydroxychalkone into Flavanone.**  
**Dehydrogenation of Flavanone to Flavone by Phosphorus Pentachloride. Synthesis of Flavone.** A. LÖWENBEIN (*Ber.*, 1924, 57, [B], 1515—1516).—Flavanone is readily obtained in 80% yield by the addition of excess of aqueous sodium hydroxide (1—2%) to a warm, alcoholic solution of *o*-hydroxyphenyl styryl ketone. It is converted by phosphorus pentachloride in the presence of boiling benzene into hydrogen chloride and a yellow, additive compound of flavone and phosphorus pentachloride from which the former is obtained in 80% yield by the action of alcohol.

H. W.

**2:4-Diarylchromenes.** A. LÖWENBEIN [with E. PONGRÁCZ and E. A. SPIESS] (*Ber.*, 1924, 57, [B], 1517—1526).—Phenyl *o*-hydroxystyryl ketone is converted by an ethereal solution of magnesium phenyl bromide into 2:4-diphenylchroman-2-ol,

$C_6H_4 \begin{smallmatrix} < \text{CHPh} \cdot \text{CH}_2 \\ \text{O} \text{---} \text{CPh} \cdot \text{OH} \end{smallmatrix}$ , m. p. 165—166°, which is dehydrated by boiling glacial acetic acid to 2 : 4-diphenyl- $\Delta^2$ -chromene,



m. p. 110°. The phenyl groups in these compounds are attached to different carbon atoms, and hence addition of the Grignard reagent to the unsaturated ketone occurs at the terminal points of the conjugated system, since phenyl *o*-hydroxystyryl ketone and magnesium *p*-tolyl bromide yield 2-phenyl-4-*p*-tolylchroman-2-ol, m. p. 141° (2-phenyl-4-*p*-tolyl- $\Delta^2$ -chromene, m. p. 85°), whereas magnesium phenyl bromide and *p*-tolyl *o*-hydroxystyryl ketone yield 4-phenyl-2-*p*-tolylchroman-2-ol, m. p. 160° (4-phenyl-2-*p*-tolyl- $\Delta^2$ -chromene, m. p. 137°). The constitution of the diphenylchromene is further confirmed indirectly, since it differs from 2 : 4-diphenyl-

$\Delta^3$ -chromene,  $C_6H_4 \begin{smallmatrix} < \text{CPh} \cdot \text{CH} \\ \text{O} \text{---} \text{CHPh} \end{smallmatrix}$ , m. p. 106°, obtained by dehydration

of 2 : 4-diphenylchroman-4-ol, m. p. 112°; the structure of the latter compound is placed beyond doubt by its production from magnesium phenyl bromide and flavanol. The two isomeric 2 : 4-diphenylchromenes are oxidised by ferric chloride to the same 2 : 4-diphenylbenzopyrylium salts (*perchlorate*, m. p. 217—218°; *additive* compound of the chloride and ferric chloride, m. p. 168°).

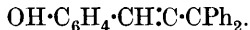
Coumarin is converted by magnesium phenyl bromide in the presence of a mixture of ether and benzene into a mixture of 2 : 4-diphenylchroman-2-ol [identical with the product from phenyl *o*-styryl ketone described above and erroneously considered by Houben (A., 1904, i, 334) to be diphenyl-*o*-hydroxystyrylcarbinol]

and 2 : 2-diphenyl- $\Delta^3$ -chromene,  $C_6H_4 \begin{smallmatrix} < \text{CH} \cdot \text{CH} \\ \text{O} \text{---} \text{CPh}_2 \end{smallmatrix}$ , m. p. 93°. The

latter substance appears to be formed from coumarin without rupture of the lactone ring; it is converted by boiling glacial acetic acid or alcoholic hydrogen chloride into the compound,

$C_6H_4 \begin{smallmatrix} < \text{CH} \\ \text{O} \end{smallmatrix} \text{C} \cdot \text{CHPh}_2$  or  $C_6H_4 \begin{smallmatrix} < \text{CH}_2 \\ \text{O} \end{smallmatrix} \text{C} \cdot \text{CPh}_2$ , m. p. 239°, pre-

sumably after hydrolysis to the allene derivative,



Magnesium  $\alpha$ -naphthyl bromide and coumarin yield 2 : 4-di- $\alpha$ -naphthylchroman-2-ol, m. p. 156°, which is converted by boiling glacial acetic acid into 2 : 4-di- $\alpha$ -naphthyl- $\Delta^2$ -chromene, m. p. 137°. The following compounds are derived from magnesium phenyl bromide and the requisite methylcoumarin: 5 : 7-dimethyl-2 : 4-diphenylchroman-2-ol, m. p. 111°, which yields 5 : 7-dimethyl-2 : 4-diphenyl- $\Delta^2$ -chromene, m. p. 118°; 4 : 6-dimethyl-2 : 4-diphenylchroman-2-ol, m. p. 110°, and thence 4 : 6-dimethyl-2 : 4-diphenyl- $\Delta^2$ -chromene, m. p. 127°; 4 : 7-dimethyl-2 : 4-diphenylchroman-2-ol, m. p. 144°, which yields 4 : 7-dimethyl-2 : 4-diphenyl- $\Delta^2$ -chromene, m. p. 86°.

[With L. POPPER.]—Phenyl *o*-hydroxystyryl ketone is converted by hydrogen chloride in the presence of ether into 2-phenylbenzo-



*pyrylium chloride*,  $C_{15}H_{11}OCl \cdot HCl$ , m. p. 85—86° (decomp.); the corresponding *perchlorate* has m. p. 186—187°. Either salt is converted by magnesium phenyl bromide into 2:4-diphenyl- $\Delta^2$ -chromene.

H. W.

**Preparation of Dehydracetic Acid from Ethyl Acetoacetate and the Mechanism of the Reaction.** F. ARNDT and P. NACHTWEY (*Ber.*, 1924, 57, [B], 1489—1491).—Dehydracetic acid is prepared in 86% yield by protracted ebullition of ethyl acetoacetate under a reflux condenser so regulated that the liberated ethyl alcohol escapes. Since dehydracetic acid is not converted by alcohol under these conditions into ethyl acetoacetate, the usual equilibrium in the decomposition of the latter depends on the action of alcohol on some intermediate product, probably the compound  $COMe \cdot CH_2 \cdot CO \cdot O \cdot CMe \cdot CH \cdot CO_2Et$ .

H. W.

**Aconite Alkaloids. I. Different Isomerides of Japaconitine.** R. MAJIMA, H. SUGINOMÉ, and S. MORIO (*Ber.*, 1924, 57, [B], 1456—1466).—The dried tubers of various species of Japanese *Aconitum* are mixed with calcium carbonate and extracted with alcohol (95%). The alcohol is removed as completely as possible, the residue is diluted with water, extracted with light petroleum, and treated with sodium carbonate solution, whereby crude japaconitine is partly precipitated, the remainder being obtained by extraction with chloroform. The crude alkaloid is extracted with ether and the soluble portion dissolved in hydrochloric acid; the solution is fractionally precipitated with sodium carbonate. The separate fractions are converted into their hydrobromides. Japaconitines of which the hydrobromides are readily crystallised from water are termed japaconitine-*A*, whereas the suffixes -*B* and -*C* denote the alkaloids of which the hydrobromides are respectively crystallisable from a mixture of alcohol and ether or not crystallisable from this mixture or water. In various species of Japanese *Aconitum* there are found isomeric alkaloids the hydrobromides of which fall within these classes; they are designated japaconitine -*A*<sub>1</sub>, -*B*<sub>1</sub>, and -*C*<sub>1</sub>.

The following individual substances are described, certain of which have been examined previously by Dunstan and Read (T., 1900, 77, 45) and Makoshi (A., 1909, i, 669). The temperatures of decomposition depend greatly on the mode of heating and are determined with reference to japaconitine-*A* or its hydrobromide. The method of "mixed melting points" fails in this series. The following compounds are described: Japaconitine-*A*,  $C_{34}H_{47}O_{11}N$ , decomp. 202—203°,  $[\alpha]_D^{25} + 20.7^\circ$  in chloroform [hydrochloride (+3.5H<sub>2</sub>O), decomp. 160—161°; (anhydrous), decomp. 165—166°;  $[\alpha]_D^{25} - 31.3^\circ$  in water; hydrobromide (+4.5H<sub>2</sub>O), decomp. 155—156°; (anhydrous), decomp. 172—173°; hydriodide, decomp. 205—209°; chloroaurate, decomp. 159—160°; triacetyl derivative, decomp. 191—193°; *perchlorate* (+H<sub>2</sub>O), decomp. (anhydrous), 215—218°]. Japaconitine-*A*<sub>1</sub>,  $C_{34}H_{47}O_{11}N$ , decomp. 208—209°,  $[\alpha]_D^{25} + 26.4^\circ$  in chloroform [hydrobromide (+3.5H<sub>2</sub>O), decomp.

(anhydrous), 172—173°,  $[\alpha]_D^{25}$  —22.5° in water; *chloroaurate*, decomp. 223—224°; *perchlorate*, decomp. 215—218°. *Japaconitine-B*,  $C_{34}H_{47}O_{11}N$ , decomp. 208—209°,  $[\alpha]_D^{25}$  +26.9° in chloroform [*hydrochloride*, decomp. 108—109°,  $[\alpha]_D^{25}$  —24.7° in water; *hydrobromide* (+H<sub>2</sub>O), decomp. 179.5—180.5°,  $[\alpha]_D^{25}$  —21.8° in water; *hydriodide*, decomp. 228—231°; *chloroaurate*, decomp. 235—237°; *perchlorate*, decomp. 215—218°; *triacetyl* derivative, decomp. 196—197°]. *Japaconitine-B<sub>1</sub>*, prisms, decomp. 194—195°,  $[\alpha]_D^{25}$  +22.0° in chloroform (*chloroaurate*, decomp. 248—249°). *Japaconitine-C*,  $C_{34}H_{47}O_{11}N$ , prisms, decomp. 195—196°,  $[\alpha]_D^{25}$  +18.3° in chloroform [*chloroaurate*, decomp. 243—245°; *perchlorate* (+2.5H<sub>2</sub>O), decomp. (anhydrous), 175—178°]; *Japaconitine-C<sub>1</sub>*, prisms, decomp. 193—195°,  $[\alpha]_D^{25}$  +23.2° in chloroform (*chloroaurate*, decomp. 248—249°).

*Japaconitine-A* is hydrolysed in the presence of aqueous sulphuric acid to acetic acid and *japbenzaconine-A*, which is isolated as the hydrochloride (+2H<sub>2</sub>O), decomp. 244—245°,  $[\alpha]_D^{25}$  —29.8° in aqueous solution, decomp. (anhydrous) 265—266°, and by water at 160—170° to benzoic acid and *japaconine-A* (*hydrochloride*,  $C_{25}H_{41}O_3N \cdot HCl \cdot 1.5H_2O$ , decomp. 173—175°; *tetra-acetyl* derivative, decomp. 235—236°,  $[\alpha]_D^{25}$  —28.9° in chloroform). Similarly, *japaconitine-B* yields *japbenzaconine-B hydrochloride*,

$C_{34}H_{45}O_{11}N \cdot HCl \cdot H_2O$ ,  
decomp. 251—252°,  $[\alpha]_D^{25}$  —24.4° in aqueous solution and *japaconine-B* which is isolated as the very hygroscopic *hydrochloride* and the *tetra-acetyl* derivative,  $C_{33}H_{49}O_{13}N$ , decomp. 228—229°,  $[\alpha]_D^{25}$  —19.1° in alcohol.  
H. W.

**Aconite Alkaloids. II. Aconitine and Pyraconitine.** R. MAJIMA and H. SUGINOMÉ (*Ber.*, 1924, 57, [B], 1466—1471).—The recognition of *japaconitine* as a mixture of isomerides (preceding abstract) has induced an examination of *aconitine* along similar lines whereby it also is found to be non-homogeneous.

*Aconitine* (Merck, ex *Aconito Napello*) is separated by aqueous hydrobromic acid into the readily crystallisable *aconitine-A hydrobromide*, decomp. 206—207°, and the amorphous *aconitine-C hydrobromide* (for use of suffixes, *A* and *C*, see preceding abstract). *Aconitine-A*,  $C_{34}H_{47}O_{11}N$ , forms hexagonal plates, decomp. 202—203°,  $[\alpha]_D^{25}$  —18.1° in chloroform (*chloroaurate*, m. p. 151—152°). It is hydrolysed to *aconine-A hydrochloride*,  $C_{25}H_{41}O_3N \cdot HCl \cdot 2H_2O$ , decomp. 169—170°,  $[\alpha]_D^{25}$  —3.7° in water. *Tetra-acetylaconine-A* decomposes at 241—242°. *Aconitine-C*,  $C_{34}H_{47}O_{11}N$ , forms prismatic crystals, decomp. 203—204°,  $[\alpha]_D^{25}$  —23.4° in chloroform (*chloroaurate*, decomp. 238—239°). It is hydrolysed to *aconine-C*, which is identified as the *tetra-acetyl* compound, decomp. 223—224°.

Thermal decomposition of *japaconitine-A* (cf. Schulze and Liebner, A., 1913, i, 1375; 1917, i, 470) yields two isomeric pyro-japaconitines designated  $\alpha$  and  $\beta$ . Non-crystalline *pyrojapaconitine- $\alpha$*  gives a *hydrobromide*,  $C_{32}H_{43}O_9N \cdot HBr$ , crystallisable from water, decomp. 262°,  $[\alpha]_D^{25}$  —43.5° in water, a *perchlorate*, decomp. 252—254°, and a *chloroaurate* (+0.5H<sub>2</sub>O), decomp. 143°. *Pyrojapaco-*

*nitine-β* could not be caused to crystallise; it yields a *hydrobromide*,  $C_{32}H_{43}O_9N, HBr, 2H_2O$ , decomp.  $226^\circ$ ,  $[\alpha]_D^{24} -68.4^\circ$  in water, a *perchlorate*, decomp.  $286^\circ$  after darkening at  $276^\circ$ , and a *chloroaurate* ( $+H_2O$ ), decomp.  $176-177^\circ$ . Similarly, *japaconitine-B* yields two *pyrojapaconitines*, one of which is identical with *pyrojapaconitine-β* from *japaconitine-A*. The other, termed *pyrojapaconitine-γ*, forms prismatic crystals, decomp.  $169-170^\circ$ ,  $[\alpha]_D^{26} -108.4^\circ$  in alcohol (*hydrobromide*,  $C_{32}H_{43}O_9N, HBr, 2H_2O$ , decomp.  $240-241^\circ$ ,  $[\alpha]_D^{25} -105.4^\circ$  in water; *perchlorate*, decomp.  $270-271^\circ$ ; *chloroaurate*, decomp.  $202^\circ$ ).

*Aconitine-A* in similar manner yields two *pyraconitines* ( $\alpha$  and  $\beta$ ) in the approximate ratio 3 : 1. The  $\alpha$ -compound resembles closely *pyrojapaconitine-α*, with which it is possibly identical. The following salts of *pyraconitine-α* are described: *hydrobromide*,  $C_{32}H_{43}O_9N, HBr$ , decomp.  $262^\circ$ ,  $[\alpha]_D^{15} -42.7^\circ$  in water; *perchlorate*, decomp.  $254-256^\circ$ ; *chloroaurate* ( $+0.5H_2O$ ), decomp.  $143-144^\circ$ . *Pyraconitine-β* yields a *hydrobromide*,  $C_{32}H_{43}O_9N, HBr, 3H_2O$ , decomp.  $207-208^\circ$ ,  $[\alpha]_D^{17} -39.2^\circ$  in water, a *perchlorate*, decomp. ca.  $282-283^\circ$ , and a *chloroaurate* ( $+H_2O$ ), decomp.  $191-192^\circ$ . One of the two isomeric *pyraconitines* obtained from *aconitine-C* is identical with *pyraconitine-β*; the other, *pyraconitine-γ*, gives a non-crystalline *hydrobromide* and *perchlorate* and a *chloroaurate*,  $C_{32}H_{43}O_9N, HCl, AuCl_3, H_2O$ , decomp.  $213-214^\circ$ . H. W.

**Aconite Alkaloids. III. So-called Jesaconitine.** R. MAJIMA and S. MORIO (*Ber.*, 1924, 57, [B], 1472-1476).—Examination of *aconitum* tubers grown in the region north of Tokyo discloses the presence of only two alkaloids, *acetylanisoylaconine* (which it is proposed to designate "*jesaconitine*") and *japaconitine-A<sub>2</sub>*; the crude material is thus a less involved mixture than that derived from the *aconitum* grown in the south of Tokyo (this vol., i, 1223). The *jesaconitine* isolated by Makoshi (A., 1909, i, 669) from tubers grown in a similar neighbourhood and considered by him to be *benzoylanisoylaconine* appears to have suffered partial degradation before examination.

The extraction of the alkaloid and the separation of it into its components is effected in the manner described for *japaconitine*. *Jesaconitine*, decomp.  $128-131^\circ$ , gives a *perchlorate*,

$C_{35}H_{49}O_{12}N, HClO_4$ ,  
decomp.  $230-232^\circ$ ,  $[\alpha]_D -16.7^\circ$  in methyl-alcoholic solution, a *chloroaurate*, decomp.  $208-209^\circ$ , and a *perbromide*, decomp.  $181-182^\circ$ . When boiled with water containing the equivalent quantity of sulphuric acid, it yields *jesoanisaconine* (*hydrochloride*,  $C_{33}H_{47}O_{11}N, HCl, 3H_2O$ , decomp.  $209-210^\circ$ ,  $[\alpha]_D^{20} -19.2^\circ$  in water) and acetic acid. Hydrolysis with water at  $160-170^\circ$  converts it into acetic and *p*-anisic acids and *jesaconine*, which is found identical with *aconine-A*. Thermal decomposition of *jesaconitine* appears to yield a single *pyrojesaconitine*, which is isolated as the *perchlorate*, anhydrous prisms, decomp.  $271-273^\circ$ ,  $[\alpha]_D^{13} -27.4^\circ$  in methyl alcohol.

*Japaconitine-A<sub>2</sub>*,  $C_{34}H_{47}O_{11}N$ , decomp.  $199-201^\circ$ ,  $[\alpha]_D^{13} +18.7^\circ$

in chloroform, yields a *hydrobromide*, decomp. 172—173°, a *chloroaurate*, decomp. 143—144°, and a *perchlorate* (+1.5H<sub>2</sub>O), decomp. 214—216°,  $[\alpha]_D^{15}$  -18.8° in methyl-alcoholic solution. It is hydrolysed to acetic and benzoic acids and japaconine-A<sub>2</sub> which is identical with aconine-A. When heated it yields pyrojapaconitine- $\alpha$  (hydrobromide, C<sub>32</sub>H<sub>43</sub>O<sub>9</sub>N.HBr, decomp. 261—262°,  $[\alpha]_D^{20}$  -42.0° in water; perchlorate, decomp. 250—254°; chloroaurate, decomp. 140—142°), which is probably identical with pyrojapaconitine- $\alpha$  and pyracoconitine- $\alpha$ .  
H. W.

**Mydriatic Alkaloids from the *Datura* Species. I.** S. OSADA (*Arch. Pharm.*, 1924, 262, 277—291; cf. T., 1908, 93, 2077).—The author proposes to investigate the structure of meteloidine, and reviews the literature dealing with teloidine and meteloidine, and the connexion of the former with tropine and scopoline. *Datura meteloides* is the only plant of the *Datura* species found to contain meteloidine, scopolamine and hyoscyamine being also present. The green- and violet-stalked varieties of *Datura alba*, Nees, each contained scopolamine, hyoscyamine, and atropine. Figures are given for the percentages of the different substances in various parts of the plants.  
B. F.

**Angostura Alkaloids. I. Synthesis of Cusparine.** E. SPÄTH and O. BRUNNER (*Ber.*, 1924, 57, [B], 1243—1251).—The synthesis of 7-methoxy-4- $\beta$ -3':4'-dimethoxyphenylethylquinoline and of the corresponding 2- $\beta$ -3':4'-dimethoxyphenylethyl compound and their non-identity with galipine disproves the constitution assigned to the latter by Troeger (A., 1913, i, 748; 1915, i, 447; 1921, i, 121). The key to the structure of cusparine and galipine is furnished by the observation that Troeger's acid, C<sub>11</sub>H<sub>9</sub>O<sub>3</sub>N, is almost certainly 4-methoxyquinoline-2-carboxylic acid. Thence 4-methoxy- $\beta$ -3':4'-methylenedioxyphenylethylquinoline is synthesised and found identical with cusparine.

2-Hydroxy-7-methoxy-4-methylquinoline, m. p. 205—206° (the *hydrochloride* is described), prepared from *m*-methoxyaniline and ethyl acetoacetate, is converted successively into 2-chloro-7-methoxy-4-methylquinoline, m. p. 112.5—113°, and 7-methoxy-4-methylquinoline, a pale yellow liquid [*picrate*, m. p. 223.5—224° (decomp.)]. The latter substance is converted by zinc chloride and 3:4-dimethoxybenzaldehyde into 7-methoxy-4- $\beta$ -3':4'-dimethoxyphenyl- $\Delta^a$ -ethinylquinoline *hydrochloride*, which is reduced by hydrogen in the presence of palladised charcoal to 7-methoxy-4- $\beta$ -3':4'-dimethoxyphenylethylquinoline, m. p. 126°. 4-Hydroxy-7-methoxy-2-methylquinoline, m. p. 252—253° [*hydrochloride*, m. p. 269° (decomp.)], is similarly transformed successively into 4-chloro-7-methoxy-2-methylquinoline, m. p. 81—82°, 7-methoxy-2-methylquinoline, a liquid [*picrate*, m. p. 217° (decomp.) after softening at 204°], 7-methoxy-2- $\beta$ -3':4'-dimethoxyphenyl- $\Delta^a$ -ethinylquinoline *hydrochloride* and 7-methoxy-2- $\beta$ -3':4'-dimethoxyphenylethylquinoline, m. p. 82.5—83°.

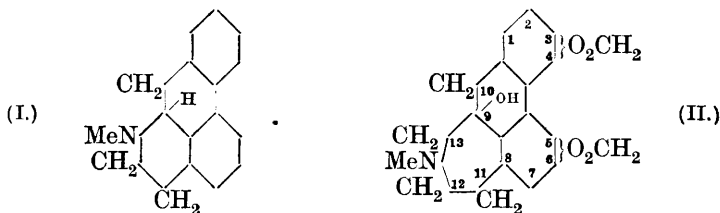
7-Methoxyquinoline, b. p. 143—145°/11 mm., prepared from

*m*-methoxyaniline, *p*-nitrophenol, glycerol, and concentrated sulphuric acid, is converted by benzoyl chloride and potassium cyanide and hydrolysis of the nitrile into 7-methoxyquinoline-2-carboxylic acid, m. p. 154°. The base is converted by methyl sulphate and potassium cyanide and treatment of the product with potassium iodide into 4-cyano-7-methoxyquinoline methiodide, m. p. 204–205° (decomp.), from which 4-cyano-7-methoxyquinoline, m. p. 153–154°, is prepared in very poor yield. The nitrile is hydrolysed to 7-methoxyquinoline-4-carboxylic acid, m. p. 273° (decomp.).

4-Methoxy-2-methylquinoline is converted by piperonal and anhydrous zinc chloride at 125° into 4-methoxy-2- $\beta$ -3':4'-methylene-dioxyphenyl- $\Delta^8$ -ethylquinoline hydrochloride, m. p. 193–195°, from which the corresponding base (dehydrocuspamine), m. p. 186°, is isolated; the latter substance is reduced by hydrogen in the presence of palladised charcoal to 4-methoxy-2- $\beta$ -3':4'-methylene-dioxyphenylethylquinoline, identical with natural cusparine.

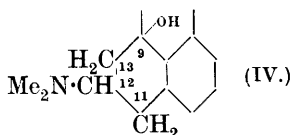
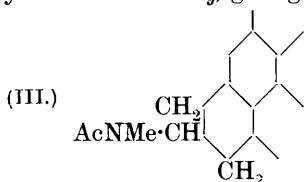
H. W.

**Chelidonium Alkaloids. III.** J. GADAMER (with H. DIETERLE, [FRL.] A. STICHEL, M. THEYSSEN, and K. WINTERFELD) (*Arch. Pharm.*, 1924, 262, 249–277; cf. A., 1920, i, 75, 872; 1921, i, 579).—This paper deals with the constitution of chelidonium. *d*-Chelidonine,  $C_{20}H_{19}O_5N$ , with cold acetic anhydride yields *d*-O-acetylchelidonine, m. p. 165–166°,  $[\alpha]_D +110^\circ$ . In the hot, however, 1 mol. of water is lost, optically inactive *N*-acetylanhydrochelidonine,  $C_{22}H_{19}O_5N$ , m. p. 152°, being formed. The nitrogen being originally tertiary, it is clear that a ring containing it has been opened and the loss of activity indicates that an asymmetrical carbon is probably involved in the reaction. On the ground of resemblances in this and other respects with the alkaloids of the so-called aporphine group (aporphine, I, is regarded as the parent



of the phenanthrene alkaloids, and its synthesis will be reported later) a formula for chelidonine has already been suggested (A., 1920, i, 75). This is now withdrawn, and replaced by the formula II, based on the reactions cited above, together with the view that in nature the substance may be formed from phenylacetaldehyde, *N*-methyl- $\beta$ -phenylethylamine, and formaldehyde, for protopine and  $\beta$ -homochelidonine (*allocryptopine*), may theoretically be decomposed into these component parts. The suggested formation in nature of chelidonine from these components is outlined. The formation of *N*-acetylanhydrochelidonine may be explained by fission of the ring between the nitrogen and C<sub>13</sub>, re-closing of the

ring between  $C_{13}$  and  $C_{12}$ , and loss of water between  $C_{10}$  and the asymmetric atom  $C_9$ , giving (III).



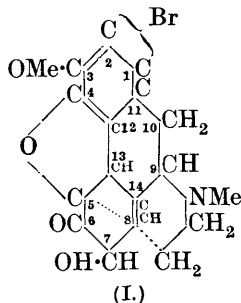
[With H. DIETERLE.]—When treated with methyl iodide, chelidonine first affords *chelidoninemethine-A*,  $C_{21}H_{21}O_5N$ , m. p. 145—146°,  $[\alpha]_D -271.3^\circ$  in chloroform (also formed by the action of methyl iodide on *O*-acetylchelidonine), and *chelidoninemethine-B*, m. p. 107—108°,  $[\alpha]_D -100^\circ$ , which occurs in the mother-liquor of the *A* methine as prepared by the first method. These two are regarded as stereoisomerides, and it is concluded that their formation is due to fission of the 7-ring and its reclosing, as in the case of the acetylation, so that the bases have formula IV. The existence of two stereoisomerides is due to the fact that a new asymmetric atom (12) has been superimposed on the original one (9). On further treatment with methyl iodide the *A* methine yields the corresponding *chelidoninemethinium methiodide*,  $C_{22}H_{24}O_5NI$ , m. p. 232—234° (decomp.),  $[\alpha]_D -50^\circ$ , which rapidly racemises in solution. The action of hot acetic anhydride on the *A* methine or its methiodide furnishes an optically inactive substance,  $C_{21}H_{18}O_6$ , m. p. 157—159° (the by-products being dimethylacetamide and trimethylamine respectively). The latter substance is an acetyl derivative, for on deacetylation by Schiff's method it yields a substance,  $C_{19}H_{16}O_5$ , m. p. 170—171°, resistant to oxidation. By the action of methyl sulphate on *O*-acetylchelidonine or chelidonine and subsequent treatment with sodium hydroxide there is formed optically inactive *methylanhydrochelidonine*,  $C_{21}H_{19}O_4N$ , m. p. 152—153°, probably by loss of water between  $C_9$  and  $C_{10}$ ; the same substance is formed by the action of methyl iodide on chelidonine under special conditions. *Methylanhydrochelidonine* forms a *methiodide*,  $C_{22}H_{22}O_4NI$ , m. p. 242—244°, which may be readily converted into the corresponding *methonitrate*,  $C_{22}H_{22}O_6N_2$ , m. p. 260—261°, and *methochloride*, m. p. 215—217°. On reduction with sodium amalgam, the latter yields trimethylamine and the substance,  $C_{19}H_{14}O_4$ , m. p. 244—245°, which is resistant towards permanganate, and is regarded as containing a phenanthrene nucleus. *Methylanhydrochelidonine methiodide*, on treatment with moist silver oxide, probably gives rise to the corresponding *hydroxide*; the latter, however, was not isolated, but immediately distilled under reduced pressure, when trimethylamine was evolved. *ψ-Anhydrochelidonine*,  $C_{20}H_{17}O_4N$ , m. p. 89—89.5°, was prepared from its *hydrochloride*, m. p. 204—205°, which results from the hydrolysis of *N*-acetylanhydrochelidonine with hydrochloric acid. Methyl iodide converts *ψ*-anhydrochelidonine into *methylanhydrochelidonine methiodide*, a substance, m. p. 133—134°, being formed as a by-product. In both methods of preparation of the *A* methine

there is formed as a by-product a *tertiary base*, m. p. 195—198°,  $[\alpha]_D + 83^\circ$  (in 2% chloroform solution). As a by-product in the treatment of chelidonine with methyl sulphate, there is formed *O-methylchelidonine*,  $C_{21}H_{21}O_5N$ , m. p. 162—163°,  $[\alpha]_D + 186^\circ$  (in 0.5% alcohol solution), converted on heating with acetic anhydride into *N-acetylanhydrochelidonine*.

For purposes of simplicity, the breaking of the 7-ring has been consistently regarded as occurring between the nitrogen and  $C_{13}$ ; actually it may also occur between N and  $C_{12}$ , which would result in the possibility of a new set of formulæ. B. F.

**Action of Reducing Agents on Bromocodeinone.** E. SPEYER and K. SARRE (*Ber.*, 1924, 57, [B], 1404—1409).—Bromocodeinone, prepared by a modification of Freund's method (A., 1906, i, 303), is reduced by hydrogen in acetic acid solution in the presence of palladised charcoal to dihydrocodeinone, identical with the product described by Freund and Speyer (A., 1921, i, 126) and by Mannich and Löwenheim (A., 1921, i, 125). When electrolytically reduced in sulphuric acid solution (25%) at lead electrodes, bromocodeinone yields *dihydrodeoxycodine*,  $2C_{18}H_{23}O_2N \cdot EtOH$ , decomp. 139—140°,  $[\alpha]_D^{13} + 58.15^\circ$  in dilute acetic acid solution, the product being formed by the replacement of bromine by hydrogen, reduction of the 6-keto to the methylene group, and rupture of the oxygen bridge with formation of a hydroxy group. It yields a *salicylate*, m. p. 198°, a *methiodide*, m. p. 199°, and a methyl ether which is isolated as the *methiodide*, m. p. 245°. Concentrated potassium hydroxide solution transforms the latter substance into the non-crystalline demethyldihydrodeoxycodine methyl ether (*hydriodide*,  $C_{20}H_{27}O_2N \cdot HI$ , m. p. 220° after softening; *methiodide*, m. p. 103°). The latter substance loses trimethylamine when heated with potassium hydroxide, but the nitrogen-free product was too unstable to be isolated. Reduction of dihydrodeoxycodine in the presence of colloidal palladium gives  $\beta$ -tetrahydrodeoxycodine (cf. Freund, A., 1920, i, 759). H. W.

**Action of Bromine on Hydroxycodine and Hydroxy-dihydrocodeinone.** E. SPEYER and K. SARRE (*Ber.*, 1924, 57, [B], 1409—1422).—Hydroxycodine hydrobromide (cf.



Freund and Speyer, A., 1917, i, 217) dissolved in cold water is converted by bromine water into *bromohydroxycodine* (I), m. p. 204—205°,  $[\alpha]_D^{13} - 80.21^\circ$  in acetic acid solution; the corresponding *hydrobromide*, decomp. 280° after softening, *acetyl* derivative, m. p. 238°, and *phenylhydrazone*, decomp. 250°, are described. The substance is converted by hydrogen in the presence of palladium into hydroxy-dihydrocodeine, m. p. 218—220°. If, however, hydroxycodine is brominated in boiling glacial acetic acid solution, a perbromide is produced which is transformed by alcohol

into *dibromohydroxycodine*, m. p. 194—195°,  $[\alpha]_D^{13} - 120.4^\circ$  in  $t^*$

acetic acid solution; this substance gives a *hydrobromide*, decomp.  $265^{\circ}$ , an *acetyl* derivative, m. p.  $219^{\circ}$ , and a *phenylhydrazone*, decomp.  $238^{\circ}$ . It resists dehalogenation by the usual methods, but is converted by catalytic hydrogenation into hydroxydihydrocodeinone, m. p.  $218-220^{\circ}$ . Since it is also produced by the bromination of bromohydroxycodeinone in boiling glacial acetic acid, the primary action is considered to consist of addition of bromine at positions 8 and 14 (see I) followed by loss of hydrogen bromide, leaving the second bromine atom in position 8. Confirmation of this hypothesis is found in the observation that dibromohydroxycodeinone is converted by sodium hyposulphite [which has been observed previously (Freund and Speyer, *loc. cit.*) to effect saturation of the double bond between the carbon atoms 8 and 14] into *bromohydroxydihydrocodeinone*, m. p.  $182^{\circ}$  (*hydrobromide*, decomp.  $227-230^{\circ}$  after softening,  $[\alpha]_D^{25} -93.15^{\circ}$  in aqueous solution; *monoacetyl* derivative, m. p.  $217^{\circ}$ ; *semicarbazone*, decomp.  $249^{\circ}$ ). Bromohydroxydihydrocodeinone is also obtained by the action of bromine water on a cold, aqueous solution of hydroxydihydrocodeinone hydrobromide and by the action of sodium hyposulphite on bromohydroxycodeinone; it is converted by palladium and hydrogen into hydroxydihydrocodeinone.

The action of bromine on hydroxydihydrocodeinone dissolved in boiling glacial acetic acid yields a crystalline *perbromide* from which *tribromohydroxydihydrocodeinone*,  $C_{18}H_{18}O_4NBr_3$ , decomp.  $228^{\circ}$  after softening,  $[\alpha]_D^{25} -225.56^{\circ}$  in acetic acid solution, is prepared. The compound is also obtained by the bromination under similar conditions of bromohydroxydihydrocodeinone, into which it is reconverted by sodium hyposulphite. The bromine atoms are hence considered to occupy the positions 1 or 2, 8 and 14 (see I). It gives a *hydrobromide*, decomp.  $255^{\circ}$ , and an *acetyl* derivative, decomp.  $220^{\circ}$  after softening. The tribromo compound is converted by 2*N*-sodium hydroxide solution into a feebly basic substance,  $C_{18}H_{20}O_6NBr \cdot H_2O$ , decomp.  $302^{\circ}$  after softening, which is regarded as bromo-7:8:14-trihydroxydihydrocodeinone; it yields, however, only a *monoacetate* ( $+H_2O$ ), decomp.  $267^{\circ}$ . Dehalogenation by means of hydrogen and palladium yields 7:8:14-trihydroxydihydrocodeinone, decomp.  $320^{\circ}$  after softening,  $[\alpha]_D^{25} -76.55^{\circ}$  in feebly alkaline solution.

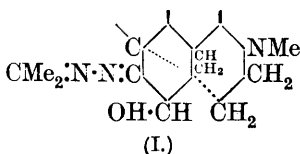
Hydroxycodeinone-*N*-oxide (cf. Freund and Speyer, *loc. cit.*) which has now been obtained in the crystalline form, decomp.  $243^{\circ}$ , is converted by acetic anhydride and sulphuric acid into "ordinary" *hydroxycodeinone-N-oxidesulphonic acid*, long rodlets, decomp. above  $260^{\circ}$ , and  $\alpha$ -*hydroxycodeinone-N-oxidesulphonic acid*, rectangular leaflets, incipient decomp.  $270^{\circ}$ . The former acid is converted by sulphurous acid into *hydroxycodeinonesulphonic acid*, decomp.  $310^{\circ}$ . Attempts to replace the sulphonic group by bromine were unsuccessful.

H. W.

**Catalytic Hydrogenation of Hydroxycodeinone- and Hydroxydihydrocodeinone-hydrazones by Palladium and Hydrogen.** E. SPEYER and K. SARRE (*Ber.*, 1924, **57**, [B], 1422-1427).—Hydroxycodeinone is readily converted by hydrazine



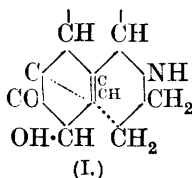
hydrate into the corresponding *hydrazone*, m. p. 221—222°, which does not appear to yield the desired methylene derivative when heated with sodium ethoxide solution under pressure. Hydroxydihydrocodeinone and hydrazine hydrate in the presence of glacial acetic acid give *hydroxydihydrocodeinonehydrazone*,  $C_{18}H_{23}O_3N_3$ , m. p. 213—214° (slight decomp.); it is not reduced by hydrogen and palladium in dilute acetic acid solution. Under similar conditions, hydroxycodeinonehydrazone absorbs 2 mols. of hydrogen with production of ammonia and *hydroxydihydrocodeinoneketimine*,  $C_{18}H_{22}O_3N_2$ , m. p. 216—217° after softening, which is readily hydrolysed by acids to ammonia and hydroxydihydrocodeinone. If



hydrogenation is effected in the presence of aqueous acetone, only 1 mol. of hydrogen is absorbed and *hydroxydihydrocodeinonedimethylketazine* (I), m. p. 159°, is produced. Hydroxycodeinonehydrazone condenses with acetone in the presence of ammonia to give *hydroxycodeinonedimethylketazine*, m. p. 171°, which could not be hydrogenated satisfactorily to the dihydro compound described above.

H. W.

**Action of Cyanogen Bromide on Hydroxycodeinone and Hydroxydihydrocodeinone.** E. SPEYER and K. SARRE (*Ber.*, 1924, 57, [B], 1427—1430).—Hydroxycyanonorcodeinone (Freund and Speyer, A., 1917, i, 217) is converted by



boiling sulphuric acid (25%) into *hydroxynorcodeinone* (cf. I), decomp. 218°,  $[\alpha]_D^{25} -123.33^\circ$  in dilute acetic acid solution. It yields a crystalline *hydrobromide* and a *nitroso* derivative, m. p. 234°. It is converted by sodium ethoxide and allyl bromide into the non-crystalline *allylnorhydroxycodeinone*, characterised as the

*hydriodide*, decomp. 192°.

Acetoxydihydronorcodeinone is converted by cyanogen bromide into *cyanoacetoxydihydronorcodeinone*, decomp. 256° after softening. It is converted by sulphuric acid into the oily *hydroxydihydronorcodeinone* (*hydriodide*, decomp. 295°,  $[\alpha]_D^{25} -114.54^\circ$  in dilute acetic acid solution; *nitroso* derivative, decomp. 259°). *Allylhydroxydihydronorcodeinone* is a liquid which gives a crystalline *hydrobromide*, decomp. 182°. The pharmacological action of the allyl derivatives is opposite to that of the parent compounds, as is to be expected when the methyl is replaced by the allyl group (cf. von Braun, A., 1917, i, 163).

H. W.

**Strychnos Alkaloids. XLIII. Decomposition of the Azide of Dihydrobrucinonic Acid.** H. LEUCHS and S. KANAO (*Ber.*, 1924, 57, [B], 1318—1320; cf. A., 1923, i, 942).—Ethyl dihydrobrucinonate is converted successively into the corresponding *hydrazide*, decomp. 205° after softening at 185°, and *azide*. The latter is decomposed by boiling water into azoimide, formalde-

hyde, and an isobrucinolone hydrate,  $C_{21}H_{24}O_6N_2$ , m. p.  $295^\circ$  (decomp.) after darkening at  $260^\circ$ ,  $[\alpha]_D^{20} +89.4^\circ$  in glacial acetic acid solution (acetyl derivative, m. p.  $210-212^\circ$ ,  $[\alpha]_D^{20} +94.8^\circ$  in glacial acetic acid). The isobrucinolone hydrate is not identical with that obtained from isobrucinolone and hydrochloric acid (Leuchs and Brewster, A., 1912, i, 210). H. W.

**Action of Halogens on Substituted Pyrroles. Synthesis of a Dipyrrolethane and of a Colouring Matter with Four Pyrrole Nuclei in its Molecule.** H. FISCHER and H. SCHEYER (*Annalen*, 1924, **439**, 185—195; cf. this vol., i, 80).—Aniline interacts with ethyl 4-methyl-2-bromomethylpyrrole-3:5-dicarboxylate (A) to give ethyl 4-methyl-2-anilinomethylpyrrole-3:5-dicarboxylate, m. p.  $125-126^\circ$ , and with ethyl 3-bromo-4-methyl-2-bromomethylpyrrole-5-carboxylate (B) to give ethyl 3-bromo-4-methyl-2-anilinomethylpyrrole-5-carboxylate, m. p.  $128-129^\circ$ . (A) also reacts with phenylhydrazine, forming  $\alpha$ -(4-methyl-3:5-dicarbethoxy-2-pyrrolylmethyl) $\alpha$ -phenylhydrazine, m. p.  $120-121^\circ$ , the asymmetric structure of which is demonstrated by the fact that with benzaldehyde it affords a hydrazone, rhombs, m. p.  $116-117^\circ$ . (B) gives a similar product, namely,  $\alpha$ -(3-bromo-4-methyl-5-carbethoxy-2-pyrrolylmethyl) $\alpha$ -phenylhydrazine, m. p.  $126^\circ$ . With hydrazine itself, (A) yields  $\alpha\alpha$ -di-(4-methyl-3:5-dicarbethoxy-2-pyrrolylmethyl)hydrazine, m. p.  $130-131^\circ$ , which affords with benzaldehyde a hydrazone, m. p.  $129-130^\circ$ , and with ethyl 2:4-dimethylpyrrole-3-aldehyde-5-carboxylate also a hydrazone, m. p.  $162-163^\circ$  after softening; when the hydrazine is treated with cuprammonium acetate solution, nitrogen is evolved, and *s*-di-(4-methyl-3:5-dicarbethoxy-2-pyrrolyl)ethane, needles, m. p.  $161^\circ$ , is produced. The latter suffers hydrolysis to the dicarboxylic acid (the sodium salt is described) when treated with sodium hydroxide solution, only the two 5-carbethoxy groups being affected; when the sodium salt of this is treated with formic and hydrochloric acids the carboxyl groups are displaced and 5:5'-di-(4''-methyl-3''-carbethoxy- $\beta$ -pyrrolylethyl)-3:3'-dimethyl-4:4'-dicarbethoxy-2:2'-dipyrrolylmethene (annexed formula), m. p.  $277^\circ$  (decomp.), is produced. This is an intensely yellow-coloured substance, closely resembling mesobilirubin in colour.

Ethyl 2:4-dimethylpyrrole-5-carboxylate is converted by treatment with bromine (2 mols.) into (B), which was previously obtained (*loc. cit.*) by another method. When 3-acetyl-2:4-dimethylpyrrole is treated with iodine 5-iodo-3-acetyl-2:4-dimethylpyrrole, m. p.  $160^\circ$  (decomp.), is obtained. The iodine atom here is not very mobile, but when the compound is treated with bromine the same methene is produced as is afforded when the unsubstituted pyrrole is treated with an excess of bromine (*loc. cit.*). Ethyl 5-iodo-2:4-dimethylpyrrole-3-carboxylate, m. p.  $146^\circ$ , ethyl 3-iodo-

2 : 4-dimethylpyrrole-5-carboxylate, m. p. 141°, and ethyl 4-iodo-2 : 5-dimethylpyrrole-3-carboxylate, m. p. 136°, are also described.

W. A. S.

**Synthesis of Phyllopyrrolecarboxylic Acid (Synthesis of the Acid Scission Products of Blood Pigment. II).** H. FISCHER and C. NENITZESCU (*Annalen*, 1924, **439**, 172—184; cf. this vol., i, 543).—2 : 4 : 5-Trimethylpyrrole-3-aldehyde reacts with malonic acid in presence of piperidine (the aldehyde forms an additive compound with piperidine, m. p. 145°) to yield 2 : 4 : 5-trimethylpyrrole-3( $\beta$ )-acrylic acid, a green, not very stable substance, m. p. 203°, which is readily reduced by sodium amalgam to 2 : 4 : 5-trimethylpyrrole-3( $\beta$ )-propionic acid, m. p. 88° (picrate, m. p. 124°) identical with phyllopyrrolecarboxylic acid obtained from hæmin. When the above aldehyde is condensed with malononitrile, 2 : 4 : 5-trimethyl-3-( $\omega\omega$ -dicyanovinyl)pyrrole, greenish-yellow needles, m. p. 185°, is obtained. This substance resists hydrolysis; by the action of sodium hydroxide, the aldehyde is regenerated, and sulphuric acid causes profound decomposition. By a similar condensation, using cyanoacetic acid, 2 : 4 : 5-trimethyl-3-( $\omega$ -cyano- $\omega$ -carboxyvinyl)pyrrole, green crystals, m. p. 214°, was prepared. This also cannot be hydrolysed, but when heated at its m. p. decomposes, giving 2 : 4 : 5-trimethyl-3-( $\omega$ -cyanovinyl)pyrrole, olive-green needles, m. p. 154°, which, when treated with sodium amalgam, undergoes reduction and hydrolysis, giving phyllopyrrolecarboxylic acid, identical with that previously obtained. 2 : 5-Dimethyl-4-carbethoxypyrrole-3-aldehyde also reacts with malonic acid to afford directly 2 : 5-dimethyl-4-carbethoxypyrrole-3( $\beta$ )-acrylic acid, yellow scales, m. p. 230° (decomp.), which, when reduced with sodium amalgam, yields 2 : 5-dimethyl-4-carbethoxypyrrole-3( $\beta$ )-propionic acid, m. p. 178°. The latter may also be obtained synthetically by heating with ammonium acetate at 160° the oily ethyl  $\alpha\beta$ -diacetyladipeate formed by interaction of ethyl acetylbromobutyrate and ethyl sodioacetoacetate; the ester obtained is readily hydrolysed by warm potassium hydroxide. When the dimethyl-carbethoxypyrrolepropionic acid of either provenance is heated at 220° with potassium methoxide and methyl alcohol, it yields phyllopyrrolecarboxylic acid.

W. A. S.

**Condensations of Acetyl-*p*-phenylenediamine to Derivatives of Pyrrole and their Hydrolytic Fission.** C. BÜLOW and W. DICK (*Ber.*, 1924, **57**, [B], 1281—1285).—Ethyl diacetylsuccinate reacts with acetyl-*p*-phenylenediamine in boiling glacial acetic acid solution to yield ethyl 1-*p*-acetamidophenyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate, m. p. 198—199°, which is hydrolysed by alcoholic potassium hydroxide solution to 1-*p*-acetamidophenyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylic acid, m. p. 252° (decomp.) [the potassium salt and the hydrochloride are described]. The acid is transformed at 250—255° into 1-*p*-acetamidophenyl-2 : 5-dimethylpyrrole, m. p. 192°, which is also obtained directly from acetonylacetone and acetyl-*p*-phenylenediamine. The ester is very slowly hydrolysed to the corresponding acid by aqueous alkali hydroxides.

but readily suffers fission of the pyrrole ring into its components under the influence of acids. With hydrazine, it yields the cyclic hydrazide,  $\text{NH}\cdot\text{CO}\cdot\text{C}(\text{Me})_2 > \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , m. p. above  $300^\circ$ .

Ethyl diacetylsuccinate and *p*-nitroaniline yield *ethyl 1-p-nitrophenyl-2:5-dimethylpyrrole-3:4-dicarboxylate*, m. p.  $94^\circ$ , which is reduced by zinc dust and hydrochloric acid to *ethyl 1-p-aminophenyl-2:5-dimethylpyrrole-3:4-dicarboxylate*, m. p.  $117^\circ$ . The diazotised ester is coupled with the requisite component to yield *ethyl 1-p-aminophenyl-2:5-dimethylpyrrole-3:4-dicarboxylate-azo- $\beta$ -naphthol*, m. p.  $166^\circ$ , *ethyl 1-p-aminophenyl-2:5-dimethylpyrrole-3:4-dicarboxylate-azoacetoacetanilide*, m. p.  $155^\circ$ , and the corresponding *p*-phenetidine, m. p.  $178^\circ$ . The latter compounds are converted by phenylhydrazine

into the substance 
$$\begin{array}{c} \text{CO}_2\text{Et}\cdot\text{C}(\text{Me})_2 \\ | \\ \text{CO}_2\text{Et}\cdot\text{C}(\text{Me})_2 \end{array} > \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C} \begin{array}{l} \text{Me}=\text{N} \\ \text{C}(\text{OH})\cdot\text{NPh} \end{array}$$
, m. p.  $154\text{--}156^\circ$ . Ethyl 1-*p*-nitrophenyl-2:5-dimethylpyrrole-3:4-dicarboxylate and ethyl 1-phenyl-2:5-dimethylpyrrole-3:4-dicarboxylate suffer fission of the pyrrole ring under the influence of mineral acids; this reaction appears therefore to be general.

H. W.

**Synthesis of 1-Aminocarbazole.** H. LINDEMANN and F. WERTHER (*Ber.*, 1924, 57, [B], 1316—1318).—7-Nitro-1-phenylbenzotriazole is reduced by stannous chloride and hydrochloric acid to 7-amino-1-phenylbenzotriazole,  $\text{NH}_2\cdot\text{C}_6\text{H}_3 < \begin{array}{c} \text{N} \\ \text{NPh} \end{array} > \text{N}$ , m. p.  $163^\circ$  (acetyl derivative, m. p.  $166^\circ$ ), which, when heated at  $300^\circ$  in paraffin, yields 1-aminocarbazole, m. p.  $193^\circ$  (diacetyl compound, m. p.  $186^\circ$ ). Since the amine is also produced by the action of sodium hyposulphite on an alkaline-alcoholic solution of the nitrocarbazole, m. p.  $187^\circ$ , isolated by Lindemann as by-product of the nitration of nitrosocarbazole (this vol., i, 550), the latter must be 1-nitrocarbazole; the compound described thus in the literature is therefore the 2- or 4-nitro derivative.

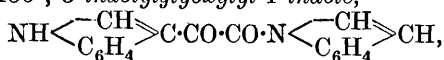
H. W.

**Carbazole Derivatives.** I. R. SEKA (*Ber.*, 1924, 57, [B], 1527—1530).—Ethyl carbazole-9-acetate is converted by alcoholic ammonia at  $120^\circ$  into carbazole-9-acetamide,  $\text{C}_{12}\text{H}_8\text{N}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , m. p.  $244^\circ$ , and by hydrazine hydrate at  $125^\circ$  into carbazole-9-acetylhydrazide, m. p.  $258\text{--}258.5^\circ$  (benzylidene derivative, m. p.  $267.5^\circ$ ; hydrochloride, m. p. above  $320^\circ$ ). The hydrazide is converted through the azide into the corresponding urethane,  $\text{C}_{12}\text{H}_8\text{N}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , m. p.  $133.5^\circ$ . Diphenyl-9-carbazolylmethylcarbinol,  $\text{C}_{12}\text{H}_8\text{N}\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$ , m. p.  $147^\circ$ , is prepared by the action of an excess of magnesium phenyl bromide on ethyl carbazole-9-acetate.

H. W.

**Synthesis in the Indole Group.** III. Formation of *N*-Acylindoles. R. MAJIMA and T. SHIGEMATSU (*Ber.*, 1924, 57, [B], 1449—1453).—The addition of ethyl acetate to a solution of magnesium indolyl iodide in ether or anisole leads to the formation of

1-acetylindole; the solvent does not play the same decisive part as in the action of magnesium indolyl iodide and formic ester (Majima and Kotake, A., 1923, i, 150). Magnesium indolyl iodide and ethyl oxalate yield a mixture 1:1'-oxalyl-di-indole,  $C_{18}H_{12}O_2N_2$ , m. p. 154.5—156°, 3-indolylglyoxylyl-1-indole,



m. p. 224—225° (which is hydrolysed by potassium hydroxide to indole, and indolyl-3-glyoxylic acid, decomp. 215° after darkening at 186°), and ethyl indolyl-3-glyoxylate, m. p. 185—186°. The compound designated 1:1-di-indolyl prepared by Oddo and Sanna (A., 1922, i, 371) by the action of oxalyl chloride on magnesium indolyl bromide is 3-indolylglyoxylyl-1-indole.

[With T. ROKKAKU.]—Ethyl malonate does not appear to react with magnesium indolyl iodide in the presence of anisole.

[With T. IKEDA.]—Ethyl succinate and magnesium indolyl iodide yield succinyl-1:1'-di-indole,  $C_{20}H_{16}O_2N_2$ , m. p. 217—218°.

H. W.

#### Syntheses in the Indole Group. IV. Indolylketonic Acids.

R. MAJIMA, T. SHIGEMATSU, and T. ROKKAKU (*Ber.*, 1924, 57, [B], 1453—1456).—The action of carbomethoxyformyl chloride on an ethereal solution of magnesium indolyl iodide gives a little 3-indolylglyoxylyl-1-indole (cf. preceding abstract) and, mainly, methyl 3-indolylglyoxylate, m. p. 220—222° (phenylhydrazone, m. p. 133—136°). The oxime, m. p. 149—151°, and the oxime of the corresponding ethyl ester, m. p. 138—142°, are prepared by means of hydroxylamine hydrochloride and potassium acetate in alcoholic solution. If, however, the ester is warmed with the equivalent quantity of free hydroxylamine, 3-indolylglyoxylic acid oxime, decomp. about 151°, is produced. Ethyl 3-indolylacetate,  $C_8H_8N \cdot CO \cdot CH_2 \cdot CO_2Et$ , m. p. 119.5°, prepared from magnesium indolyl iodide and carbethoxyacetyl chloride, is readily transformed by alcoholic potassium hydroxide solution into methyl 3-indolyl ketone. The ester is converted by phenylhydrazine into 1-phenyl-3-β-indolylpyrazolone,  $C_{17}H_{13}ON_3$ , m. p. 201—203°, and by hydroxylamine into 3-β-indolylisooxazolone,  $C_{11}H_8O_2N_2$ , m. p. 188—188.5°.

[With T. IKEDA.]—Ethyl β-3-indolylpropionate, prepared from magnesium indolyl iodide and β-carbethoxypropionyl chloride, has m. p. 129.5—130.5°; the corresponding acid, m. p. 235—236°, is described. The ester is decomposed by molten potassium hydroxide with production of indole-3-carboxylic acid in small amount.

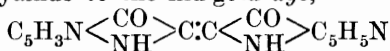
[With I. MIYAGAWA.]—Cyanogen chloride and magnesium indolyl iodide yield 3-cyanoindole, m. p. 178—180.5°. 3-Cyano-2-methylindole, m. p. 210—212°, is unusually resistant to hydrolysis by alkali hydroxide.

H. W.

**New Class of Indigoid Dyes.** F. REINDEL (*Ber.*, 1924, 57, [B], 1381—1386).—2-Aminopyridine is converted by chloroacetic acid into pyridylglycine,  $C_7H_8O_2N_2$ , m. p. 250° (decomp.), which is transformed by boiling sodium hydroxide solution into the sodium

salt of *pyrindoxyl*,  $C_5H_3N \langle \begin{smallmatrix} C(ONa) \\ NH \end{smallmatrix} \rangle CH$  or  $NH:C_5H_3 \langle \begin{smallmatrix} C(ONa) \\ N \end{smallmatrix} \rangle CH$ .

The constitution of the salt is thus far established by its ability to give a *monobenzoyl* derivative, m. p. 293° (decomp.) after softening at 275°, which is soluble in alkali hydroxide solution, and an insoluble *dibenzoyl* compound, m. p. 172—173°, when benzoylated according to the Schotten-Baumann reaction, whereas when treated with benzoyl chloride in the presence of pyridine it yields a *benzoyl* derivative, m. p. 130°, which is insoluble in alkali hydroxide. The *barium*, *copper*, *lead*, *cobalt*, and *nickel* salts of pyrindoxyl have been examined; the *hydrochloride*,  $C_7H_7ON_2Cl$ , m. p. 243° (decomp.) after darkening at 230°, and the *picrate*, decomp. 207—208°, are described. The sodium salt is oxidised by an aqueous solution of potassium ferricyanide to the indigoid *dye*,



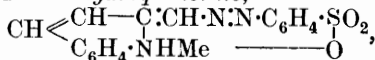
or  $C_5H_3(NH) \langle \begin{smallmatrix} CO \\ N \end{smallmatrix} \rangle C:C \langle \begin{smallmatrix} CO \\ N \end{smallmatrix} \rangle C_5H_3NH$ , a red amorphous powder which is readily reduced beyond the indigo-white stage by sodium hyposulphite, but yields a typical vat with zinc dust and sodium hydroxide. On cotton mordanted with tannin and tartar emetic, it gives raspberry-red shades which are fast to light but not to milling.

H. W.

### Reactions of 2-Methylene-1-alkyl-1 : 2-dihydroquinolines.

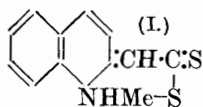
#### I. Diazo Coupling of the Methylene Base in Neutral Solution.

E. ROSENHAUER [with O. DANNHOFER] (*Ber.*, 1924, 57, [B], 1291—1294).—2-Methylene-1-methyl-1 : 2-dihydroquinoline dissolved in ether couples with a neutral, aqueous solution of benzenediazonium chloride without loss of the *N*-methyl group (contrast König, A., 1923, i, 862) to form 2-benzeneazomethylene-1-methyl-1 : 2-dihydroquinoline hydrochloride, decomp. 243°, from which the free base, m. p. 140—141°, is obtained; the latter compound is identical with that prepared from 2-bromomethylquinoline methobromide and phenylhydrazine (Rosenhauer, this vol., i, 768). When cautiously oxidised with potassium permanganate, it yields 1-methyl-2-quinolone. Similarly, the methylene base and diazobenzene-sulphonic acid give the "internal" *p*-sulphonate of 2-benzeneazomethylene-1-methyl-1 : 2-dihydroquinoline,



decomp. above 300°, which is transformed by sodium hydroxide into the *sodium* salt of 2-*p*-sulphobenzeneazomethylene-1-methyl-1 : 2-dihydroquinoline.

[With A. SCHMIDT and W. SCHLEIFENBAUM.]—2-Methylene-



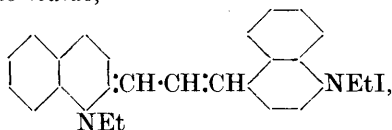
quinoline.

1-methyl-1 : 2-dihydroquinoline dissolved in benzene is converted by a large excess of carbon disulphide into the compound I, decomp. 185°. A similar substance,  $C_{13}H_{13}NS_2$ , decomp. 185°, is derived from 2-methylene-1-ethyl-1 : 2-dihydro-

H. W.

**Degradation of Pyridine to Glutacondialdehyde and Reconversion of the Latter into Pyridine.** I. P. BAUMGARTEN.—(See i, 1166.)

**Cyanine Dyes. VIII. Synthesis of a 2:4'-Carbocyanine.**  
**Constitution of the Dicyanines.** W. H. MILLS and R. C. ODAMS (*J. Chem. Soc.*, 1924, **125**, 1913—1921).—When a mixture of 4-methyl- and 2-methyl-quinoline ethonitrates is heated in pyridine solution with diformylmethylaminodiphenyl disulphide (cf. Mills, Clark, and Aeschlimann, T., 1923, **123**, 2358) six products are formed and may be separated by fractional extraction with and crystallisation from water, benzene, or methyl alcohol, if necessary after conversion into the respective iodides. They are (i) bis-2-methylbenzothiazoline-1:1-spiran (Mills and Braunholtz, T., 1923, **123**, 2804); (ii) and (iii) pinacyanole and kryptocyanine (in very small amount); (iv) 2-methyl-1'-ethylthioisocyanine iodide, m. p. 248—249°, which was prepared also from 4-methylquinoline ethonitrate; (v) 2-methyl-1'-ethylthiopseudocyanine iodide, m. p. 254—256°, also prepared separately from 2-methylquinoline ethonitrate; and (vi) the main product (the quantity of which showed that condensation between two dissimilar molecules readily takes place), namely, 1:1'-diethyl-2:2'-carbocyanine iodide,

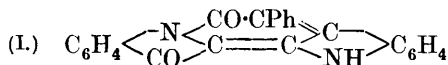


m. p. 240—241° (the crystals contain 1 MeOH). This substance is spectrometrically intermediate between pinacyanole and kryptocyanine.

The dicyanine, m. p. 244—252°, from 2:4-dimethylquinoline ethiodide (cf. Mikeska, Haller, and Adams, A., 1921, i, 54) was prepared by oxidising the base, in methyl-alcoholic solution, by exposure to the air. The absorption spectrum of this compound is almost identical with that of the above 2:4'-carbocyanine; this result and analytical figures show that the compound is 2':4'-dimethyl-1:1'-diethyl-2:2'-carbocyanine iodide. Presumably it is formed by the linking of 2 mols. of the ethiodide by means of a methenyl group furnished by disruptive oxidation of a portion of the material.

W. A. S.

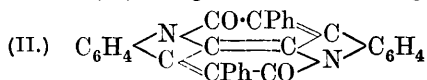
**Indigotin Group. IV. New Vat Dye Prepared from Indigotin and Ethyl Phenylacetate.** T. POSNER and W. KEMPER (*Ber.*, 1924, **57**, [B], 1311—1315).—Ethyl indigotinphenylacetate (I), dark violet crystals, m. p. above 320°, is obtained by



protracted ebullition of powdered indigotin with a very large excess of ethyl phenylacetate. A substance,  $C_{24}H_{17}O_2N$ , m. p. 302°, which has not been investigated further, is obtained as by-product.

It is converted by reduction with sodium hyposulphite in the presence of sodium hydroxide and addition of benzoyl chloride to the solution into *ethyl benzoyldihydroindigotinphenylacetate*, m. p. 235°, and by benzoyl chloride in the presence of boiling pyridine into *ethyl benzoylindigotinphenylacetate*, m. p. 307° (decomp.), thus establishing the presence of the carbonyl and imino groups. Since it is transformed by protracted boiling with ethyl malonate into ethyl anhydrophenylacetylindigotinmalonate, identical with the product obtained by Posner and Pyl (A., 1923, i, 254) from ethyl indigotinmalonate and phenylacetyl chloride, it must contain the group  $-\text{CO}\cdot\text{C}:\text{C}\cdot\text{NH}-$ . The compound and ethyl indigotinmalonate are of peculiar interest since they can only be derived from the *trans* form of indigotin.

The constitution (II), assigned without stringent proof to Ciba-



red B, is established by its production from ethyl indigotinphenylacetate and ethyl phenylacetate or phenylacetyl chloride. H. W.

**Quinazolines. XXXVII. Behaviour of Phthalic Anhydride with the Reactive Methyl Groups of certain Quinazolines.** M. T. BOGERT and F. P. NABENHAUER (*J. Amer. Chem. Soc.*, 1924, 46, 1932—1936; cf. A., 1912, i, 214).—An attempt has been made to prepare dyes of the quinoline-yellow type by condensing several quinoxalines with phthalic anhydride and sulphonating the products. 2-Methyl-, 2:4-dimethyl-, 2-phenyl-, and 2-phenyl-4-methylquinazolines were prepared (in the main) by methods already described. 4-Methylquinazoline, pale yellow prisms, m. p. 36—37° (corr.), b. p. ca. 260° (corr.), was prepared by boiling 4-methylquinazoline-2-carbonamide with hydrochloric acid; *picrate*, m. p. 183.5° (corr.). These quinazolines when heated with phthalic anhydride at about 200° showed varying degrees of reactivity; the condensation was more rapid and complete when the methyl group was in the 2-position and the product was insoluble in dilute alkali. The condensation product (phthalone) from the 4-methylquinazoline was soluble in dilute alkali. Since only a small portion of the product from 2:4-dimethylquinazoline was soluble in alkali it appears that the 2-methyl had reacted rather than the 4-methyl group. The phthalones in all cases were amorphous and difficult to purify, those from 4-methyl- and 2-phenyl-4-methylquinazolines being incapable of purification. 2-Methylquinazolinephthalone,  $\text{C}_{17}\text{H}_{10}\text{O}_2\text{N}_2$ , is a yellowish-brown powder, soluble with a yellow colour in sulphuric acid and organic solvents. Its sulphonation product dyes silk a dull golden-yellow, not very fast to washing. 2:4-Dimethylquinazolinemonophthalone,  $\text{C}_{18}\text{H}_{12}\text{O}_2\text{N}_2$ , was obtained (impure) as a dark brown powder, insoluble in water and dilute alkali. The ammonium salt of the sulphonation product dyes silk a brown shade. The condensation product (purity, 80%) from 4-methylquinazoline and phthalic anhydride was strikingly different from the above phthalones, being insoluble in ethyl-



benzene and soluble in dilute alkali to a brown solution. Acids precipitated it as a brownish-yellow powder. It is a very strong dye, the dyeings (on silk), however, being less fast to washing than to light. 2-Phenyl-4-methylquinazoline formed only a small amount of condensation product with phthalic anhydride even after 8 hours' heating at 210°; a little of this was soluble in dilute alkali, the insoluble part (still containing unchanged quinazoline) on sulphonation giving a *product* which dyed silk orange. The dyes obtained appear to be decidedly inferior to quinoline-yellow.

A. C.

[Derivatives of *cyclo*Triazobutane.] R. STOLLÉ (*Ber.*, 1924, 57, [B], 1558).—The compound described by Diels and Behncke (this vol., i, 674) as *cyclotriazomethene-4:4-dicarboxylic acid* is identified as the hydroxytriazolecarboxylic acid,  $\begin{array}{c} \text{N:C(OH)—} \\ \text{N:C(CO}_2\text{H)—} \end{array} \text{>NH}$ , whereas 2:4-carbonyl*cyclotriazomethene* is the hydroxytriazole,  $\begin{array}{c} \text{N:C(OH)—} \\ \text{N:CH—} \end{array} \text{>NH}$ .

H. W.

### *iso*Oxazoline Oxides. III. Triphenyl*isooxazoline* Oxide.

E. P. KOHLER and G. R. BARRETT (*J. Amer. Chem. Soc.*, 1924, 46, 2105—2113).—By the condensation of nitrostilbene with phenyl-nitromethane in the presence of sodium methoxide (cf. Knoevenagel and Walter, A., 1905, i, 65), 3:4:5-*triphenylisooxazoline oxide*,  $\begin{array}{c} \text{CHPh}\cdot\text{CHPh} \\ \text{CPh}=\text{NO} \end{array} \text{>O}$ , m. p. 162°, is obtained, in which

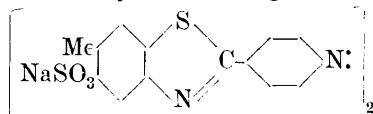
the only reactive group present is the system C:NO characteristic of *isooxazoline* oxides (cf. this vol., i, 571, 998). The reaction probably proceeds according to the scheme:  $\text{CHPh}\cdot\text{CPh}\cdot\text{NO}_2 + \text{CH}_2\text{Ph}\cdot\text{NO}_2 \rightarrow \begin{array}{c} \text{CHPh}\cdot\text{CHPh}\cdot\text{NO}_2 \\ \text{CPh}\cdot\text{NO}_2 \end{array} \rightarrow \begin{array}{c} \text{CHPh}\cdot\text{CHPh} \\ \text{CPh}=\text{NO} \end{array} \text{>O}$ , the dinitro compound having been previously isolated by Hein (A., 1911, i, 717). Triphenyl*isooxazole* (Meisenheimer, A., 1922, i, 176) is the main by-product of the reaction and its formation is due to "stripping" of the *isooxazoline oxide* by excess of sodium methoxide since this is rapidly converted into the *isooxazole* on boiling with concentrated aqueous-alcoholic sodium hydroxide. Dilute bases have little action (cf. *loc. cit.*), and the mechanism of the "stripping" is not clear, as no evidence could be obtained of the intermediate formation of a ketolic oxime,  $\text{HO}\cdot\text{N:CPh}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{OH}$ . The oxide is not "stripped" by acetic acid, but loses water when heated alone, yielding *isooxazole* and benzonitrile. Nitrous acid in acetic acid and permanganate in acetone do not attack the oxide, but with chromic acid in acetic acid phenyldibenzoylmethane (Meisenheimer, *loc. cit.*) was obtained. Bromine in acetic acid gave, besides *isooxazole*, a small amount of a nitrogen-free substance, m. p. 125°. In other reactions also, the new *isooxazoline oxide* shows marked differences from the oxides previously obtained, which contained acyl groups. With phosphorus pentachloride, it behaves like diphenylfuroxan, oxygen being removed, yielding 3:4:5-*triphenyl-*

*isooxazoline*, m. p. 136—137°, which does not react with magnesium ethyl bromide, and is oxidised to triphenylisooxazole by chromic acid. Reduction with zinc and acetic acid converts the oxide into a stable substance, m. p. 188°, which yields an *acetyl* derivative, m. p. 100—110° (decomp.), a *benzoyl* derivative, m. p. 130°, and a *copper* derivative with cupric acetate; the structure 2-hydroxy-3:4:5-triphenylisooxazoline is accordingly assigned to it (cf. Posner, A., 1907, i, 55), the acidic properties being attributed to the NOH group. Concentrated sulphuric acid transforms this reduction product into (1) a 3:4:5-triphenylisooxazoline, m. p. 208°, isomeric with the product obtained by the action of phosphorus pentachloride on the isooxazoline oxide; (2) triphenylisooxazole, and (3) 3:4:5-triphenylisooxazolidine, m. p. 96°, which reacts with magnesium ethyl bromide, yields a nitroso compound, and is identical with the main product of the action of sulphuric acid on the oxide. Only small amounts of the isooxazole are formed, and the relative amounts of this and the isooxazolidine do not accord with a reciprocal oxidation-reduction reaction. Triphenylisooxazoline oxide reacts with a large excess of magnesium ethyl bromide, giving, in 50% yield, the above 2-hydroxy-3:4:5-triphenylisooxazoline.

R. B.

#### Constitution of Columbia-yellow (Chloramine-yellow).

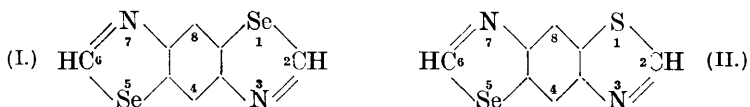
M. T. BOGERT and F. H. BERGEIM (*Proc. Nat. Acad. Sci.*, 1924, 10, 318—322).—Columbia-yellow is assigned the formula



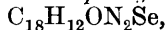
The position of the sulphonate groups is still in doubt. Specimens of the dye purified through the free sulphonic acid and its cerium salt give analyses and molecular weights agreeing with this formula. The dye was synthesised by reducing 2-*p*-nitrophenyl-6-methylbenzthiazole to the azo compound by means of zinc and alkali, and subsequently sulphonating; the product was physically, chemically, and tinctorially identical with Columbia-yellow. The lower homologue of this dye was prepared by oxidising sodium 2-*p*-aminophenylbenzthiazolesulphonate with sodium hypochlorite and proved to be a substantive dye of a lighter shade but very similar properties. Hence the methyl groups are not essential for the production of this type of dye, and in the usual method of preparation of Columbia-yellow by the action of sodium hypochlorite on sodium dehydrothio-*p*-toluidinesulphonate it is the amino group which is oxidised, and not, as has been suggested, the methyl group, giving rise to a stilbene derivative. The oxidation of the amino group may produce an azo compound, a quinone, a quinoneimine, a chloroimine, or a chloroamine. Since the purified dye contains no chlorine, the two latter are excluded. The resistance to oxidation and reduction exhibited by Columbia-yellow is an argument against quinone structure and further evidence in this direction was supplied by the observation that 2-*p*-hydroxyphenyl-

6-methylbenzthiazolesulphonic acid (prepared by diazotisation from dehydrothio-*p*-toluidinesulphonic acid) did not give a dye or a colour reaction when oxidised by sodium hypochlorite. S. S.

**Selenium Organic Compounds. IV. Synthesis of Benzo-bis-selenazoles and Selenazolobenzothiazoles; New Heterocyclic Systems.** M. T. BOGERT and H. H. HOPKINS (*J. Amer. Chem. Soc.*, 1924, **46**, 1912—1917).—The new heterocyclic types: (I) benzobis-selenazoles and (II) selenazolobenzthiazoles have been prepared by fusion of benzylideneaminobenzoselenazoles with selenium and with sulphur. 2 : 6-Diphenyl-*p*- $\beta$ -benzobis-selenazole



lemon-yellow needles, m. p. 217°, was obtained in 17% of the theoretical yield by boiling 6-benzylideneamino-2-phenylbenzoselenazole with selenium. As proof of its structure it was also synthesised by fusing dibenzylidene-*p*-phenylenediamine with selenium. A mixture of the two products had the same m. p. It forms an unstable *acetyl chloride additive* product; a *nitro* derivative, m. p. 296.1—297.1°; a *dinitro* derivative, m. p. 332.4—333.4°. The nitro compound on reduction with tin and hydrochloric acid gives *amino*-2 : 6-diphenyl-*p*- $\beta$ -benzobis-selenazole (yield 30%), orange needles, m. p. 279.4—281°; it formed a *benzylidene* derivative, m. p. 233.5—235.5°, when heated in boiling *n*-butyl-alcoholic solution with benzaldehyde. 2 : 6-Diphenyl-*p*- $\beta$ -selenazolobenzthiazole, m. p. 220.4—221.5°, b. p. 345—350°/11 mm., was obtained as lustrous yellow needles from the mass formed on fusing 6-benzylideneamino-2-phenylbenzoselenazole with sulphur at 250—260°; the *tetrabromide* decomposed at 238—243°, and slowly on keeping; an *acetyl chloride additive* product melted at 224—225° with evolution of acetyl chloride; the *dinitro* derivative had m. p. 295—297°, and probably contained some mononitro derivative. The selenazolothiazole did not combine with methyl iodide in a sealed tube at 100°. One of the experiments for the preparation of the selenazolothiazole resulted in a 25% yield of a new *base*, C<sub>27</sub>H<sub>18</sub>N<sub>2</sub>S<sub>2</sub>Se, long, straw-coloured needles, m. p. 5° higher than the selenazole and quite distinct from it. The base gave a *dinitro* derivative, m. p. 283°, which on reduction yielded the compound C<sub>27</sub>H<sub>20</sub>N<sub>4</sub>SSe, brownish-yellow needles, m. p. 305° (decomp., with evolution of hydrogen sulphide). The character of the base was not ascertained, since, although numerous attempts were made, it could not be formed again. 6-Furfurylideneamino-2-phenylbenzoselenazole,



yellow needles, m. p. 147.5°, was prepared by heating 6-amino-2-phenylbenzoselenazole with excess of furfuraldehyde. Attempts to combine it with selenium were unsuccessful, as it charred below the m. p. of selenium. No pure product was obtained on heating the furfurylideneamino compound with sulphur. A. C.

**Naphthalene and its Derivatives.** N. VOROSKOV (*Bull. Soc. chim.*, 1924, [iv], 35, 996—1021).—The dissociation in aqueous solution of the *sodium hydrogen sulphite* compounds of benzene-azo- $\alpha$ -naphthol, yellow needles, benzeneazo- $\beta$ -naphthol ( $+2\text{H}_2\text{O}$ ), brilliant golden-yellow spangles, obtained by the action of sodium hydrogen sulphite on the pure azo compound, and of 5-hydroxy-naphthaleneazophenol, obtained by coupling phenol with the diazotised sodium hydrogen sulphite compound of 1:5-amino-naphthol, has been examined. In all cases, dissociation into azo compound and sulphite increases with the dilution and with the alkalinity of the solution, a very small increase in the number of hydroxyl ions producing a marked increase in the dissociation, whilst in acid solution the dissociation is very slightly retarded, and decreases slightly with increasing concentration of the acid. These results show that the three sulphite compounds have a similar structure and are to be regarded essentially as additive compounds, in opposition to Bucherer's views (*A.*, 1904, i, 309). The formation of such additive compounds will depend on the nature of the conjugated system and the positions of the substituents in the ring, the systems  $-\text{C}(\text{OH})\cdot\text{C}\cdot\text{C}\cdot\text{CX}-$  and  $-\text{C}(\text{OH})\cdot\text{CX}-$  favouring the reaction, whilst the systems  $-\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CX}\cdot\text{CH}-$  and  $-\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CX}-$ , existing in the 3-substituted  $\alpha$ -naphthols and 4-substituted  $\beta$ -naphthols, do not favour addition, and consequently the Bucherer reaction does not take place (cf. Meyer and Lenhardt, *A.*, 1913, i, 704, 723). The different behaviour of the two amino groups in 1:5- and 1:8-naphthylenediamine with sodium hydrogen sulphite finds an explanation in the different character of the two benzene rings in the naphthalene molecule; one ring behaves as a conjugated olefinic system and yields the additive compound, leading to the naphthol, whilst the other behaves as an aromatic ring system and yields no additive product. The alkylation of the naphthols is similarly explained as due to the formation of an intermediate additive compound, and the conversion of naphthols into naphthylamines and the reverse reaction in the absence of sulphites are given a similar interpretation. The naphthols and naphthylamines from this point of view are intermediate in reactivity between the reactive conjugated open-chain compounds, such as ethyl acetoacetate or  $\beta$ -aminocrotonate, and the typical aromatic phenols and amines of the benzene series. The readiness with which phenols, such as nitrosophenol, phloroglucinol, and nitroso- $\beta$ -naphthol, which are capable of tautomeric change, are converted into amines also supports the theory (cf. Fuchs and Stix, *A.*, 1922, i, 451; Friedländer, *A.*, 1921, i, 443).

R. B.

**Optically Active Dyes. II. Adsorption, Absorption Spectra, and Rotation.** W. R. BRODE and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, 46, 2032—2043).—In continuance of their projected investigation of the question whether the absorption of dyes by animal or vegetable fibres is a physical or chemical process, using the previously described  $\beta$ -naphthol derivatives of *d*-, *l*-, and *dl*-*p*-diazobenzamidophenylacetic acid (Ingersoll and Adams, *A.*,

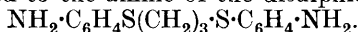
1923, i, 200), the authors have established that the adsorption of the two optically active forms of the dye by inactive adsorbing agents, such as charcoal and ball-clay, is identical, but is rather less than that of the racemic form, which also exists more in a colloidal state than do the *d*- and *l*-compounds. The absorption spectra of the active forms of the dye show bands of the same frequency, and variation of the hydrogen-ion concentration of the solutions changes the intensity, but not the wave-length of the bands (cf. A., 1922, ii, 602). Within the range of hydrogen-ion concentration change caused by the addition of common adsorbing agents, the change of colour of the active forms of the dye and the possible difference in the intensity is negligible as far as colorimetric determinations are concerned. Beer's law is valid for the dilute solutions used in these experiments and as far as studied the rotation of the two active dyes is normal. On long standing with sodium hydroxide, racemisation of the active forms takes place, and from saturated solutions of the active forms, the less soluble *dl*-form separates. In view of these facts, it is concluded that any difference in the adsorption of the *d*- and *l*-forms of the dye in the dyeing experiments may be taken as evidence of chemical reaction in the dyeing process.

R. B.

**Influence of Sulphur on the Colour of Azo Dyes.** D. G. FOSTER and E. E. REID (*J. Amer. Chem. Soc.*, 1924, **46**, 1936—1948).—By methods very similar to those employed for the para-analogues (cf. this vol., i, 95), a number of *o*-aminophenyl alkyl sulphides have been made by condensing sodium *o*-nitrothiophenoxide with alkyl halides and reducing the nitro compound with iron and acetic acid. Diamines of the type  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S})_2\text{R}$ , with sulphur have been made in the same way from alkylene dihalides. In many cases, the *o*-nitrophenyl alkyl sulphides were not isolated but reduced at once to the corresponding amino compounds, but the following were prepared in the pure state: *ethyl*, b. p. 149—150°/15 mm., *propyl*, b. p. 172—174°/7 mm., *allyl*, m. p. 54°, the respective yields being 46, 64, 32% of the theoretical. The *allyl sulphide*, m. p. 38—39°, and the *cyclohexyl sulphide*, m. p. 56—57° of the para-analogue were also prepared. All the amines of this series are oils which decompose below their boiling points, even under diminished pressure. They were isolated as hydrochlorides as white, crystalline solids,  $\text{R} \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{HCl}$  (the figures represent the % of the theoretical yield on the alkyl halide). *Methyl* (74), *ethyl* (73), *propyl* (54), *isopropyl* (99), *butyl* (55), *isobutyl* (72), *isoamyl* (71), *cyclohexyl* (32), *allyl* (75). *Allyl*- and *cyclohexyl*-*p*-aminophenyl sulphides were isolated as sulphates in 45 and 93% of the theoretical yields, respectively. The following *o*: *o'*-dinitrodiphenyl disulphides are described:  $(\text{C}_6\text{H}_4 \cdot \text{NO}_2)_2\text{S}_2\text{CH}_3$ , m. p. 170° from methylene iodide;  $(\text{C}_6\text{H}_4 \cdot \text{NO}_2)_2\text{S}_2(\text{CH}_2)_2$ , m. p. 205°, from ethylene dibromide;  $(\text{C}_6\text{H}_4 \cdot \text{NO}_2)_2\text{S}_2(\text{CH}_2)_3$ , m. p. 140°, from trimethylene bromide, and  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{C}_2\text{H}_4 \cdot \text{S} \cdot \text{C}_2\text{H}_4 \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$  (a trisulphide), m. p. 107—108°, from *pp*-dichlorodiethyl sulphide and sodium *o*-nitrothiophenoxide. The last four substances are

very sparingly soluble yellow solids. On reduction the corresponding diamines were obtained as brown oils; their hydrochlorides (which hydrolyse very rapidly) could not be obtained crystalline, but were precipitated from alcohol by means of ether:

$(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2\text{S}_2\text{CH}_2\cdot 2\text{HCl}$ ,  $(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2\text{S}_2(\text{CH}_2)_2\cdot 2\text{HCl}$ ,  
 $(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2\text{S}_2(\text{CH}_2)_3\cdot 2\text{HCl}$  and  $(\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{S}\cdot\text{C}_2\text{H}_4)_2\text{S}_2\cdot 2\text{HCl}$   
 were obtained in 91, 21, 89, and 90% of their respective theoretical yields. For the purpose of demonstrating the effect of the sulphone group (on the character of the dyes described below), as compared with the sulphur atom alone, the following *o*-nitrophenylsulphones (white, crystalline solids) were prepared by the method described for the para compounds:  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Me}$ , m. p.  $104-105^\circ$ ;  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Pr}$ , m. p.  $50^\circ$ ;  $(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_2)_2\text{CH}_2$ ,  $156-157^\circ$  in 65, 86, and 72% of the respective theoretical yields. The *o*-nitrophenylmethyl and propyl sulphones gave the corresponding amines,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Me}$ , an oil, and  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Pr}$ , m. p.  $50^\circ$ , in 69 and 53% of the theoretical yields, but the trimethylene nitrosulphone was reduced to the amine of the disulphide,



One of the sulphones of the para series behaved similarly. Dyes were made from all the above *o*-nitrophenyl alkyl sulphides and disulphides and sulphones by diazotisation and coupling with R-salt; only the free mercaptan,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SH}$ , failed to couple and give a dye. They dyed wool red, orange, and yellow shades. A comparison with similar sulphur-free dyes from known intermediates gave: -Me *deep salmon*, -OMe *carmine*, -SMe *yellowish-red*, -SO<sub>2</sub>Me *orange*, i.e., in the dyes containing sulphur the characteristic wave-length moves from the red towards the yellow whilst the methoxyl group appears more strongly bathochromic than the alkyl sulphide. In general, the bathochromic effect is much less marked than with sulphur in the para position. In the simple alkyl sulphides, increase in the molecular weight of the alkyl group attached to the sulphur produces a general hypsochromic effect, showing a periodicity in colour similar to that shown in certain physical constants of aliphatic homologous series. The dyes formed from the *o*-diamine bases are markedly different from the benzidine dyes both as to colour and in the fact that none of the ortho dyes are substantive. A hypsochromic effect is shown with reference to the sulphur-free dye when the two sulphur atoms are separated by only one carbon atom. Increasing separation and the introduction of a third atom of sulphur show a bathochromic influence with respect to the other sulphur dyes of the series. The colour relation to the sulphur-free dye is difficult to place. A. C.

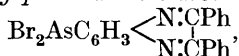
**Formation of Dyes on Animal Fibres by Reaction of the Material Itself.** J. GROOT (*Chem. Weekblad*, 1924, **21**, 450-455).—Wool, silk, hair, and other animal fibres react with nitrous acid, acquiring an intense yellow colour, which may be discharged by sunlight, heating, or the action of alkalis. The action is slow, requiring about 20 hours in the cold. After treatment and thorough washing, the fabric on treatment with phenols or amines acquires

distinctive colours. The coupling takes place in faintly acid or alkaline solutions, and the colours are fast to light and washing, but not to acids and alkalis. Subsequent treatment with metallic salts or with dichromate modifies the colours obtained; the mechanical strength of the fabrics is not adversely affected. The reaction appears to be a true diazotisation of the amino groups of the fibre proteins.

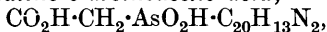
S. I. L.

**Condensation Products of Aminoarsanilic Acid (3 : 4-Diaminophenylarsinic acid).** W. L. LEWIS, P. L. CRAMER, and R. S. BLY (*J. Amer. Chem. Soc.*, 1924, **46**, 2058—2065).—With a view to study their therapeutic properties a number of arsinated quinoxalines have been prepared by the condensation of 3 : 4-diaminophenylarsinic acid with *o*-diketones. The condensation of 3 : 4-diaminodiphenylarsinic acid with cyanogen and with *o*-bromoacetophenone yields dihydroquinoxalines, but with monocarbonyl compounds, such as benzaldehyde, a series of arsenated Schiff's bases is obtained:  $\text{H}_2\text{O}_3\text{As}\cdot\text{C}_6\text{H}_3(\text{NH}_2)_2 + 2\text{PhCHO} = 2\text{H}_2\text{O} + \text{AsH}_2\text{O}_3\cdot\text{C}_6\text{H}_3(\text{N}:\text{CHPh})_2$ . The behaviour of ethyl acetoacetate is exceptional and a condensation product of 1 mol. of amino-acid with 1 mol. of acetone is obtained:  $\text{AsH}_2\text{O}_3\cdot\text{C}_6\text{H}_3(\text{NH}_2)_2 + \text{Ac}\cdot\text{CH}_2\text{CO}_2\text{Et} \rightarrow \text{EtOH} + \text{CO}_2 + \text{AsH}_2\text{O}_3\cdot\text{C}_6\text{H}_3(\text{NH}_2)(\text{N}:\text{CMe}_2)$ , a product which cannot be obtained directly from acetone.

3 : 4-Diaminodiphenylarsinic acid, obtained by Berthelm's method (A., 1911, i, 1055), using Jacobs and Heidelberger's method of reduction with ferrous hydroxide (A., 1919, i, 50), with diacetyl in absolute alcohol, yields 2 : 3-dimethylquinoxaline-6-arsinic acid, lustrous, pink flakes, m. p. 212—215° (decomp.). Similarly, in boiling methyl-alcoholic solution benzil gives 2 : 3-diphenylquinoxaline-6-arsinic acid, a white or slightly yellow substance (yield 64%), which on treatment with 50% hydrobromic acid in boiling acetic acid yields 2 : 3-diphenylquinoxaline-6-arsenious bromide,

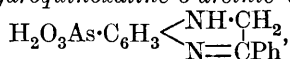


lustrous, yellow plates, m. p. 232°; the corresponding dihydroxide is white and the chloride has m. p. 185—187°; the iodide is described. The dihydroxide condenses with chloroacetic acid in alkaline aqueous-alcoholic solution (cf. Adams and Quick, A., 1922, i, 600), yielding 2 : 3-diphenylquinoxaline-6-arsinoacetic acid,



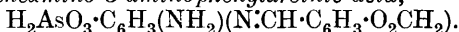
m. p. 122—125° (decomp.). 3 : 4-Diaminodiphenylarsinic acid and dinitrobenzil (Barnett and Kay, A., 1922, i, 844) in methyl alcohol give (yield 75%) 2 : 3-di-m-nitrophenylquinoxaline-6-arsinic acid, m. p. above 230° and giving a deep red solution in alkali. Similarly with anisil, prepared from oxalyl chloride and anisole by Staudinger's method (A., 1912, i, 567), is obtained, in 61% yield, 2 : 3-di-p-methoxyphenylquinoxaline-6-arsinic acid, light yellow needles, and with furil, 2 : 3-difurylquinoxaline-6-arsinic acid, m. p. above 250°. In glacial acetic acid are obtained similarly, from phenetil (*pp'*-diethoxybenzil), m. p. 150—151° (cf. Vorländer, A., 1911, i, 865), prepared by Staudinger's method, 2 : 3-di-p-ethoxyphenylquinoxaline-

6-arsinic acid, light yellow (yield 84%); from piperil (3 : 4-dimethylenedioxy-3' : 4'-methylenedioxybenzil, 2 : 3-di-3 : 4-methylenedioxy-phenylquinoxaline-6-arsinic acid, yellow crystals (yield 92%); and from tetramethyldiaminobenzil, 2 : 3-di-p-dimethylaminophenylquinoxaline-6-arsinic acid, yellow powder, m. p. above 260° (yield 45%). 3 : 4-Diaminophenylarsinic acid and cyanogen combine in methyl alcohol, giving 2 : 3-di-imino-1 : 4-dihydroquinoxaline-6-arsinic acid,  $\text{H}_2\text{O}_3\text{As}\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{NH}\cdot\text{C}\cdot\text{NH} \\ \text{NH}\cdot\text{C}\cdot\text{NH} \end{smallmatrix}$ , orange powder, m. p. 200—205° (decomp.), and  $\omega$ -bromoacetophenone similarly yields 3(?)-phenyl-1 : 2-dihydroquinoxaline-6-arsinic acid,

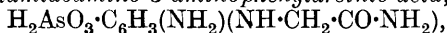


orange crystals, m. p. above 250°.

[With E. A. LARSEN.]—With ethyl acetoacetate in boiling methyl alcohol, 3 : 4-diaminodiphenylarsinic acid gives in 88% yield 4-dimethylmethyleamino-3-aminophenylarsinic acid, m. p. above 260°. Similarly, aldol gives (yield 26%) 3 : 4-di- $\gamma$ -hydroxybutyleneaminophenylarsinic acid,  $\text{H}_2\text{AsO}_3\cdot\text{C}_6\text{H}_3[\text{N}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CHMe}(\text{OH})]$ , m. p. below 260°; with crotonaldehyde is obtained 3 : 4-dicrotonylideneaminophenylarsinic acid,  $\text{H}_2\text{AsO}_3\cdot\text{C}_6\text{H}_3(\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHMe})_2$ , m. p. above 260°; with benzaldehyde, 3 : 4-dibenzylideneaminophenylarsinic acid, yellow, m. p. above 250° (yield 28%); with *o*-methoxybenzaldehyde, 4-*o*-methoxybenzylideneamino-3-aminophenylarsinic acid, m. p. above 250°; with anisaldehyde, 4-*p*-methoxybenzylideneamino-3-aminophenylarsinic acid, yellow powder, and with piperonal, 4-piperonylideneamino-3-aminophenylarsinic acid,



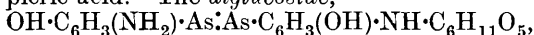
With the object of obtaining a substance with pharmacological properties analogous to tryparsamide (Jacobs and Heidelberger, A., 1920, i, 108), 3 : 4-diaminodiphenylarsinic acid in sodium hydroxide was condensed with chloroacetamide, giving (yield 58%) 4(?) -acetamidoamino-3-aminophenylarsinic acid,



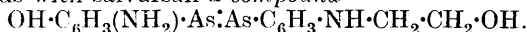
decomp. 220—232°.

R. B.

**Arsenobenzene Derivatives.** A. CONTARDI and U. CAZZANI (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 329—338; from *Chem. Zentr.*, 1924, i, 2512).—3 : 3'-Diamino-4 : 4'-dihydroxyarsenobenzene (salvarsan) forms with dilute (2.5—20%) solutions of dextrose a monoglucoside,  $[\text{As}\cdot\text{C}_6\text{H}_3(\text{NH}_2\cdot\text{HCl})\cdot\text{O}\cdot\text{C}_6\text{H}_{11}\text{O}_5]_2\cdot 2\text{H}_2\text{O}$ , a yellow powder having  $[\alpha]_D^{20} -137.1^\circ$ . It forms a picrate with 2 mols. of picric acid. The diglucoside,



formed with more concentrated solutions of dextrose is similar to the monoglucoside. Similar glucosides are given by galactose,  $\alpha$ -arabinose, and rhamnose. Neosalvarsan, "neojacol," and "sulpharsenol" also yield glucosides with dextrose. Ethylene glycol yields with salvarsan a compound



G. W. R.



**New Organic Arsenic Compounds.** O. MARGULIES (Brit. Pat. 220668).—When mono- or poly-amino derivatives of aromatic aldehydes or ketones, or of mixed aliphatic-aromatic ketones, are diazotised and treated with an arsenite in aqueous solution, the carbonyl group is not attacked and arsinic acids of therapeutic value are obtained. Preparations, by this method, of the following compounds are described: *Nitroxyacetophenonearsinic acid*, m. p. about 200°; *acetophenone-p-arsinic acid*, m. p. about 176°; *benzophenone-p-arsinic acid*, m. p. 195—197°; *benzophenone-4:4'-diarsinic acid*, m. p. 236°; *p-aldehydophenylarsinic acid*; *3-hydroxybenzophenone-4'-arsinic acid*, m. p. 180°; *4-acetamidobenzophenone-3'-arsinic acid*, m. p. 253°; *ω-phthalimidoacetophenone-p-arsinic acid*, m. p. not below 270°; *phenyl-p-arsinic acid benzyl ketone*, m. p. 160° (decomp.); *propiophenone-p-arsinic acid*, m. p. not below 275°; and *nitro-p-aldehydophenylarsinic acid*, decomp. 130°. [Cf. B., Nov. 28th.] F. G. W.

**Preparation of o-Nitrodiphenylarsinic Acid.** E. SAKELLARIOS (Ber., 1924, 57, [B], 1514—1515).—o-Nitrodiphenylarsinic acid is prepared in 87% yield by the addition of a solution of phenylarsenious oxide in sodium hydroxide and sodium acetate to a diazotised solution of o-nitroaniline in hydrochloric acid. H. W.

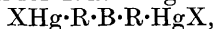
**Preparation and Properties of Diphenyl-4:4'-diarsinic Acid.** [MISS] A. E. HILL (J. Amer. Chem. Soc., 1924, 46, 1855—1857).—It has been sought to extend the inhibiting effect on the growth of certain bacilli possessed by organic substances having the so-called benzidine configuration (cf. Lewis, J. Exp. Med., 25, 441) by combining it with other substances which are known to be therapeutically active in other directions. *Diphenyl-4:4'-diarsinic acid* was prepared by the Bart reaction from tetrazotised benzidine (cf. A., 1913, i, 115, 415). The acid forms white crystals, is characterised by extreme inertness and stability, and is insoluble in the common organic solvents; it dissolves in boiling water to the extent of 0.1%, in hot sulphuric acid and in hot glycerol without change, and is not attacked by bromine or iodine. It is not sulphonated by fuming sulphuric acid. It is tetrabasic and differs from the diphenylarsinic-o-arsinic acid of Kalb (cf. A., 1921, i, 375). The *tetrasodium* salt, white, columnar crystals, contained 14H<sub>2</sub>O (cf. following abstract). A. C.

**Diarsonodiphenyl [Diphenyl-4:4'-diarsinic acid] and Derivatives.** W. W. BAUER and R. ADAMS (J. Amer. Chem. Soc., 1924, 46, 1925—1931).—Various arsenic derivatives of diphenyl of possible therapeutic value have been prepared. Tetrazotised benzidine and alkaline sodium arsenite afforded diphenyl-4:4'-diarsinic acid, not melting below 300°, being practically insoluble in ordinary solvents. A brown by-product, not obtained pure, appears to be 4-hydroxydiphenyl-4'-arsinic acid. Attempts to nitrate the diarsinic acid were unsuccessful, complex oxidation resulting. It was, however, found possible to prepare, from

3 : 3'-dinitrobenzidine, 3 : 5'-dinitrodiphenyl-4 : 4'-diarsinic acid (yield, 65%), a light yellow, insoluble solid. The amino groups in 2 : 2'-dinitrobenzidine could not be readily displaced by arsinic acid groups. 3 : 5'-Diaminodiphenyl-4 : 4'-diarsinic acid was obtained as a yellowish-white powder (79% yield), by the reduction of the corresponding dinitro compound with alkaline ferrous hydroxide. It showed all the properties of aminoarsinic acids of the benzene series, and gave a white *diacetyl* derivative. Tetrazotised 3 : 5'-diaminodiphenyl-4 : 4'-diarsinic acid couples with 2 mols. of H-acid to form a dye,  $C_{32}H_{26}O_{20}N_6S_4As_2$ , of the trypan-blue type, a bronze-coloured solid soluble in water to a bluish-red solution. *o*-Tolidine afforded similar compounds : 3 : 5'-dimethyldiphenyl-4 : 4'-diarsinic acid (yield, 44%) is a white powder, insoluble in water and organic solvents, and does not melt below  $310^\circ$ . On oxidation with alkaline permanganate, it gives 3 : 5'-dicarboxydiphenyl-4 : 4'-diarsinic acid, fine, white crystals insoluble in water. Compounds containing an arsinic acid radical attached to one ring and a hydroxyl or amino group attached to the other were also prepared. The best method consisted in forming the tetrazo compound, coupling one diazonium group with a component which could be reduced to an amino group, and then replacing the second diazonium group by an arsinic acid radical. 4-Aminodiphenyl-4'-arsinic acid was prepared in this manner, using H-acid for the coupling. After the introduction of the arsinic acid group, the product is reduced with sodium hyposulphite and the resulting 4 : 4'-di-*p*-aminodiphenylarsenobenzene,  $(NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot As)_2$ , separated from the amino-H-acid, making use of its insolubility in alkali. The arseno compound, when oxidised with alkaline hydrogen peroxide, gives the aminoarsinic acid (*acetyl* derivative, a white solid). Pharmacological tests showed the *acetyl* derivative to have about the same toxicity as arsanilic acid, whilst 3 : 5'-diaminodiphenyl-4 : 4'-diarsinic acid is much less toxic (cf. preceding abstract).

A. C.

**Complex Organic Compounds of Mercury.** W. SCHOELLER (D.R.-P. 387850; U.S. Pat. 1457675; from *Chem. Zentr.*, 1924, i, 2397—2398).—Complex organic compounds of mercury are prepared having the general formulæ  $XHg \cdot R \cdot R \cdot HgX$  and

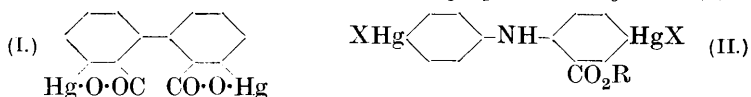


respectively, where X denotes a simple group such as Cl,  $SO_4$ , or OAc and R and B complex organic groups. Such compounds when treated with ammonium sulphide yield cyclic compounds in which the two mercury atoms are connected by a sulphur atom. Diethyl diallylmalonate gives with mercuric acetate a complex ester, which yields on treatment with sodium chloride solution and subsequent hydrolysis a *dicarboxylic acid*,



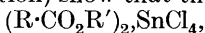
Complex mercury compounds may also be prepared with diallylbarbituric acid and ethyl diallylacetate, respectively. Diethyl *o*-phenylenediacrylate yields with mercuric acetate a complex mercury compound,  $C_6H_4(CH[OMe] \cdot CHgX \cdot CO_2Et)_2$ . From diphenic

acid and mercuric acetate *bismercuroxydiphenic anhydride* (I) is



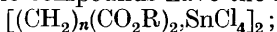
obtained. Similarly, ethyl diphenylamine-2-carboxylate yields the complex type (II).  
G. W. R.

**Ring Formation in Additive Compounds. I. Cyclic Molecular Compounds of the Stannic Halides.** W. HIEBER (*Annalen*, 1924, **439**, 97—131; cf. Pfeiffer and others, A., 1917, i, 205, etc.; and "Organische Molekülverbindungen," Stuttgart, 1922).—Molecular-weight determinations (by the cryoscopic method in ethylene bromide solution) show that the compounds,



formed by union of various esters with stannic chloride, are dissociated to varying degrees in solution. Those from the esters of benzoic acid are almost completely dissociated, but the ethyl  $\beta$ -phenylpropionate compound is more stable and that from ethyl cinnamate is hardly split up at all. Stability here runs parallel with melting-point and resistance to attack by moisture. The extent to which dissociation takes place depends in each case on the concentration and also on the nature of the solvent; nitrobenzene is more active than ethylene bromide, although even in the former the benzaldehyde-stannic chloride additive compound is stable.

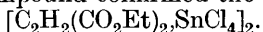
The above determinations were made as a preliminary to an investigation of the molecular structure of the compounds obtained from stannic halides and the esters of dibasic acids and related compounds. These compounds are formed by union of equimolecular proportions of the components, and Pfeiffer's formula (*loc. cit.*), which is unsatisfactory for stereochemical reasons, is shown to be incorrect. Molecular-weight determinations indicate that in every case the compounds have the formula



they are dissociated to varying degrees in solution, but the observed molecular weight is always greater than that required by the simple formula.

The following new compounds are described (a number of others, already described by Pfeiffer and others, were also investigated); all were prepared in a special apparatus designed to secure anhydrous conditions. The *additive* compounds of stannic chloride with various esters have melting points as follows: methyl oxalate, 86°; methyl malonate (needles), 154°; methyl adipate (needles), 132°; methyl pimelate, 116°; methyl suberate (prisms or needles), 110°; methyl azelaate and methyl sebacate, 95° and 90°, respectively. The existence of these compounds by itself, apart from the above results, suggests that they cannot be formed by union molecule for molecule as it is difficult to imagine the two so widely separated carbonyl groups being associated with the auxiliary valencies of the one tin atom. Further, similar results were

obtained with other compounds: methyl and ethyl fumarates yield stannic chloride *additive* compounds of m. p. 91—92° and 81—82°, respectively; methyl and ethyl maleates yield similar, but quite distinct, compounds, m. p. 123° and 114—115°, respectively. These substances regenerate the parent ester unchanged when treated with water; the formation of the additive compounds is therefore independent of the configuration and is not the result of intramolecular change. A molecular-weight determination on the ethyl fumarate compound confirmed the formula



Similar *compounds* are formed by methyl phthalate (m. p. 146°), methyl *isophthalate* (needles, m. p. 71°), methyl terephthalate (m. p. 137°), and ethyl terephthalate (m. p. 65°).  $\alpha$ -Stilbenediol diacetate yields a *compound*, m. p. 122° (decomp.), the  $\beta$ -isomeride a different *compound*, m. p. 98°; and the *cis*- and *trans*-forms of dibenzoyl ethylene both give analogous *compounds*, that from the former being very unstable, and that from the latter having m. p. 120° (decomp.).

Stannic chloride has the normal molecular weight in ethyl malonate, succinate, or glutarate and the compound of stannic chloride and ethyl oxalate is completely dissociated in these solvents.

Analogous *compounds* are formed by stannic bromide; thus, with methyl malonate, leaflets, m. p. 69°; with methyl adipate, m. p. 45°; ethyl maleate, scales, m. p. 35—36°; methyl phthalate, m. p. 20°. Similar observations to those described above were made on these compounds.

Both ethyl fumarate and maleate combine with antimony pentachloride, the *compounds*,  $C_2H_2(CO_2Et)_2, 2SbCl_5$ , having m. p. 140° (decomp.) and 120°, respectively. The analogous *compound* from ethyl terephthalate forms leaflets.

Certain other observations are recorded, for details of which the original should be consulted.

W. A. S.

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### Biochemistry.

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**Gas and Electrolyte Equilibria in the Blood. VII. Effect of Carbon Monoxide on Acidity of Hæmoglobin.** A. B. HASTINGS, J. SENDROY, jun., C. D. MURRAY, and M. HEIDELBERGER (*J. Biol. Chem.*, 1924, **61**, 311—335).—The experiments on the base-binding power of oxygenated and reduced hæmoglobin (this vol., i, 1008) have been extended to carbon monoxide-hæmoglobin, which was found to behave identically with oxyhæmoglobin. Electrometric titration curves for reduced hæmoglobin and carbon monoxide-hæmoglobin over the range  $p_{\text{H}}$  6.2—8.6 have been obtained. It is concluded that the increase in base-binding power of hæmoglobin, which occurs to the same extent on combination

with either oxygen or carbon monoxide, is due to an increase in the dissociation constant of one labile carboxyl group in the hæmoglobin molecule.  
C. R. H.

**Protein Coagulation in Drops. V. Influence of Genus, Sex, and Age of Animals on the Precipitability of the Blood-serum.** E. PŘIBYL, V. ŠUK, and J. ZLÁMAL (*Biochem. Z.*, 1924, **148**, 529—540).—The precipitability of horse, ox, and pig sera by various reagents (formaldehyde, alcohol, acids, various metallic salts, pyrogallol, tannin) differs in type and in range as studied by Bečka's drop method, and shows further variations with the age and sex of the animal. The sera of castrated animals are less readily precipitated than is the serum of normal animals. J. P.

**Protein Coagulation in Drops. VI. Influence of Nitrogen Compounds on the Precipitation.** J. BEČKA and A. ŠIMÁNEK (*Biochem. Z.*, 1924, **149**, 150—157).—Amino-acids inhibit, urea increases the precipitating action of copper sulphate on 1% horse-serum solutions; 1% ox-serum is more readily precipitated by cupric, zinc, and ferrous salts in the presence of amino compounds than in their absence. The action of the amino group in these respects is not affected by alterations in the concentration of the protein or of the sodium chloride present. The action of amino nitrogen in increasing the precipitation of horse-serum by tannin can be utilised for the detection of the former in dilutions as great as  $M/10,000$ .  
J. P.

**Chlorides of Serum, Blood, and Corpuscles in Pathological Conditions.** H. C. GRAM (*J. Biol. Chem.*, 1924, **61**, 337—343).—A study of cases of various diseases shows that a deviation from the normal in the concentration of chloride in the serum is accompanied by a corresponding percentage deviation in the chloride of the whole blood; assuming that corpuscle chlorides vary directly with serum chlorides, it is possible to calculate the chloride concentration of the whole blood from that of the serum together with a determination of the corpuscle volume. The observed results agree with those calculated in this manner to within 3%.  
C. R. H.

**Refractometric and Interferometric Quantitative Analysis. II. Blood-serum.** J. BEČKA (*Z. physiol. Chem.*, 1924, **139**, 52—56).—When serum is mixed with dilute sodium chloride, the refraction of the mixture is usually smaller than that calculated. The deviations from the calculated value differ with different species and depend on the age of the animal from which the serum was obtained and also on the age of the serum itself. E. S.

**Refractometric and Interferometric Analysis. III. Changes in the Refractive Power of Serum.** J. BEČKA and V. ZEMANEC (*Z. physiol. Chem.*, 1924, **139**, 97—106).—Under the influence of carbon dioxide, warmth, and light, the refractive index of sterile serum is increased on standing for 24 hours; in presence of oxygen, it is diminished; these changes are greater in ox-serum

than in horse-serum and are more rapid in the serum of young than of old animals.

C. R. H.

**Surface Tension of Serum. X. Thickness of a Unimolecular Layer of Serum.** P. L. DU NOÛY (*J. Exp. Med.*, 1924, **40**, 133—149; cf. this vol., i, 900).—Consideration of the minimum value of the surface tension in relation to the dilution of a serum solution leads to the supposition that a unimolecular layer exists at a certain dilution. The thickness of the protein molecule is then calculated to be  $35.4 \times 10^{-8}$  cm. The result for crystalline egg-albumin was  $52.8 \times 10^{-8}$  cm. CHEMICAL ABSTRACTS.

**Nature of Blood-sugar.** W. DENIS and H. V. HUME (*J. Biol. Chem.*, 1924, **60**, 603—612).—In a repetition of the work of Winter and Smith (*A.*, 1923, i, 513), the authors have failed to observe any decrease in the power of normal blood filtrates on keeping for 3 days to decolorise permanganate. Although changes in the rotatory power of such filtrates have been occasionally observed, these have always coincided with the growth of mould in the polarimeter tube and have never occurred when sodium or potassium fluoride has been used as anti-coagulant. Thus no support is given to the view that  $\gamma$ -glucose is present in normal blood.

E. S.

**Blood-sugar and Gastric Hunger Contractions.** E. BULATAO and A. J. CARLSON (*Amer. J. Physiol.*, 1924, **69**, 107—115).—Intravenous injection of dextrose inhibits gastric hunger contractions which, in insulin hypoglycæmia, increase at a blood-sugar concentration of 0.07—0.08%. Dextrose, but not lactose, inhibits the gastric tetany of hypoglycæmia.

A. A. E.

**Hypoglycæmia and Acidosis.** F. B. TALBOT, E. B. SHAW, and M. E. MORIARTY (*J. Amer. Med. Assoc.*, 1924, **83**, 91—93).—Acidosis during fasting is accompanied by low blood-sugar concentrations (45 mg. per 100 c.c.). A certain proportion of the fatty acids is not completely oxidised, and the keto-acids thus produced deplete the alkali reserve; this is accompanied by a shift of the  $p_H$  of the blood towards the acid side. The administration of carbohydrate frees the body from an excess of acids by completing the combustion of the ketone substances.

CHEMICAL ABSTRACTS.

**Lead. IX. Solubility of Various Lead Compounds in Blood-serum.** L. T. FAIRHALL (*J. Biol. Chem.*, 1924, **60**, 481—484).—Determinations have been made of the solubilities of various lead compounds in blood-serum at 25°. Whilst the values obtained for lead salts (carbonate 0.0333, sulphate 0.0437 g.p.l.) do not differ greatly from the corresponding solubilities in water, that for lead monoxide is distinctly greater (1.1520 g.p.l. against 0.0171 g.p.l. in water at 20°). Metallic lead has a solubility in blood-serum of 0.578 g.p.l. at 25°. Saturation of the serum with carbon dioxide decreased the value for lead to 0.1930, but produced no marked effect on the other solubilities. The results are of significance as indicating the ease with which lead oxides can enter the circulation from the respiratory tract.

E. S.

**Effect of Ultra-violet Light on the Condition of Calcium in the Blood.** J. H. CLARK (*Amer. J. Hyg.*, 1923, 3, 481—482).—The diffusible calcium of blood-serum, measured by dialysis in collodion sacs against physiological saline, was found to be higher after the serum was exposed to radiation of a quartz mercury arc. The diffusible calcium in rabbit-serum rose from 38 to 58%, in dog-serum from 44 to 53%.

CHEMICAL ABSTRACTS.

**Creatinine in the Blood.** P. FONTEYNE and P. INGLEBRECHT (*Ann. med.*, 1923, 14, 470).—The creatine and creatinine content of the blood was determined in 100 healthy and sick subjects. The coefficient of secretion of creatinine remains longer intact than Ambard's ureosecretory coefficient. The amount of creatinine in the blood is comparatively independent of the diet.

CHEMICAL ABSTRACTS.

**Chemistry of the Blood during Pregnancy.** H. J. STANDER (*Bull. Johns Hopkins Hosp.*, 1924, 35, 133—137).—In non-pregnancy and pregnancy, respectively, 100 c.c. of blood contained, in mg.: non-protein nitrogen, 32, 28; urea nitrogen, 18.5, 12.48; uric acid, 3.3, 3.3; carbon dioxide combining power of plasma, 52, 44.5; ratio of urea nitrogen to non-protein nitrogen, 57, 44.5.

CHEMICAL ABSTRACTS.

**Enzyme Content of the Blood. II. Variations in the Catalase and Protease Figures during 24 Hours in Animals and Man.** E. IVANITZKY-VASSILENKO and A. BACH (*Biochem. Z.*, 1924, 148, 469—473).—Extreme daily variations in the blood catalase values are: in rabbits +33%, -10%; in cats +18%, -10%; in man +9%, -9% of the mean values in each case. The protease content shows wide variations up to  $\pm 100\%$  of the mean.

J. P.

**Enzyme Content of the Blood. III. Catalase Values of the Blood of Thyroidectomised Goats.** A. BACH and E. CHERASKOVA (*Biochem. Z.*, 1924, 148, 474—475).—Thyroidectomy has no influence on the mean blood catalase value in goats.

J. P.

**Eosinophile Granule Substance of the Blood and its Preparation, Nature, and Properties. I. Technique of Isolation.** A. NEUMANN (*Biochem. Z.*, 1924, 148, 524—528).—The isolation of the eosinophile granule substance from horse-blood fibrin is described. This substance is characterised by an intense benzidine peroxydase reaction and is very resistant to the action of acids and alkalis.

J. P.

**Animal Calorimetry. XXV. Relative Specific Dynamic Action of Various Proteins.** D. RAPPORT [with J. EVENDEN] (*J. Biol. Chem.*, 1924, 60, 497—511).—The specific dynamic action of a number of proteins (beef, casein, gliadin, codfish, chicken, gelatin) has been found to be approximately the same despite the large differences in their amino-acid composition. The addition of cystine to gelatin, which, it was considered, might lead to the



production of glutathione in the organism, did not increase the specific dynamic action of this protein. E. S.

**Animal Calorimetry. XXVI. Inter-relations between certain Amino-acids and Proteins with Reference to their Specific Dynamic Action.** R. WEISS and D. RAPPORT [with J. EVENDEN] (*J. Biol. Chem.*, 1924, **60**, 513—544).—Although the specific dynamic actions of glycine and alanine, when administered simultaneously to a dog, are largely additive, the administration of glycine or alanine either orally, subcutaneously, or intravenously, simultaneously with the oral administration of protein (gelatin, casein), does not lead to a summation of effect unless the protein is fed in an amount which is small relative to the amount of amino-acid administered. The protein is apparently able to "neutralise" the action of the amino-acid. The specific dynamic actions of proteins, when fed together, are, however, additive. The authors consider it probable that certain amino-acids or polypeptides derived from the proteins combine with the glycine and so neutralise its specific dynamic effect. E. S.

**Animal Calorimetry. XXVII. Administration of Various Proteins with Benzoic Acid to a Pig.** F. A. CSONKA (*J. Biol. Chem.*, 1924, **60**, 545—582).—When benzoic acid is included in the diet of a pig, it is eliminated in the urine in the form of hippuric acid, benzoylglycuronic acid (cf. Magnus-Levy, A., 1907, ii, 979), and free benzoic acid. The relative amounts of the two former substances excreted depend on the quantity of preformed glycine (free amino-acid or combined as protein) ingested. An increase in the latter leads to an increase in the excretion of hippuric acid and a decrease in that of benzoylglycuronic acid. Hence the equality in the specific dynamic actions of equal amounts of different proteins with varying contents of glycine (cf. preceding abstracts) does not depend on the synthesis of this amino-acid in the organism. E. S.

**Animal Calorimetry. XXVIII. Respiratory Metabolism of a Young Pig as Influenced by Food and Benzoic Acid.** D. RAPPORT, R. WEISS, and F. A. CSONKA [with J. EVENDEN] (*J. Biol. Chem.*, 1924, **60**, 583—601).—No definite effect on the heat production of the pig is produced by the ingestion, under varied dietary conditions, of benzoic acid (hence by the synthesis of hippuric acid) or of hippuric acid. Following a starchy meal, the conversion, by the pig, of carbohydrate into fat (cf. Lusk, A., 1915, i, 614) may continue for more than 21 hours; the maximum conversion observed amounted to 77% of that theoretically possible. E. S.

**Metabolism of some Pyrimidines.** H. J. DEUEL, jun. (*J. Biol. Chem.*, 1924, **60**, 749—763).—No pyrimidines are excreted in normal urine. When fed to dogs in single doses of 1 to 3 g., thymine and uracil are partly metabolised (as shown by the rise, which usually occurs, in urinary carbamide) and partly excreted unchanged, but when the same amounts are administered in small

doses they are completely destroyed in the organism. Following the ingestion of 50 g. of thymus-nucleic acid, the urine of a dog gave qualitative tests for pyrimidines. These results suggest that, contrary to current views, the destruction of pyrimidines contained in nucleic acid takes place after liberation from the latter. E. S.

**Inorganic Metabolism. III. Significance of Phosphates in the Production of Tetany.** F. P. UNDERHILL, E. G. GROSS, and W. COHEN (*J. Metab. Res.*, 1923, **3**, 679—709; cf. this vol., i, 452, 453).—Intravenous or intraperitoneal injection of sodium or potassium phosphate causes, with dogs and rabbits, a corresponding diminution of calcium. The intravenous administration of sodium hydrogen carbonate also produces tetany, but no diminution of calcium. The amount of calcium in the bones of rabbits is not affected by intravenous injection of comparatively large quantities of sodium orthophosphate. CHEMICAL ABSTRACTS.

**Rate of Sugar Absorption in the Newborn.** R. G. FLOOD (*J. Amer. Med. Assoc.*, 1924, **82**, 1595—1596).—The various sugars have different rates of absorption, dextrose being the most readily absorbed. The disaccharides show some of the characteristics of their component monosaccharides. Sucrose is not readily absorbed by very young infants, but the ability to utilise this sugar increases with the age of the infant. CHEMICAL ABSTRACTS.

**Extraction and Precipitation of Soluble Proteins of Muscle.** P. E. HOWE (*J. Biol. Chem.*, 1924, **61**, 493—522).—The concentration of a salt necessary for its maximum solvent action on muscle proteins has been shown to bear a definite relationship to the concentration of the same salt which will bring about precipitation of the blood proteins. When the solvent action of salt solutions towards muscle proteins was tested over a continuous range of varying concentrations, there were observed, for any one salt, certain zones of concentration in which the amount extracted was the same; these zones were taken to represent individual protein fractions. A method, based on this hypothesis, has been developed, whereby, using as solvent different molecular concentrations of a solution containing mono- and di-potassium phosphates in the ratio 1 : 2, it is possible to separate the proteins of muscle into six fractions. The work of Halliburton (A., 1887, 984) and of von Fürth (A., 1896, ii, 48) is reviewed in the light of this new fractionation, and details are given of the results of the method when applied to the muscles of various animals. C. R. H.

**Creatine Content of Frog's Muscle during Work. I.** H. SCHLOSSMANN (*Z. physiol. Chem.*, 1924, **139**, 87—94).—Stimulation of frog's muscle perfused with Ringer solution with or without the addition of creatine produces an increase in the creatine content of the muscle in the case of winter frogs but not in that of summer frogs. This corresponds with the smaller creatine content of the muscles of the former; stimulation evidently causes it to approach that of the latter. E. S.

**Animal Nutrition. IV. Nitrogen, Ash, and Phosphorus Distribution in Beef Flesh.** W. S. RITCHIE, C. R. MOULTON, P. F. TROWBRIDGE, and L. D. HAIGH (*Univ. Missouri Agr. Exp. Sta. Res. Bull.*, 1923, **59**, 1—78).—The ash of the fat of the rib is higher than that of the lean; total phosphorus is much higher in lean flesh than in fat. The ratio of soluble to total phosphorus increases as the animal grows thinner. The effects of age and of the plane of nutrition are investigated. CHEMICAL ABSTRACTS.

**Photochemistry of the Visual Purple.** S. HECHT (*J. Gen. Physiol.*, 1924, **6**, 731—740).—The velocity of bleaching of visual purple by light, under comparable conditions of concentration, volume, and surface exposed, is directly proportional to the intensity. D. R. N.

**Aminogenesis in the Grey and White Substances of the Brain during Hunger.** A. PALLADIN and D. ZUWERKALOW (*Z. physiol. Chem.*, 1924, **139**, 57—63).—During fasting in dogs, the coefficient of aminogenesis—i.e., the amino-acid nitrogen expressed as a percentage of the total nitrogen—of the grey substance of the brain is depressed and that of the white substance increased. E. S.

**Chemistry of Bull's Testicles (Extractives).** L. LEIBFREID (*Z. physiol. Chem.*, 1924, **139**, 82—86).— $\alpha\alpha$ -Dimethylguanidine has been isolated in the form of its chloraurate, which was identical with that prepared by Schenck (A., 1912, i, 424). E. S.

**Uric Acid Content of Human Amniotic Fluid.** J. L. WILLIAMS and J. A. BARGEN (*Amer. J. Obst. Gyn.*, 1924, **7**, 406).—Uric acid and creatinine are present in human amniotic fluid in greater concentration than in blood. The amounts of carbamide, non-protein nitrogen, and uric acid in the fluid increase as the term of pregnancy is prolonged. CHEMICAL ABSTRACTS.

**Spinal Fluid Sugar.** B. J. ALPERS, C. J. CAMPBELL, and A. M. PRENTISS (*Arch. Neurol. Psychiatry*, 1924, **11**, 653—663).—The spinal fluid dextrose normally varies from 50 to 84 mg. per 100 c.c.; average figures are given for various pathological conditions. CHEMICAL ABSTRACTS.

**Natural Porphyrins. XI.** H. FISCHER, H. KÄMMERER, and A. KÜHNER (*Z. physiol. Chem.*, 1924, **139**, 107—117).—The sterile autolysis of beef always gives rise to Kämmerer's porphyrin, which can be demonstrated spectroscopically after about 10 days; after 6 weeks the spectrum of coproporphyrin can also be observed. These results are similar to those previously obtained in the putrefaction of meat (this vol., i, 894). C. R. H.

**Hydrogen-ion Concentration of the Cerebro-spinal Fluid of Children.** K. WALTNER (*Biochem. Z.*, 1924, **149**, 145—149).—The  $p_H$  of the cerebro-spinal fluid from normal children is 7.50 to 7.55, in tuberculous meningitis it is unchanged, whilst in purulent

meningitis it may be somewhat lower. Successive fractions taken during a lumbar puncture tend to become more acidic. J. P.

**Comparison of the Metabolism of some Mineral Constituents of Cow's Milk and of Human Milk.** C. C. WANG and L. H. DAVIS (*Amer. J. Diseases Children*, 1924, 27, 569—577; cf. *ibid.*, 352).—The greater intake of chlorine with cow's milk causes an increase in the excretion of chlorine. The utilisation of chlorine runs parallel to the urinary chlorine; there is no marked difference in percentage utilisation of chlorine intake between the two milks. As age increases there is a decrease in the amount of chlorine retained with cow's milk, but not with human milk.

CHEMICAL ABSTRACTS.

**Reaction of the Urine of the Horse.** F. PÁDÁR (*Biochem. Z.*, 1924, 149, 200—205).—Electrometric determinations of the influence of varying carbon dioxide tensions on the reaction of horse's urine show that it behaves like a bicarbonate solution, low carbon dioxide tensions producing a much steeper relative fall in the curve of hydroxyl-ion concentration than do higher tensions. J. P.

**Gastric Secretion and the "Alkaline Tide" in Urine.** R. S. HUBBARD, S. A. MUNFORD, and E. G. ALLEN (*Amer. J. Physiol.*, 1924, 68, 207—212).—The alkaline tide was absent in the urine of individuals whose gastric juice did not contain hydrochloric acid. A. A. E.

**Uric Acid Excretion.** A. E. KOEHLER (*J. Biol. Chem.*, 1924, 60, 721—736).—Ingestion of uric acid does not appreciably raise the level of uric acid in the blood nor does it increase its excretion in the urine. After intravenous injection approximately 50% may be recovered from the urine. The amount of uric acid retained in the blood 2 hours after injection and its rate of excretion may serve as guides in determining renal insufficiency. E. S.

**Origin of Urinary Ammonia.** R. F. LOEB, D. W. ATCHLEY, and E. M. BENEDICT (*J. Biol. Chem.*, 1924, 60, 491—495).—That the ammonia content of the renal venous blood of the dog is much greater than that of arterial blood (Nash and Benedict, A., 1922, i, 191) has been confirmed and it has been further found that venous blood from other sources has an ammonia content slightly greater than that of arterial blood. With an animal (rabbit) which does not excrete appreciable amounts of ammonia in the urine the ammonia content of the renal venous blood is practically identical with that of arterial blood. These results give further support to the theory of Nash and Benedict that the kidney is the seat of formation of urinary ammonia. E. S.

**Variations in Rate of Excretion of Acetone Compounds.** R. S. HUBBARD and F. R. WRIGHT (*J. Biol. Chem.*, 1924, 61, 377—385).—Subjects fed on diets of which the ketogenic ratio (cf. Shaffer, A., 1922, i, 83) was between 1:1 and 2:1 showed an increased excretion of acetone compounds, although not so much as is required

by the theory that 1 mol. of antiketogenic material can bring about the combustion of only 1 mol. of ketogenic material. The rate of excretion showed considerable diurnal variations, being usually at its height soon after food and not running parallel with the rate of excretion of urine. C. R. H.

**Ether Anæsthesia. III. Rôle of Lactic Acid in the Acidosis of Ether Anæsthesia.** E. RONZONI, I. KOECHIG, and E. P. EATON (*J. Biol. Chem.*, 1924, **61**, 465—492).—The acidosis observed in ether anæsthesia appears, from a series of experiments on dogs, to be chiefly due to the accumulation of lactic acid derived from the tissues; in view of the loss of phosphate from the muscles during anæsthesia observed by Stehle and Bourne (this vol., i, 900), this may indicate a breakdown in the muscle of a hexosephosphate such as the lactacidogen of Embden (A., 1921, i, 528). The view of Anrep and Cannan (*J. Physiol.*, 1923—24, **58**, 244) that accumulation of lactic acid is controlled by the  $p_H$  of the blood through the tension of carbon dioxide, is not supported by the experiments. C. R. H.

**Excretion of Phosphoric Acid during Anæsthesia.** W. BOURNE and R. L. STEHLE (*J. Amer. Med. Assoc.*, 1924, **83**, 117—118; cf. A., 1922, i, 1085, and *J. Biol. Chem.*, 1924, **60**, 17).—Eleven of fifteen cases of surgical anæsthesia showed in consequence a definitely increased excretion of phosphorus. The effect is usually most pronounced during the anæsthesia, but with chloroform, and with ether preceded by morphine, it is later. The chloride excretion does not show any significant variations. Apparently phosphoric acid is responsible for the acidosis of anæsthesia.

CHEMICAL ABSTRACTS.

**Low Nitrogen Metabolism with Low Carbohydrate Diet in Diabetes.** K. PETREN (*J. Biol. Chem.*, 1924, **61**, 355—363).—The total nitrogen metabolised, as indicated by the ratio, grams total urinary nitrogen : kg. body-weight, may be maintained at a very low level for prolonged periods in diabetics receiving a diet poor in protein and carbohydrate but rich in fat; this indicates that the sparing effect of fat ingestion on nitrogenous metabolism is greater than has hitherto been supposed. C. R. H.

**Lipæmia. I. Micro-determination of Blood Fat.** H. I. BING and H. HECKSCHER (*Biochem. Z.*, 1924, **149**, 79—82).—The blood is absorbed on filter-paper, extracted by a suitable fat solvent, and the turbidity of a solution of the fat in 99.5% alcohol, after treatment with an aqueous solution of 1% barium chloride, is compared with standard opacity suspensions in a Heckscher nephelometer (*Compt. rend. Soc. Biol.*, 1921, **85**, 378). J. P.

**Lipæmia. II. Blood Fat in Normal Human Subjects.** H. I. BING and H. HECKSCHER (*Biochem. Z.*, 1924, **149**, 83—89).—In 155 cases out of 213 examined, the fat content of the normal blood in a fasting condition lay between 0.05% and 0.13%. The remaining 58 cases showed values between 0.14% and 3.16%. The

incidence shows a maximum at 0.10%. The individual fasting blood-fat value remains practically constant. The blood fat reaches a maximum in from 3 to 5 hours after a meal, but the form of the blood-fat curve varies with the nature of the diet. Direct observation of the turbidity of the blood-serum is not a trustworthy indication of the fat content. J. P.

**Lipæmia. III. Pathological Changes in the Blood-fat Value.** H. I. BING and H. HECKSCHER (*Biochem. Z.*, 1924, **149**, 90—99).—Children and young people often have blood-fat values below normal. Hypolipæmia was found in three cases of Basedow's disease, hyperlipæmia in cases of acute lung and uncompensated heart affections, in cases of icterus, in various types of nephritis, in diabetes mellitus, and in cases of disturbed endocrine function involving fat metabolism. In some cases the hyperlipæmia was latent, e.g., in arthritis urica the fasting value was normal and the abnormality was revealed only after a meal. J. P.

**Amino-acids in Physiological Fluids.** G. WOLPE (*Münch. med. Woch.*, 1924, **71**, 363—365; from *Chem. Zentr.*, 1924, i, 2377).—Increased amino-acid content in the blood-serum in malaria and leucæmia is due to increased decomposition of blood proteins. There appears to be a correlation between the resistance of the organism and the amino-acid content in physiological fluids. Amino-acid production may be connected with disturbances in the endocrine glands. G. W. R.

**Relation of Acidosis and Hyperglycæmia to the Excretion of Acids, Bases, and Sugar in Uranium Nephritis.** B. M. HENDRIX and M. BODANSKY (*J. Biol. Chem.*, 1924, **60**, 657—676).—The acidosis which, together with hyperglycæmia and glycosuria, is produced in dogs by administration of uranium acetate is accompanied in the early stages by an increased excretion of basic phosphates and salts of organic acids, and in the later stages by a marked decrease in phosphate excretion. No constant relationship appears to exist between the degree of acidosis and the hyperglycæmia and glycosuria. E. S.

**Chemistry of Osteohæmochromatosis in Animals.** D. VON DESEÖ (*Biochem. Z.*, 1924, **149**, 191—199).—The pigment occurring in the bones of animals with osteohæmochromatosis has chemical and spectroscopic properties which suggest that it originates from blood pigment and is possibly a hæmatoporphyrin. J. P.

**Rate of Excretion of Urea in the Toxæmias of Pregnancy.** H. J. STANDER, E. C. DUNCAN, and B. L. MOSES (*Bull. Johns Hopkins Hosp.*, 1924, **35**, 97—103).—Average results are given for non-pregnant, pregnant, and pathological conditions.

CHEMICAL ABSTRACTS.

**Excretion of Tryparsamide.** A. G. YOUNG and C. W. MUEHLBERGER (*J. Pharm. Exp. Ther.*, 1924, **23**, 461—464).—At least part of the tryparsamide is excreted unchanged in the urine and in three out of four normal individuals 88—95% of the arsenic  
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of the drug was excreted within the first 24 hours. Some individuals show a much slower rate of excretion, and may therefore be more susceptible to cumulative effects of the drug. D. R. N.

**Test-tube Reaction for Damage and Death of Tissues.** P. ROSTOCK (*Fermentforsch.*, 1924, 8, 72—85).—After testing the various reactions which have been proposed for distinguishing between living and dead tissues, the author concludes that the most trustworthy are the dinitrobenzene reaction of Lipschitz (*Pflüger's Arch.*, 199) and the nitroanthraquinone reaction of Bieling (*Zentr. Bakt.*, 1923, 90). C. R. H.

**Effect of Potassium on the Acid Metabolism of Surviving Skeletal and Cardiac Muscles of the Frog.** F. R. GRIFFITH (*J. Gen. Physiol.*, 1924, 6, 683—695).—The potassium contraction of skeletal muscle and relaxation of cardiac muscle have been correlated with the carbon dioxide and total acid production of these tissues. The immersion of surviving sartorius muscles of the frog in isotonic potassium chloride solution causes a marked increase in the rate of acid production, carbon dioxide being probably the principal acid involved. Surviving cardiac muscle treated in a similar manner shows a pronounced depression in the rate of acid production. It is believed that these changes in metabolism may be independent of the stimulation and inhibition of contraction which potassium simultaneously produces in these tissues. D. R. N.

**Factors influencing Chemical Processes of Fracture Healing.** R. SCHWARZ, R. EDEN, and E. HERMANN (*Biochem. Z.*, 1924, 149, 100—108).—Ossification after fracture consists primarily in the addition of calcium to organic substances and the secondary combination of phosphoric acid with the fixed calcium until a ratio  $\text{Ca} : \text{P} = 1 : 0.6$  is attained, at which stage the cartilage becomes ossified. J. P.

**Mechanism of Phloridzin Diabetes.** T. P. NASH, jun., and S. R. BENEDICT (*J. Biol. Chem.*, 1924, 61, 423—428).—The fact that insulin may be obtained by the usual procedure from the pancreas of phloridzinised dogs is evidence against the view of Ringer (this vol., i, 446) that the effect of phloridzin is to injure the pancreas, rendering it unable to produce insulin. C. R. H.

**Action of Quinine on Protein Metabolism, Respiratory Exchange, and Heat Function. I. Protein Metabolism.** S. W. HARDIKAR (*J. Pharm. Exp. Ther.*, 1924, 23, 395—448).—The view generally held that quinine diminishes heat production by lowering nitrogen metabolism is not substantiated. Quinine has no influence on protein metabolism even in doses which may be toxic in themselves. D. R. N.

**Pressor Anæsthetics.** C. S. MARVEL and V. DU VIGNEAUD. —(See i, 1193.)

**Experiments with Anæsthetic Gases, Propylene, Methane, and Methyl Ether.** W. E. BROWN (*J. Pharm. Exp. Ther.*, 1924, **23**, 485—496).—Propylene induces anæsthesia at a concentration as low as 37% when mixed with either oxygen or air. Anæsthesia may be maintained satisfactorily at a concentration as low as 20%. In concentrations of about 65% or higher it is poisonous. Methane produces anæsthesia only at high concentrations (87%) whilst 90% methane administered to a cat caused irregular respirations which gradually ceased. Methyl ether produces anæsthesia at concentrations of 65%; 85% causes profound anæsthesia with gradual cessation of respiration.  
D. R. N.

**Chloroform Poisoning.** H. J. STANDER (*Bull. Johns Hopkins Hosp.*, 1924, **35**, 46—49).—In a fatal case of delayed chloroform poisoning there was an increased output of urinary nitrogen with a marked decrease of the urea-nitrogen % and a steadily rising ammonia coefficient; a very definite drop in the carbon dioxide-combining power of the blood to 27.4 vols. %, an increase in the blood of non-protein nitrogen, urea, uric acid, and amino-acids, and a fall in blood-sugar to 0.058%. These changes indicate an increased destruction but incomplete oxidation of the proteins.

## CHEMICAL ABSTRACTS.

**Physiological Actions of Cyanides.** T. H. BODINE (*J. Gen. Physiol.*, 1924, **7**, 19—23).—The physiological action of hydrocyanic acid and its salts depends on (a) the ease with which hydrogen cyanide penetrates living cells as such and then ionises; (b) the presence of large amounts of the free acid even in the presence of cyanides; (c) specific effects due to chemical activity. Hydrocyanic acid in acid, neutral, or slightly alkaline media produces intracellular acidity on account of its rapid penetration into the cell. It acts specifically on certain protozoa, the resistance towards it being the reverse of that to mineral acids.  
O. O.

**Toxicity of a Polymeride of Hydrocyanic Acid.** CH. BEDEL (*J. Pharm. Chim.*, 1924, [vii], **30**, 189—193).—Dicyanomethylamine hydrocyanide,  $[\text{HCN}]_4$ , is much less toxic than hydrocyanic acid, the minimum lethal dose being about 0.75 g. per kg. body-weight when given by mouth. The symptoms of poisoning are similar to those of hydrocyanic acid, but sodium thiosulphate is without effect as an antidote.  
C. R. H.

**Biochemistry of Carotinoid Pigments in Animals.** L. S. PALMER (*Minnesota Agr. Exp. Sta., Ann. Rept.*, 1922, 43—44).—The yellow lipochrome of cod-liver oil is not a carotinoid and cannot be removed completely by treatment with charcoal. The yellow pigment in the blood serum of pigeons has been identified as xanthophyll. The red pigment in the feet and legs resembles carotin in its solubility, but not in other respects. Alcoholic solutions treated with lime-water yield an amorphous pigment, which gives a blue colour when treated with ferric chloride instead of a green, characteristic of carotin and xanthophyll. Human organisms lose carotinoid pigments by the process of oxidation.



Carotinoid skin colorations are due to lowered oxidation processes of the body and super-abundance of carotinoids in the diet.

CHEMICAL ABSTRACTS.

**Concentration of Silver Ions in Solutions of Colloidal and Complex Silver Preparations with Special Reference to their Medicinal Use.** H. SCHLEE (*Biochem. Z.*, 1924, **148**, 383—432).—Excess of sodium chloride in a solution of silver chloride diminishes the silver-ion concentration in accord with the solubility-product equation. Egg-albumin has a similar but more marked effect on solutions of silver nitrate, and this persists after the protein has been dialysed to remove naturally occurring sodium chloride. Blood-serum has a still more marked effect in diminishing the silver-ion concentration. The findings of Paul (*Z. Elektrochem.*, 1912, **18**, 521) with regard to the classification of medicinal silver preparations into three groups are confirmed. It is possible from such behaviour to draw conclusions as to the nature of the silver in these preparations. Determinations were made of the silver-ion concentration of the blood after injections of certain colloidal silver preparations.

J. P.

**Photodynamic Phenomena. III. Fixation of Active Dyes in the Cell.** P. METZNER (*Biochem. Z.*, 1924, **148**, 498—523).—Photodynamically active dyes show in general negative phototaxis. Cresyl fast violet exhibits induced photokinesis. In the cell, the active portion of the dye is adsorbed and shows absorption and fluorescent spectra which differ from those of the substance when in solution, being displaced towards the red. It is suggested that the active adsorbent is a phosphatide or a tyrosine compound. The activity spectra and absorption spectra are approximately proportional without showing exact correspondence, and the former is also displaced towards the red in the adsorbed dye. It is concluded that photodynamic dyes become active only within the cell.

J. P.

**Permeability of Living and Dead Cells. III. Penetration of certain Alkalis and Ammonium Salts into Living and Dead Cells.** M. M. BROOKS (*U.S. Pub. Health Rpts.*, 1923, **38**, 2074—2086, *Reprint No.* 866).—The rate of penetration of bases into living cells has been measured, using the marine alga, *Valonia ventricosa*, and the method previously described (cf. *ibid.*, 1923, **38**, 1449). Ammonia, ammonium chloride, sulphate, and carbonate cause an increase in the  $p_H$  of the sap of *Valonia*, due to the penetration of free ammonia. On removal of the ammonia by aëration, the  $p_H$  of the sap returns to normal. Both ions of ammonium carbonate penetrate and can be removed by aëration. Solutions of sodium and potassium hydroxides penetrate into the cell sap very much more slowly than an ammonia solution having the same  $p_H$ . Dead cells rapidly assume the  $p_H$  of the surrounding solution. The results confirm the view that the relative  $p_H$  of the sap of living cells and of the solution surrounding them is greatly influenced by the nature of the ions present in the solution.

C. T. G.

**Permeability of Living and Dead Cells. IV. Penetration of Tervalent and Quinquevalent Arsenic into Living and Dead Cells.** M. M. BROOKS (*U.S. Pub. Health Rpts.*, 1923, **38**, 2951—2966, *Reprint No.* 888).—Determinations have been made of the amount of arsenic passing from surrounding solutions into the sap, protoplasm, and cell-wall of *Valonia* (cf. preceding abstract). Arsenic, whether in the quinquevalent form (as  $\text{As}_2\text{O}_5$  and atoxyl) or in the tervalent form (as  $\text{As}_2\text{O}_3$ ), penetrates least when the solution is nearly neutral. With increasing alkalinity or acidity more arsenic is taken up. Tervalent arsenic, from acid solutions, penetrates less readily into the protoplasm but more readily into the sap than quinquevalent arsenic; in alkaline solutions, the behaviour of the two forms is similar. Previous exposure of the cells in sodium hydrogen carbonate solution (when carbon dioxide accumulates in the sap) increases by 150% the quinquevalent arsenic and reduces by 25% the tervalent arsenic taken up by protoplasm; on the other hand, the tervalent arsenic taken up by the sap is increased by about 100% and the quinquevalent arsenic only by about 25%. Penetration of arsenic into dead cells is much more rapid than into living cells. The use of phosphate buffer solutions to maintain a constant  $p_{\text{H}}$  sometimes led to untrustworthy results.

C. T. G.

**Formation of Pigment. I. Enzymic Pigment Formation as an Aid to Classification.** H. SCHMALFUSS (*Fermentforsch.*, 1924, **8**, 1—41, 86—115). **Formation of Pigment. II.** H. SCHMALFUSS and F. WERNER (*ibid.*, 116—134).—The formation of pigment from *l*- $\alpha$ -amino- $\beta$ -3:4-dihydroxyphenylpropionic acid (called for brevity the “D-reaction”) by an enzyme from caterpillar’s blood, is increased by the presence of oxygen; nitrogen, hydrogen, acetylene, carbon monoxide and dioxide, and nitrous oxide are indifferent, whilst sulphur dioxide, hydrogen sulphide, hydrocyanic acid, cyanogen, chlorine, bromine, and ammonia inhibit the reaction. The effect of other organic substances, both alone and in presence of “D,” on pigment formation by this enzyme was tested in a large number of cases. The substances investigated fell into four groups, according to whether or not they inhibited the formation of pigment from “D,” and whether or not they could themselves act as precursors of pigment. The application of these criteria made it possible in many instances to distinguish between isomerides, *e.g.*, between *o*-, *m*-, and *p*-cresol. Formation of melanin could be demonstrated when strips of filter-paper, previously treated with a solution of egg-albumin in strong potassium hydroxide, were immersed in solution either of “D” or of pyrocatechol.

The above experiments were extended to enzyme preparations derived from the body fluids of a number of different animal species; by the application of the same criteria a series of results was obtained which, it is claimed, may form a useful support to morphological grounds of classification.

Although in the case of the precursor “D” the formation of pigment by the enzyme from caterpillar’s blood is very much

accelerated by oxygen, the effect of the latter with other precursors is less marked. The reaction does not take place in anhydrous solvents and is not affected by light. The effect of heat shows that two active agents are involved, one heat-labile, which reaches its optimum at 40° and is inactivated at 70°, and the other heat-stable, which increases in activity up to 100°. The enzyme is destroyed by acids and inhibited by bases. Preparations from caterpillar's blood become more active with keeping, both as regards catalase and oxydase, but both fresh and old preparations are destroyed with equal ease by dilute sulphuric acid.

C. R. H.

**Investigation of Amylase.** P. RONA and C. VAN EWYK (*Biochem. Z.*, 1924, **149**, 174—187).—A method for investigating amylolytic activity is described in which glycogen is used as the substrate, its concentration being determined continuously throughout the course of the reaction by means of the nephelometer.

J. P.

**Amylase.** K. SJÖBERG and E. ERIKSSON (*Z. physiol. Chem.*, 1924, **139**, 118—139).—Amylase from barley after germination can carry the hydrolysis of starch further than that obtained before germination; with the most active amylase, however, there could not be obtained a greater yield of maltose than 80%. Separate experiments with amylose and amylopectin as substrates showed that these substances individually were hydrolysed to the extent of 80% also. The affinities of the enzyme for amylose and amylopectin are of the same order of magnitude, but not identical. The inhibiting effects of maltose and dextrose are different according to whether they are measured by the rate of maltose production or by the rate of disappearance of the iodine reaction. This supports the hypothesis that two enzymes are concerned in the hydrolysis of starch by amylase.

C. R. H.

**Antiamylase.** H. LÜERS and F. ALBRECHT (*Fermentforsch.*, 1924, **8**, 52—72).—The serum of rabbits which have been injected subcutaneously with preparations of amylase contains a substance which inhibits the action of the enzyme; such serum also gives a precipitin reaction with solutions of the amylase injected. These reactions are in a high degree specific to the particular amylase employed. The anti-body to the enzyme is stable when heated at 56°. After the injection of amylase, previously inactivated by heat, the precipitin reaction is still obtained, but the serum has no inhibitory action towards the enzyme. There are therefore involved two distinct immunity reactions, the production of an anti-body to the enzyme itself, and of another to the protein which accompanies it.

C. R. H.

**Relation between Catalase and Autoxidisable Substances.** D. RYWOSCH (*Fermentforsch.*, 1924, **8**, 48—51).—The presence of catalase in the body fluids of invertebrates has been demonstrated to run parallel with the presence therein of an autoxidisable chromogen.

C. R. H.

**Stability of Yeast Catalase.** K. NAKAMURA (*Z. physiol. Chem.*, 1924, **139**, 140—146).—The observed rate of inactivation of

yeast catalase during autolysis of yeast is about 20,000 times greater than can be accounted for by the effect of temperature alone; this is apparently due to the presence of enzymes which destroy catalase.

C. R. H.

**Rôle of the Mineral Constituents in Plants. I. Influence of Neutral Salts on Catalase.** A. J. SMIRNOV and S. P. ALISSOVA (*Biochem. Z.*, 1924, **149**, 63—78).—The reaction of aqueous extracts of wheat containing naturally occurring buffer salts is not altered by the addition of the chlorides of univalent metals, whilst the chlorides of the bivalent metals lower the  $p_H$  by 0.2 to 0.6. By increasing the  $p_H$  from 3.5 to 7.3, the relative activity of the catalase present increases from 4.76 to 135.98. Bivalent cations inhibit the activity of catalase twice as strongly as univalent cations, whilst a similar relation between inhibitory power and valency is not observed in the case of the anions, the series being  $SO_4 < PO_4 < Cl < NO_3$  in the order of increasing inhibition. Univalent cations are active in concentrations of  $M/320$ , bivalent cations at  $M/640$ . At still greater dilutions down to  $M/5120$ , a zone of very weak or of no inhibition is followed by one at which the inhibition again appears.

J. P.

**Influence of Culture of Yeast on Galactose on its Power of Fermenting this Carbohydrate.** E. ABDERHALDEN (*Fermentforsch.*, 1924, **8**, 42—47).—The fact, previously recorded by other observers, that yeast, grown in a medium containing galactose, acquires an increased power of fermenting this carbohydrate, has been confirmed; similar results were obtained with the maceration juice of yeast so treated. No evidence could be obtained of increased permeability of the yeast-cells to galactose. It is suggested that, prior to fermentation, galactose must be transformed into dextrose or lævulose, and that suitable conditions for such a transformation are established in the cells by the presence of galactose in the culture medium.

C. R. H.

**Fermentation Co-enzyme (Co-zymase) of Yeast. V. The Rôle of the Co-enzyme in Fermentation.** H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **139**, 15—23).—A parallelism, which is not disturbed by variations in the co-enzyme content of the yeast, has been found to exist between the evolution of carbon dioxide and the esterification of phosphates during the fermentation of dextrose by yeast. It is concluded that the co-enzyme takes part in the formation of the hexosediphosphate or perhaps in an earlier transformation of the sugar.

E. S.

**Dependence of Alcoholic Fermentation on Acidity.** K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **139**, 30—38).—A comparison has been made between the conditions of activity of a bottom yeast, with which esterification of phosphates (decrease of free phosphates) accompanied fermentation, and a top yeast, which produced no detectable decrease in free phosphates; dry preparations were used in each case. No essential difference was found between the velocity- $p_H$  curves. From this result, together with the effect of

phosphates on the course of the fermentation, it is concluded that the two yeasts differ only in the rate at which they decompose hexosephosphates; this rate is small with the bottom yeast and hence an accumulation of hexosephosphates occurs. E. S.

**Rotation of the Maltose produced by Fermentation of Starch by Malt Extract.** H. VON EULER and K. HELLEBERG (*Z. physiol. Chem.*, 1924, **139**, 24—29).—Preliminary experiments indicate that the maltose so produced contains a preponderating amount of the  $\beta$ -form. E. S.

**Enzymic Methylglucoside Equilibrium.** H. VON EULER and K. JOSEPHSON (*Arkiv Kem., Min., Geol.*, 1924, **9**, No. 7, 1—8).—For the reversible enzymic hydrolysis of  $\beta$ -methylglucoside, represented by the equation  $[\beta\text{-methylglucoside-enzyme}] + [\text{water}] \rightleftharpoons [\text{glucose-enzyme}] + [\text{methyl alcohol}]$ , there exist the equilibria  $[\text{methylglucoside-enzyme}]/[\text{methylglucoside}] \cdot [\text{enzyme}] = K_1$  and  $[\text{glucose-enzyme}]/[\text{glucose}] \cdot [\text{enzyme}] = K_2$ . The velocity equations are, for the hydrolysis of the glucoside,  $v_1 = k_1[\text{glucoside-enzyme}] \cdot [\text{water}]$  and for the synthesis,  $v_2 = k_2[\text{glucose-enzyme}] \cdot [\text{alcohol}]$ . The progress of the reaction in the system, glucoside-glucose-alcohol-water-enzyme is hence determined by the expression,  $dx/dt = v_1 - v_2 = k_1[\text{glucoside-enzyme}] \cdot [\text{water}] - k_2[\text{glucose-enzyme}] \cdot [\text{alcohol}] = k_1 K_1 [\text{glucoside}] \cdot [\text{enzyme}] \cdot [\text{water}] - k_2 K_2 [\text{glucose}] \cdot [\text{enzyme}] \cdot [\text{alcohol}]$ . For a condition of equilibrium,  $dx/dt = 0$ , and hence

$$k_1/k_2 = K_2[\text{glucose}] \cdot [\text{alcohol}]/K_1[\text{glucoside}] \cdot [\text{water}] = K.$$

Only when  $K_1 = K_2$  can the position of equilibrium in this system coincide with that in the corresponding non-enzymic system.

Bourquelot (*J. Pharm. Chim.*, 1914, [vii], **10**, 361) has shown that the same equilibrium position is arrived at in the hydrolysis as in the synthesis of  $\beta$ -methylglucoside in presence of emulsin. By means of Bourquelot's results, the authors show that the value of  $K_1$  in the expression,  $[\text{methyl alcohol}][\text{glucose}] = K_1[\text{water}][\text{glucoside}]$  remains practically constant at 0.25 for concentrations of the alcohol not exceeding about 50% and afterwards gradually rises, probably owing to increasing inactivation of the enzyme, thus altering the final state and resulting in a false equilibrium. Thus, according to the theory outlined above, the affinity of  $\beta$ -glucosidase for glucose is about four times as great as that for methylglucoside, whereas the value of the equilibrium constant derived from the velocities of the two reactions should be 1. The affinities between the  $\beta$ -methylglucosidase used by Bourquelot and the reacting substances are not known, but for the emulsin employed by Willstätter, Kuhn, and Sobotka (*A.*, 1923, i, 1034; see also Kuhn, *A.*, 1923, i, 589; Willstätter and Kuhn, *A.*, 1923, i, 721), the ratio between such affinities is calculated to be 3.3, which differs but little from the value 4 for the different preparation of enzyme used by Bourquelot. T. H. P.

**Blood Diastases.** I. S. J. COHEN (*Amer. J. Physiol.*, 1924, **69**, 125—131).—Since hyperglycæmia produced by adrenaline or

morphine, but not by ingestion of carbohydrate, and hypoglycæmia produced by insulin are associated with a fall in the blood diastase and an increase in the liver-tissue diastase, it is suggested that the function of the blood diastases is to assist in the breaking down of glycogen, and to be available for mobilisation to the organs where there is immediate need for their action. A. A. E.

**Enzyme Action. XXVIII. Spontaneous Increase in the Activities of Lipase and Protease of Tissue Extracts.** (MISS) H. M. NOYES, K. SUGIURA, and K. G. FALK (*J. Amer. Chem. Soc.*, 1924, **46**, 1885—1889; cf. A., 1923, i, 872).—The tissues investigated were whole rats ( $3\frac{1}{2}$  and 22 days old), rabbit liver, lung, and muscle, mouse carcinoma, and human fibromyoma of uterus. They were ground up, extracted with water, and the filtered extracts tested for lipase and protease immediately and at intervals after standing at the ordinary temperature in the presence of toluene. The lipase was determined by adding 3.4 milli-equivalents of ten different esters to 15 c.c. portions of the extracts, incubating at 37° for 22 hours, and then titrating with 0.1N-sodium hydroxide. For the protease actions, 0.1 g. portions of peptone, casein, and gelatin were added to the extracts to be tested and titrated by the formol method after similar incubation. The mixtures were all brought to  $p_H$  7.0 initially. In the lipase experiments spontaneous increases were observed with some tissues and substrates and not with others. Spontaneous increases in protease action usually occurred with casein, and not with the other two substrates. A. C.

**Application of Folin's Method for the Determination of Amino-nitrogen to Peptic Digestion.** Y. UWATOKO (*Z. physiol. Chem.*, 1924, **139**, 76—81).—No increase in amino-acid nitrogen occurs during the digestion of casein or glycine anhydride with pepsin. Some ammonia is produced from the casein, but this is also formed by treatment with 1% hydrochloric acid at 37° alone. E. S.

**Kinetics of Trypsin Digestion.** J. H. NORTHPROP (*J. Gen. Physiol.*, 1924, **6**, 723—729).—The rate of digestion of concentrated casein solutions with small amounts of trypsin has been followed with a view to prove the validity or otherwise of Schutz's rule, according to which the amount of hydrolysis should be proportional to the square root of the product of the time into the enzyme concentration. Neither Schutz's rule nor Arrhenius' equation holds accurately owing to the incorrectly assumed relation between the rate of hydrolysis and the substrate concentration. D. R. N.

**Enzymic Action of Extracts of the Duodenal Region of Domestic Animals.** H. D. BERGMAN, H. H. DUKES, and J. H. YARBOROUGH (*J. Amer. Vet. Med. Assoc.*, 1924, **65**, 313—326).—Extracts were made from the duodenal substance of the horse, ox, sheep, and pig. The extracts invariably contained an amylolytic enzyme active in neutral solution. This action was greater than that of extracts of the submucosa of these regions,

leading to the belief that the duodenal cells themselves produce amylase. Protease and lipase were generally not found.

CHEMICAL ABSTRACTS.

**Nucleosidases. I. General Properties.** P. A. LEVENE, M. YAMAGAWA, and I. WEBER (*J. Biol. Chem.*, 1924, **60**, 693—706).—The kinetics of the decomposition of adenosine by nucleosidase have been investigated. Solid preparations of the enzyme were obtained by extracting the minced organs (spleen, kidney) with a phosphate buffer solution ( $p_H$  7.0) and pouring the press-juice, after concentration, into a large volume of acetone. These, however, rapidly lost their activity; hence the press-juice was mostly employed without further purification. The optimum conditions for the action of nucleosidase are at  $p_H$  7.5 and  $37^\circ$ , although irreversible inactivation occurs at much lower temperatures. With a relatively large excess of enzyme, the reaction follows the unimolecular law; deviations from this law are considered to be due to the formation of the complex enzyme-inhibitor, but attempts to calculate the dissociation constant of the latter yielded values which differed with different enzyme preparations. Both products of the reaction (adenine, ribose) exert an inhibitory action; the effect of ribose is twice that of adenine. E. S.

**Nucleosidases. II. Purification of the Enzyme.** P. A. LEVENE and I. WEBER (*J. Biol. Chem.*, 1924, **60**, 707—715).—The nucleosidase was extracted by suspending the washed and ground organs (2.2 kg.) in a phosphate buffer solution (4 litres) at  $p_H$  7.0, allowing them to autolyse for 24 hours at  $40^\circ$ , and filtering. When kidneys were employed, the activity of the extract was increased by digesting the filtrate for a further 24 hours at  $40^\circ$ ; with pancreas this further digestion produced inactivation. Purification was effected by fractional precipitation with colloidal iron and alcohol. Addition of 20% (by volume) of iron solution and 20% of alcohol removed the inhibitory substances; the further addition to the filtrate of 40% of iron solution and 40% of alcohol (95%) completely precipitated the enzyme. The latter was extracted from the adsorbate by disodium phosphate or sodium hydroxide at  $p_H$  8.7. After filtration from the iron, the extract was neutralised, concentrated under diminished pressure, and the enzyme precipitated by a large excess of acetone. The solid preparation so obtained retained its activity for 10 months. It contained large amounts of inorganic material (76% ash) which could not be removed by dialysis without disappearance of the enzyme. Further purification could sometimes be effected by bringing a solution of this preparation to  $p_H$  1.2 by addition of hydrochloric acid, when a highly active product separated as a flocculent precipitate (ash 8%); this method was not, however, invariably successful. The most active preparation gave a pink biuret reaction, but no distinct reaction with Millon's reagent; it did not reduce Fehling's solution. Nucleosidase is adsorbed by kaolin, but not by aluminium hydroxide; in the former case, the adsorbate possesses the whole of the original activity, but the enzyme cannot be recovered. E. S.

**Nucleosidases. III. Degree of Specificity of Nucleosidase and Distribution of it in Various Organs and in Various Species.** P. A. LEVENE and I. WEBER (*J. Biol. Chem.*, 1924, **60**, 717—720).—The optimum acidity for the decomposition of inosin by nucleosidase is identical with that for adenosine (cf. preceding abstracts). Nucleosidase is absent from dog's pancreas and from pancreatic and intestinal juices, but is present in the pancreas of cattle. It has no action on adenine hexoside.

E. S.

**Action of Antiphenolase in an Adsorbed Condition.** W. ENGELHARDT (*Biochem. Z.*, 1924, **148**, 463—468).—Antiphenolase, together with the serum proteins, is adsorbed from immune sera by ferric and aluminium hydroxides, charcoal, and kaolin. The adsorption is practically irreversible, and the adsorbed enzyme retains undiminished its specific affinity for phenolase in the cases of the first three adsorbents, whilst its activity is but slightly diminished in the case of kaolin.

J. P.

**Coagulating Property of Papain.** L. ROSENFELD (*Biochem. Z.*, 1924, **149**, 158—173).—Papain solution precipitates an aqueous solution of the mucilage prepared from the seeds of *Cydonia*. Pepsin, trypsin, rennin, and plant protease do not precipitate the mucilage. The specific affinity of papain for *Cydonia* mucilage is such that the latter may be identified and separated from mixtures with other similar substances. *Cydonia* mucilage carries a negative charge whilst papain is positive. The precipitation is therefore explained on physical grounds. The precipitate consists of both constituents and separation is difficult, although the precipitated enzyme is still capable of coagulating milk. Alkalis, inorganic acids, neutral salts, and the globulin of blood-serum inhibit the action of papain, whilst organic acids have the opposite effect. Papain also coagulates agar-agar.

J. P.

**Milk-coagulating Enzyme of *Solanum elaeagnifolium*.** A. BODANSKY (*J. Biol. Chem.*, 1924, **61**, 365—375).—The chymase obtained from the berries of the above plant acts best at 80—85° and is more stable to heat than rennin from animal sources; the preparation showed no change in activity after dialysis; with boiled milk, coagulation takes place in some cases only. The time of coagulation is inversely proportional to the amount of enzyme present.

C. R. H.

**Soluble Enzymes of the Bryony Root (*Bryonia dioica*).** N. F. GIRARDET (*J. Pharm. Chim.*, 1924, [vii], **30**, 75—81).—Amylase, invertase, and peroxydase have been found in the root. It also contains a characteristic enzyme which acts on one or more of its constituents producing a dextrorotatory sugar. Basic ammoniacal lead acetate, but not neutral lead acetate, precipitates this enzyme.

D. R. N.

**Utilisation of Dextrose in Mineral Media by Bacteria with reference to Acid Formation.** J. S. JOFFE and H. J. CONN (*Abstr. Bact.*, 1924, **8**, 10—11).—In inorganic media with



dextrose as a source of energy, various soil organisms utilise the constituents of the medium and impart a reaction irrespective of the course of dextrose fermentation. With ammonium dihydrogen phosphate (at  $p_H$  6.6) the reaction became more acid; with sodium nitrate, alkaline. In the latter case, the nitrate was completely utilised, leaving sodium ions. Differential decomposition of the dextrose and adsorption phenomena also affect the final  $p_H$ .

A. A. E.

**Enzyme in *Penicillium glaucum* which Hydrolyses Sucrose.**

H. VON EULER, K. JOSEPHSON, and B. SÖDERLING (*Z. physiol. Chem.*, 1924, **139**, 1—14).—The invertase contained in *Penicillium glaucum* (A., 1921, i, 482) cannot be removed from the cell by extraction with water, and no success has been attained in attempts to liberate it by autolysis. The optimum conditions of acidity for its action lie between  $p_H$  4 and  $p_H$  6, and thus differ from those of invertases of different origin. The "constant" calculated for a unimolecular reaction decreases rapidly during the reaction. The action of *P. glaucum* invertase, like that of taka-saccharase (Kuhn, A., 1923, i, 1033), is inhibited by dextrose, but not by lævulose. E. S.

**Fermentation of Pentoses by *Bacillus granulobacter pectinovorum*.** W. H. PETERSON, E. B. FRED, and E. G. SCHMIDT (*J. Biol. Chem.*, 1924, **60**, 627—631).—Xylose and arabinose yield the same products as dextrose; slightly greater amounts of volatile acids and slightly smaller amounts of solvents (acetone, butyl alcohol) are, however, produced from the pentoses (cf. Speakman, this vol., i, 371). The fermentation of the pentoses is practically complete in 72 hours (cf. Robinson, A., 1922, i, 971). E. S.

**Proteolytic Action of *Bacillus granulobacter pectinovorum* and its Effect on the Hydrogen-ion Concentration.** W. H. PETERSON, E. B. FRED, and B. P. DOMOGALLA (*J. Amer. Chem. Soc.*, 1924, **46**, 2086—2090).—In the fermentation of maize mash a rapid hydrolysis of the proteins is produced by *Bacillus granulobacter pectinovorum*, from 50 to 75% of the total proteins being converted into soluble products during the fermentation, which is approximately complete in 3 to 4 days. There is little amino-acid or peptide formation during the first 24 hours, but after this the soluble protein and intermediate products increase more slowly and finally, after 48 hours, decrease, while amino-acid and peptide formation increase rapidly. At the end of 96 hours, the nitrogen is mainly in the form of proteoses, peptones, and peptides. Glutamic acid was isolated from the filtrate after phosphotungstic acid precipitation. Due to the buffer action of hydrolytic products and to acids with low dissociation, a high titratable acidity may be produced without much change in the hydrogen-ion concentration. R. B.

**Decomposition of Cellulose by Various Groups of Micro-organisms of the Soil.** H. HEUKELEKIAN (*Abstr. Bact.*, 1924, **8**, 9).—Under similar conditions, fungi decompose cellulose in the form of filter-paper more readily than either bacteria or actinomycetes; a definite correlation appears to exist between the

cellulose decomposed and the nitrogen assimilated, the ratio for most of the strong cellulose-decomposing fungi being 30 : 1. The results apply in the case of the decomposition of cellulose in the soil; when no available nitrogen is added, together with the cellulose, the amount of the latter decomposed will indicate to a certain extent the availability of the nitrogen of the soil. A. A. E.

**Decomposition of Proteins and Amino-acids by Various Groups of Soil Micro-organisms.** S. LOMANITZ (*Abstr. Bact.*, 1924, 8, 9—10).—*Bacterium fluorescens* attacks amino compounds (glycine, alanine, and asparagine), but not casein in solution; *B. cereus* attacks casein, but not glycine or alanine, and asparagine only to a limited extent. *Actinomyces viridochromogenus*, *Trichoderma Kőningi*, and *Zygorhynchus Mölleri* utilise all four compounds as sources of carbon and nitrogen. The amount of nitrogen assimilated by the organism depends on the presence or absence of dextrose. A. A. E.

**Influence of Micro-organisms on the Carbon : Nitrogen Ratio of the Soil.** S. A. WAKSMAN (*Abstr. Bact.*, 1924, 8, 10).—The definite ratio (about 10 : 1) existing between the carbon and nitrogen contents of the soil is due to the activities of micro-organisms. Addition of organic matter results in its decomposition by soil micro-organisms, with the effect of narrowing down the original carbon : nitrogen ratio; whether nitrogen is made available or nitrogen starvation sets in depends on the carbon : nitrogen ratio of the organic matter of the soil, and the micro-organisms concerned. A. A. E.

**Structure and Life-history of the Sulphur Bacteria. I.** D. ELLIS (*Proc. Roy. Soc. Edinburgh*, 1923—1924, 44, 153).

**Preparation of Insulin.** A. SORDELLI (*Compt. rend. Soc. Biol.*, 1924, 90, 254; from *Chem. Zentr.*, 1924, i, 2446).—A method is described for the preparation of insulin in which the acid alcoholic extract of pancreas is precipitated with picric acid. G. W. R.

**Insulin-like Substances from Beans and their Action on Carbohydrate Metabolism.** M. EISLER and L. PORTHEIM (*Biochem. Z.*, 1924, 148, 566—572).—Preparations made from extracts of dried beans (*Phaseolus multiflorus*) contain a substance which lowers the blood-sugar of rabbits without producing convulsions. Such extracts—including certain preparations devoid of insulin-like action—inhibit the action of salivary and taka-diaestases on starch, and also lower the starch and sugar content, and increase the acetaldehyde content of pulped beans (*P. vulgaris*) when incubated with the latter at 36° in physiological saline. J. P.

**Chemical Constitution of Insulin.** A. CRUTO (*Atti R. Accad. Lincei*, 1924, [v], 33, ii, 42—45).—A highly purified preparation of "insulin sulphate" examined by the author was free from phosphorus and had the percentage composition: C, 47.73; H, 7.27; N, 14.53; S, 1.73; O, 22.84;  $H_2SO_4$ , 5.90. T. H. P.

**Influence of Insulin on the Dextrose-fermenting Action of *Bacillus coli*.** G. MCGUIRE and K. G. FALK (*J. Biol. Chem.*, 1924, **60**, 489—490).—No influence was observed. E. S.

**Fat-soluble Vitamins. XVII. Induction of Growth-promoting and Calcifying Properties in a Ration by Exposure to Ultra-violet Light.** H. STEENBOCK and A. BLACK (*J. Biol. Chem.*, 1924, **61**, 405—422).—Food free from vitamin-A can be activated by exposure to the light of a mercury vapour lamp and is not subsequently inactivated by heating at 96°; muscle and liver from rats which have been exposed to ultra-violet light contain vitamin-A, whereas from non-irradiated animals these tissues do not contain this vitamin. C. R. H.

**Concentration of Vitamin-B.** P. A. LEVENE and B. J. C. VAN DER HOEVEN (*J. Biol. Chem.*, 1924, **61**, 429—443).—A series of attempts was made to concentrate vitamin-B by precipitation or adsorption with various reagents and subsequent recovery from the precipitate, using as starting material the fraction prepared according to Osborne and Wakeman (*A.*, 1920, **i**, 208). Adsorption with kaolin was unsuccessful. A slight purification was effected by adsorption with Lloyd's reagent and subsequent extraction with alkali ( $p_H$  9.0), also by precipitation with barium hydroxide and subsequent removal of barium with sulphuric acid. The best result was obtained by adsorption with silica gel; from the adsorbate the active material could be partly extracted at  $p_H$  3.0, a larger and more active fraction being obtained by further extraction at  $p_H$  9.0. C. R. H.

**Spinacin, a New Protein from Spinach Leaves.** A. C. CHIBNALL (*J. Biol. Chem.*, 1924, **61**, 303—308).—By the application of the author's method (*A.*, 1923, **i**, 635) for the extraction of cytoplasmic material from leaf-cells, a new protein, "spinacin," has been isolated from the common spinach. The substance is free from carbohydrate, is insoluble in water and neutral salt solutions, but readily soluble in a small excess of either acid or alkali; it is precipitated by salts from either solution, more readily from the acid one; its isoelectric point lies between  $p_H$  4.0 and 4.6. C. R. H.

**Biochemical Hydrolysis of Rutin. Presence of Rutin in Plants and Identification of the Glucoside and its Hydrolysis Products.** C. CHARAUX (*Bull. Soc. Chim. biol.*, 1924, **6**, 631—640, and 641—647).—A list of plants from which rutin may be extracted is given. The pure glucoside,  $C_{27}H_{30}O_{16}$ , crystallises from water in fine needles with  $2H_2O$ , and melts indefinitely at 188—190°. On heating on the water-bath with 4% sulphuric acid, an insoluble precipitate was obtained which was identified by means of its bromo derivative as quercetin. The acid mother-liquor, after removal of the quercetin, yields rhamnose and dextrose. Partial hydrolysis of rutin was brought about by an enzyme from the seeds of *Rhamnus utilis*; in this experiment the carbohydrate part of the molecule was obtained as a disaccharide ("rutinose")

which was slightly dextrorotatory, softened at 140°, and melted at 189—192° (decomp.), giving dextrose and rhamnose on acid hydrolysis.

C. R. H.

**Glucoside Hydrolysable by Emulsin in the Genera, *Veronica*, *Euphrasia*, *Odontites*, *Bartsia*, and *Pentstemon*.** M. BRAECKE (*Bull. Soc. Chim. biol.*, 1924, 6, 665—671).—Observations of the effect on the optical rotation and the reducing power of extracts of these plants brought about by emulsin show that they all contain glucosides hydrolysable by this enzyme. Invertase has, in most cases, no effect on the extracts.

C. R. H.

**Solanine Content of Potatoes.** C. GRIEBEL (*Z. Unters. Nahr. Genussm.*, 1924, 47, 436—408).—In many parts of Germany the potatoes grown during the year 1922 contained an unusually large quantity of solanine (0.038 to 0.079%) and their consumption caused illness; when re-grown during 1923, these potatoes produced tubers of normal solanine content (0.005%). Experiments showed that the quantity of solanine in potatoes may be doubled by exposing the latter to light for 4 days, and it would appear that the poisonous potatoes had been unduly exposed during the harvest, transport, or storage.

W. P. S.

**Constituents of *Astragalus sinicus*, L.** K. YOSHIMURA and S. FUJISE (*J. Chem. Soc. Japan*, 1924, 45, 32—41).—The fresh grass contained: water, 90.17%; protein, 2.19%; ether extract, 0.60% (fats, 0.25%, and colouring matters, 0.35%); fibre, 2.66%; soluble non-nitrogenous compounds, 3.41%, and ash, 0.97%. From an aqueous extract of 40 kg. of the grass, the following organic compounds were isolated: malonic acid, 2.7 g.; adenine hydrochloride, 1.5 g.; histidine, trace; arginine nitrate, 0.3 g.; choline chloraurate, 1.5 g.; trigonelline hydrochloride, 0.12 g. No betaine was found.

K. K.

**Constituents of "Hang-ge."** S. NAKAYAMA (*J. Pharm. Soc. Japan*, 1924, No. 509, 551—564).—The drug "Hang-ge" (Chinese: Pwan-hia) is the root nodule of *Pinellia tuberifera*, Ten., and is used as an anti-emetic. The powdered material was extracted first with ether, then with alcohol, and finally with water. The ethereal extract (1.02—1.10% of the fresh material) is composed of an ethereal oil and a fatty oil (semi-solid in ordinary temperature, iodine value 80.92, saponification value 133.32, acid value 1.91). On hydrolysis with alcoholic potash, the fatty oil gave about 20% of unsaponifiable substance, from which a phytosterol ( $C_{26}H_{44}O, H_2O$ , m. p. 136°,  $[\alpha]_D^{20} - 31.37^\circ$ , acetate, m. p. 121°) was isolated. Among the saturated fatty acids, palmitic acid was detected. From the unsaturated acid fraction, an acid,  $C_{18}H_{34}O_2$ , m. p. 44°, b. p. 208—216°/3 mm., probably isooleic acid, was isolated. From the alcoholic extract (1.25—3.90%), oxalic acid (0.29—0.38% of the material) was isolated and from the water extract (3.67—4.10%) a sugar.

K. K.

**New Constituent of *Atractylis ovata*, Thunb.** S. TAKAGI and G. HONGO (*J. Pharm. Soc. Japan*, 1924, No. 509, 539—551).—By steam distillation of *Atractylis ovata*, Thunb. (*Compositae*), a light yellow, viscous oil is obtained ( $d_4^{20}$  0.985,  $[\alpha]_D^{25} + 46.5^\circ$ , acid value 0, saponification value 16.95). It slightly reddens fuchsin-sulphurous acid solution and reduces Fehling's solution when heated. When subjected to fractional distillation in a vacuum, crystals appear in the distillate (yield: 20% of the oil). The name *atractylon* is given to this substance (colourless plates, m. p.  $42^\circ$ , b. p.  $131-132^\circ/4$  mm.,  $[\alpha]_D^{25} + 39.65^\circ$ ,  $d_4^{25}$  1.0269 and  $n_D^{25}$  1.52627). Its formula is  $C_{14}H_{18}O$ , and it can be recrystallised from methyl alcohol. The mother-liquor contains no atractylol,  $C_{15}H_{26}O$  (cf. Gadamer and Amenomiya, A., 1903, i, 353). Atractylon is unstable in air, changing into a resin. With vanillin and hydrochloric acid, it gives a cherry-red coloration. The pine-shaving hydrochloric acid reaction gives a violet colour. It does not reduce Fehling's solution. It reacts violently with bromine in acetic acid solution, and contains no methoxyl. No acyl derivative could be obtained. It does not combine with hydroxylamine, phenylhydrazine, or semicarbazide, and could not be reduced with sodium and ethyl or amyl alcohol. From these results, atractylon is concluded to be an ether-like compound. Reduction with hydrogen in acetic acid solution, using platinum black as a catalyst, yielded *hexahydro-atractylon*,  $C_{14}H_{24}O$ , a colourless, stable oil, b. p.  $135-136^\circ/4$  mm.,  $d_D^{20}$  0.9919,  $[\alpha]_D^{25} - 34.36^\circ$ ,  $n_D^{20}$  1.50186. K. K.

**Constituents of the Tomato. I.** K. YOSHIMURA and K. NISHIDA (*J. Chem. Soc. Japan*, 1924, 45, 57—65).—From an aqueous extract of 100 kg. of tomato (*Lycopersicum esculentum*, Mill., water content 96.01%), the following compounds were isolated: malic acid, 4.45 g.; citric acid, 4.70 g.; adenine hydrochloride, 1.20 g.; arginine, trace; trigonelline chloroaurate, 1.35 g.; choline chloroaurate 0.20 g. K. K.

**Nitrogenous Compounds in Pumpkin and Cucumber.** K. YOSHIMURA and K. NISHIDA (*J. Chem. Soc. Japan*, 1924, 45, 49—57).—The pumpkin contained 82% of water. Analysis of the dried substance gave the following results: protein, 13.23%; fats, 2.47%; crude fibre, 8.95%; soluble non-nitrogenous substance, 68.42%; ash, 6.93%. From the aqueous extract of 16 kg. of pumpkin, free from seeds, the following compounds were isolated: adenine hydrochloride, 0.25 g.; arginine nitrate, 1.68 g.; trigonelline hydrochloride, 0.50 g. On extracting 22 kg. of cucumber (water content 96.15%) with hot water, adenine hydrochloride, 0.27 g., and trigonelline chloroaurate, 0.5 g., were isolated. A trace of arginine was detected. K. K.

**Microchemical Detection of Acetaldehyde in Fruits.** C. GRIEBEL.—(See ii, 791.)

**Methylpentosans in Cereals.** G. TESTONI.—(See ii, 790.)

**Nitrogenous Compounds in the Oil Cake of *Brassica campestris*, var. *Chinensis*.** T. ITO. K. YOSHIMURA and S. FUJISE (*J. Chem. Soc. Japan*, 1924, 45, 42—49).—The cake contained 10·84% of water. Analysis of the dried material gave the following results: total nitrogen, 6·15%; protein nitrogen, 5·60%; non-protein nitrogen, 0·55%; fats, 13·47%; ash, 11·63%. From an aqueous extract of 40 kg. of the cake the following bases were isolated: adenine hydrochloride, 1·2 g.; arginine copper nitrate, 0·6 g.; choline hydrochloride, 43·3 g.; and betaine hydrochloride, 0·85 g. K. K.

**Microchemical Detection of Mustard Oils.** A. PIETSCHMANN.—(See ii, 793.)

**Nitrogenous Constituents of the Juice of the Alfalfa Plant [*Lucerne*]. I. Amide and Amino-acid Nitrogen.** H. B. VICKERY (*J. Biol. Chem.*, 1924, 60, 647—655).—The filtrate obtained from the press-juice after raising the alcohol content to 53% (cf. Osborne, Wakeman, and Leavenworth, A., 1922, i, 99, 1104) has been fractionally precipitated with a variety of reagents and the distribution of nitrogen determined in each fraction. Amino-acids are present only in small amount and account for 13·6% of the total nitrogen in the filtrate; small quantities of polypeptides, as shown by the increase in amino-nitrogen after hydrolysis, are also present. Tyrosine and asparagine have been isolated in a pure state; the yield of the latter represented 35·7% of the amide-nitrogen and 5·82% of the total nitrogen in the filtrate. E. S.

**Effects of the Method of Desiccation on the Nitrogenous Constituents of Plant-tissue.** K. P. LINK and E. R. SCHULZ (*J. Amer. Chem. Soc.*, 1924, 46, 2044—2050).—Experiments with the leaves of the sugar-beet, the barberry, and maize, and with ears of maize show that the temperature of drying does not affect the total nitrogen content of the tissues but generally produces a decrease in the proportion of total soluble nitrogenous compounds, due to coagulation of the proteins. The effects of desiccation depend largely on the nature of the tissue involved. Drying at high temperatures (80° to 90°) causes a considerable decrease in water-soluble nitrogen, this effect being more pronounced with beet leaves and maize ears than with maize and barberry leaves. At lower temperatures (30° to 45°) proteolytic decomposition takes place, which in some cases is balanced by coagulation of the soluble nitrogenous constituents. At 65° a decrease in the amount of soluble nitrogen is the only significant alteration (cf. Tottingham, Schulz, and Lepkovsky, this vol., i, 598). R. B.

**Effect of Titanium on Plant Growth.** E. BLANK and F. ALTEN (*J. Landw.*, 1924, 72, 103—110).—The authors were unable to confirm the results of Němec and Káš (A., 1923, i, 1161) and find that the addition of sodium titanate may depress the dry weight of mustard and maize plants. This depression appears to be directly proportional to the amount of titanate added. O. O.

**Have Green Plants the Power of Fixing Elementary Nitrogen from the Atmosphere?** C. B. LIPMAN and J. K. TAYLOR (*J. Franklin Inst.*, 1924, 198, 475—506).—Wheat and barley in culture solutions with and without nitrate nitrogen fix atmospheric nitrogen without bacterial intervention. Incomplete experiments suggest that *Bromus villosus* is able to fix nitrogen, but that peas cannot. Barley does not fix as much elementary nitrogen as wheat in the presence of nitrates in solution. In the case of wheat, there appears to be a minimum supply of nitrate nitrogen below which decrease in the amount of such nitrogen has no effect on the nitrogen content of the dry matter produced. O. O.

**Significance of Oxygen for the Formation of Enzymes in Germinating Plant Seeds.** A. OPARIN and A. BACH (*Biochem. Z.*, 1924, 148, 476—481).—The increases in the peroxydase, protease, and amylase contents of moistened wheat seedlings, kept for two days out of contact with oxygen, become more marked if oxygen be admitted. Autolysis of the material in the absence of oxygen causes a diminution in catalase, whilst in the presence of this gas a still greater diminution is noted. On subjecting the seedlings or extracts made from them to anodic oxidation the enzymes first increase to a maximum and then diminish in amount. Peroxydase is present in plant fibrin after tryptic digestion followed by anodic oxidation, but it is not detectable in the original material. A similar treatment of egg-albumin and crystallised plant-globulin yields negative results. J. P.

**Can Measurements of Enzyme Action be Employed for Ascertaining the Vitality of Important Cultivated Plants?** T. BIÉCHY (*Fermentforsch.*, 1924, 8, 135—166).—Comparison of the activity of the catalase contained in the expressed juice of the stems of potato plants grown under different conditions shows that this measurement may afford useful evidence regarding the vitality of the plant. It is suggested that this method of investigation be extended to other species. C. R. H.

**Resistance to Disease in Plants.** J. J. WILLAMAN, C. A. MORROW, and A. K. ANDERSON (*Minnesota Agr. Expt. Sta., Ann. Rept.*, 1922, 35 pp.).—The principal products of metabolism of the flax wilt organism (*Fusarium lini*) are stated to be carbon dioxide and alcohol, with smaller amounts of organic acids.

CHEMICAL ABSTRACTS.

**Apparently Specific Test for Tannins.** A. H. WARE.—(See ii, 789.)

**Influence of Electrolytes on the Total Surface of Soil Particles.** L. SMOLIK (*Compt. rend.*, 1924, 179, 211—213).—The effect of electrolytes on the hygroscopic behaviour of soils has been examined. The addition of an electrolyte apparently coagulates the soil colloids, and thus reduces the surface and the power of absorbing moisture. Removal of the electrolytes by washing has the converse effect. [Cf. B., 1924, 920.] M. S. B.

## Organic Chemistry.

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**Action of Ozone on Hydrocarbons with Special Reference to the Production of Formaldehyde. III. Action of Ozone on *n*-Hexane.** E. W. BLAIR, T. S. WHEELER, and W. LEDBURY (*J. Soc. Chem. Ind.*, 1924, **43**, 287—289T).—The action of ozone on boiling *n*-hexane yields formaldehyde, acetaldehyde, and other aldehydes up to *n*-hexaldehyde; acids up to *n*-hexoic acid (produced in greatest quantity); also traces of carbon monoxide and dioxide and water. *n*-Hexyl *n*-hexoate and other esters are also formed.

**Action of Bromine on *n*-Hexane.** E. W. BLAIR, W. LEDBURY, and T. S. WHEELER (*J. Soc. Chem. Ind.*, 1924, **43**, 289—290T).—*p*-Dibromobenzene and *trans*-benzene hexabromide are produced when nitrogen carrying the vapour of either benzene or *n*-hexane is passed through bromine at the ordinary temperature. It is probable that the hexane is converted into *cyclohexane* and then into benzene by oxidation.

**Liberation of Hydrogen from Carbon Compounds. I. Interaction of Acetylene, Methyl Alcohol, and Formaldehyde with Fused Alkali Hydroxides.** H. S. FRY, E. L. SCHULZE, and H. WEITKAMP (*J. Amer. Chem. Soc.*, 1924, **46**, 2268—2275).—The reaction between dry acetylene and an equimolecular mixture of sodium and potassium hydroxides at 300—325° yields various quantities of orthocarbonates, but no acetates as reported by Feuchter (A., 1914, i, 406). The quantity of carbonate produced is approximately proportional to the amount of acetylene introduced into the alkali hydroxides, but owing to decomposition of the acetylene, evidenced by deposition of free carbon, the amounts of hydrogen and methane are not in accord with the equation  $C_2H_2 + 4NaOH \rightarrow H_2 + CH_4 + C(ONa)_4$ . Minute traces of unsaturated hydrocarbons are also formed. Similarly, methyl alcohol yields a mixture of carbonates and hydrogen, the ratios of the amounts of methyl alcohol consumed and carbon dioxide and hydrogen produced being in agreement with the equation  $MeOH + 2NaOH \rightarrow Na_2CO_3 + 3H_2$ . Formaldehyde behaves similarly, the ratio of the amounts of aldehyde consumed and carbon dioxide and hydrogen produced according approximately with the equation  $CH_2O + 2NaOH \rightarrow Na_2CO_3 + 2H_2$ . The reactions are in accordance with the general type reaction,  $R(H)_n + nMOH \rightarrow R(OM)_n + nH_2$ , and are analogous to the reactions between glycol and potassium hydroxide and resorcinol and sodium hydroxide. The mechanism of the reactions is suggested by the



scheme  $\text{HC}\equiv\text{CH} + 2\text{NaOH} \rightarrow \text{CHMe}(\text{ONa})_2$ ;  $\text{CHMe}(\text{ONa})_2 + \text{NaOH} \rightarrow \text{CMe}(\text{ONa})_3 + \text{H}_2$ ;  $\text{CMe}(\text{ONa})_3 + \text{NaOH} \rightarrow \text{CH}_4 + \text{C}(\text{ONa})_4$  (cf. Peters, this vol., ii, 174). The oxidation of cellulose by fused alkali hydroxides, yielding oxalates, conforms to the proposed type reaction.

R. B.

### Metallic Acetylides. II. Action of Acetylene on Metals.

J. F. DURAND (*Bull. Soc. chim.*, 1924, [iv], **35**, 1141—1144; cf. this vol., i, 602).—By the direct action of acetylene on the metal at 450—500° (cf. Novak, A., 1909, i, 865; 1910, ii, 778) the author has obtained *beryllium acetylide*, *cadmium acetylide*, and a new *aluminium acetylide*, probably  $\text{BeC}_2$ ,  $\text{CdC}_2$ , and  $\text{Al}_2(\text{C}_2)_3$ , respectively, and the zinc acetylide,  $\text{ZnC}_2$ , previously described (A., 1923, i, 449). These acetylides, which have not been obtained free from carbon or excess of the metal, are distinguished from magnesium acetylide in not giving rise to allylene derivatives; on treatment with water or dilute hydrochloric acid, acetylene is the only hydrocarbon produced, except in the case of aluminium acetylide when some methane is probably also formed (cf. Kusnetzoff, A., 1907, i, 669). Gold, palladium, uranium, and mercury give no acetylide under these conditions, and no acetylene could be obtained from the deposited carbon. The action of acetylene on aluminium and lead amalgams etc., and of iron, lead, etc. on acetylene in acetone solution, gave inconclusive results.

R. B.

**Comparison of Molecular Volume Numbers.** R. LORENZ and W. HERZ.—(See ii, 823.)

**Chlorination of Chloroform.** H. GAULT and R. TRUFFAULT (*Compt. rend.*, 1924, **179**, 467—469).—Chlorine is without action on chloroform in the dark or when exposed to red or yellow light, but light of shorter wave-length favours the reaction, the velocity of which is most marked in the ultra-violet region. Dry chlorides of calcium, zinc, or aluminium act in some degree as catalysts, but ferric chloride appears totally to inhibit the reaction. This is due to its absorption of the radiations of effective wave-length, as no chlorinating action occurs when a screen of ferric chloride solution is interposed. When in very dilute solution, absorption of the activating radiation is incomplete and a small yield of carbon tetrachloride is obtained. The velocity of the reaction increases with temperature.

H. J. E.

**Organic Reactions at the Surfaces of Dehydrogenating Catalysts.** H. ADKINS and W. A. LAZIER (*J. Amer. Chem. Soc.*, 1924, **46**, 2291—2305; cf. this vol., ii, 159).—The behaviour of ethyl alcohol, ethyl acetate, acetal, ether, acetaldehyde, and acetic acid at the surfaces of various catalysts containing nickel, copper, iron, and zinc has been investigated with a view to determine whether the reactions taking place are dependent on the physical nature of the surface or are characteristic of the metal present. Two distinct types of nickel are produced through reduction by

alcohol at 350–420° and by hydrogen at 300–400°. The former is at least twice as active as the latter in dehydrogenating alcohol and much more active in breaking down acetaldehyde to carbon monoxide and methane, practically no acetaldehyde being obtained from ethyl alcohol with this catalyst. In the hydrogenation of ethylene, it is only slightly superior, but with pure acetaldehyde, ethyl ether, and acetal it is many times as effective as nickel prepared with hydrogen. Neither catalyst is effective with ethyl acetate, whilst a catalyst reduced from nickel oxide by ethyl acetate itself is effective both against the ester and the alcohol; these facts, with the observations that nickel reduced with ethyl ether or acetal is reactive towards these compounds, whereas nickel reduced with hydrogen is not, lend some support to Boswell's theory of the activity of nickel catalysts. The evidence that oxygen must be present at a nickel surface in order that the nickel may function as a catalyst is inconclusive. If a nickel catalyst reduced by hydrogen is treated with oxygen, its activity towards dehydrogenation or decomposition is much increased, but this reactivation is not due to the addition of oxygen. Treatment of a hydrogen-reduced catalyst with oxygen followed by reduction with an organic reducing agent produces a much more effective catalyst than the original, the new catalyst producing a different proportion of reactions. A nickel catalyst reduced with alcohol does not lose its activity on treatment with hydrogen. The results obtained by passing a mixture of ethyl alcohol and acetic acid over nickel catalysts are in harmony with the activities when the two substances are reduced alone, the decomposition of ethyl alcohol being the more rapid reaction. The reactions under consideration are not successive reactions, the proportion of reaction products being determined by the nature of the catalyst, whilst the amount of reaction is dependent on variable factors such as time and temperature. The evidence indicates that the true catalyst is not a nickel oxide, but metallic nickel, and that the spacing of the active points is of fundamental importance, as it is in the case of non-reducible oxide catalysts. All nickel catalysts are characterised by their power of breaking carbon linkings, and this may be connected with the ability of nickel to pull electrons from their normal position between atoms.

When alcohol is passed over iron oxide obtained by drying precipitated ferric hydroxide or by igniting the nitrate or oxalate, the reactions involving the formation of methane and ethane and those of dehydrogenation occur in the proportion of 1 : 4 or 1 : 5. Iron oxide obtained from *methyl* or *ethyl ferrite*, however, behaved like reduced iron, yielding almost entirely a straight dehydrogenation to acetaldehyde and hydrogen. Copper catalysts obtained by ignition of copper nitrate, oxalate, and formate and by reduction of cuprous oxide give a similar straight dehydrogenation of ethyl alcohol. Zinc oxide obtained from zinc hydroxide dehydrogenates six times as much alcohol as it dehydrates, whilst with zinc oxide from *zinc isopropoxide*, the ratio dehydrogenation/dehydration is only 4/1, and in the latter case 5–6% of carbon dioxide is produced,

whereas in the first case only 1—2% is formed. The catalyst from zinc butoxide is intermediate between these two catalysts. The oxide obtained from the isopropoxide gives results with acet-aldehyde almost identical with those from iron oxide in the proportions of the reaction products, whereas the catalyst from zinc hydroxide gives 25% less carbon dioxide, 30% more carbon mon-oxide, and 40% less hydrogen. Generally, the catalyst from zinc isopropoxide is much the more active. The cases of zinc and ferric oxides are thus similar to alumina and titania in that the relative activities of the catalysts for different simultaneous reactions on their surfaces are determined by the solid compound which is converted into the catalyst, in contrast to nickel catalysts, the relative activity of which is determined by the process by which the nickel compound is reduced (cf. Kelber, this vol., ii, 244). The experimental results of Sabatier and Mailhe are criticised as inconclusive owing to their nickel having been partly reduced by hydrogen and partly by alcohol.

R. B.

#### Catalytic Dehydration of Alcohol and Ether by Alumina.

J. B. SENDERENS (*Bull. Soc. chim.*, 1924, [iv], 35, 1144—1145).—The results obtained by Pease and Young (this vol., i, 363) have already been described by the author (A., 1909, i, 127; 1912, i, 406).

R. B.

**Odour and Chemical Constitution.** A. MÜLLER (*Deuts. Parfümerie Ztg.*, 1923, 9, 5—6; from *Chem. Zentr.*, 1924, i, 2778).—The dimethyloctanols prepared by reducing active citronellal and inactive citral with nickel and hydrogen have different odours, the alcohol from citronellal smelling like isopulegol. Carefully purified inactive dimethylnonanol had a cruder and more intense odour than the active alcohol.

F. A. M.

**Density of Gaseous Dimethyl Ether.** T. BATUECAS (*Compt. rend.*, 1924, 179, 440—443).—The mean value of a series of twenty determinations of the weight of a litre of gaseous dimethyl ether under standard conditions is 2.1097 g. This is in agreement with the value obtained by Baume (A., 1908, ii, 372). The gas used was prepared by two different methods.

H. J. E.

**Velocity of Hydrolysis of Ethyl Ether.** A. SKRABAL and H. AIROLDI.—(See ii, 842.)

**Action of Chlorine on Trimethylene Trisulphide.** J. GIRON (*Bull. Sci. Pharmacol.*, 1924, 31, 25—27; from *Chem. Zentr.*, 1924, i, 2774).—On passing a stream of chlorine over methylene sulphide and fractionating the product, a substance, (?)  $\text{CH}_2\text{Cl}\cdot\text{S}\cdot\text{CHCl}_2$ , b. p. 85—86°/29 mm.,  $d_4^{24}$  1.6374, is obtained.

F. A. M.

**Ionisation of Some Organic Acids dissolved in Mixtures of Water and Ethyl Alcohol.** M. DUBOUX and D. TSAMADOS.—(See ii, 827.)

**Preparation of  $\beta$ -Chloropropionic Acid.** C. MOUREU and R. CHAUX (*Bull. Soc. chim.*, 1924, [iv], **35**, 1360—1364; cf. A., 1917, i, 534; 1921, i, 495; 1922, i, 105).—Dry hydrogen chloride is passed into acraldehyde at  $-15^\circ$  until the theoretical gain in weight has taken place. The product is then oxidised in small quantities at a time by adding it slowly, with agitation, to fuming nitric acid (*d* 1.49). At first, the temperature is kept between  $30^\circ$  and  $35^\circ$ , but the action is completed on the water-bath. The yield of  $\beta$ -chloropropionic acid averages 65%, but with specially pure nitric acid it may reach 70%.  
W. E. E.

**Optically Active  $\alpha\beta$ -Dibromopropionic and  $\alpha\beta$ -Dichloropropionic Acids.** P. KARRER and W. KLARER (*Helv. Chim. Acta*, 1924, **7**, 929—931).—By the action of cold nitrosyl bromide *d*- $\alpha\beta$ -diaminopropionic acid is converted into *d*- $\alpha\beta$ -dibromopropionic acid, b. p.  $129^\circ/9$  mm., m. p.  $64$ — $66^\circ$ ,  $[\alpha]_D^{20} +6.5^\circ$  to  $+7.0^\circ$  in water. In the same way, nitrosyl chloride gives *d*- $\alpha\beta$ -dichloropropionic acid, b. p.  $113^\circ/12$  mm., m. p.  $36^\circ$ ,  $[\alpha]_D^{20} +18.8^\circ$ . In both cases, it is possible that racemisation has taken place. *d*- $\alpha\beta$ -Dibromopropionic is transformed into *l*-glyceric acid.  
W. E. E.

**Autoxidation of Crotonaldehyde. Preparation of Crotonic Acid.** A. DUCHESNE and M. DELÉPINE (*Bull. Soc. chim.*, 1924, [iv], **35**, 1311—1317).—Oxygen is bubbled through three flasks of crotonaldehyde connected in series; the first two flasks are maintained at  $70^\circ$ . After the third or fourth day, the first flask is removed and its place taken by the second; the third flask takes the second place and a fresh flask of aldehyde is connected at the end. Besides crotonic acid (yield 45—50%), acetic acid and a resin are formed. In small quantities, ferric oxide and manganese hydroxide accelerate the oxidation, but foreign acids are still produced and the yield is little improved. Dilution of the crotonaldehyde with ether or benzene reduces the yield of acid obtainable; the presence of alcohol, water, or light petroleum (b. p.  $100^\circ$ ) in sufficient quantity prevents oxidation altogether.  
W. E. E.

**Fish Oils. Quantitative Analysis of Sardine Blubber.** A. EIBNER and E. SEMMELBAUER (*Chem. Umschau*, 1924, **31**, 189—197; 201—209).—A sample of sardine blubber, forming a viscous, brownish-yellow oil which deposited crystalline fats at ordinary temperatures, had the following constants: iodine value, 136.0; acid value, 18.8; ester value, 179.8; saponification value, 194.9; unsaponifiable matter, 0.5%; ash, 0.18%. It contained clupanodonic acid, 12.7%;  $\alpha$ -linoleic acid, 9.8%; isolinoleic acid, 10.1%; oleic acid, 28.6%; hydroxy-acids, 8.7%; saturated acids, 22.0%; glycerol, 4.1%; and cholesterol, 0.5%. Tsujimoto's formula for clupanodonic acid (A., 1923, i, 297) was confirmed, and the presence in the blubber of dipalmitostearin, oleodipalmitin, and probably the triglyceride of clupanodonic acid was established. [Cf. B., 1924, 986.]  
F. G. W.

**Velocity of Hydrolysis of Ethyl Orthoacetate.** A. SKRABAL and M. BALTADSCHIEWA.—(See ii, 842.)

**Mutual Relationship of the Formation of Oxalic and Citric Acids with Different Species of *Aspergillus niger*.** C. WEHMER (Ber., 1924, 57, [B], 1659—1665).—The action of various species of *Aspergillus niger* on sugar solutions in the presence of potassium nitrate, potassium dihydrogen phosphate, magnesium sulphate, and calcium carbonate leads to the production of calcium oxalate and, frequently, of calcium citrate. The formation of calcium citrate is particularly noticeable when potassium nitrate is replaced by ammonium nitrate as source of nitrogen. The hypothesis that the production of oxalic acid from sucrose occurs through the intermediate formation of calcium hydrogen citrate is supported by the observation that oxalic acid is freely produced by the action of *A. niger* on solutions of sodium, ammonium, or calcium hydrogen citrates in which these salts are the sole source of carbon; normal calcium citrate does not undergo a similar change. With certain species of *Aspergillus*, notably *A. niger japonicus*, production of oxalic acid does not occur. Calcium hydrogen citrate is converted by this mould into the normal citrate, the citric acid appearing to be transformed directly into carbon dioxide; it is noticeable that the salt is never decomposed completely. Cessation of activity is attributed to the diminishing acidity of the solution; with moulds which yield oxalic acid, such diminution does not occur, since the utilised citric acid is replaced by oxalic acid. H. W.

**Glutaconic Acids. XVII. Tendency towards Reversion to Type.** C. K. INGOLD, J. H. OLIVER, and J. F. THORPE (*J. Chem. Soc.*, 1924, 125, 2128—2136).—When mobile derivatives of the glutaconic acids are transformed into static derivatives, the latter exhibit a remarkable instability and tendency to revert to a mobile form. The reversion of static dibromo-additive products into glutaconic acids is believed to take the following course,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}_2\text{H} \rightarrow \text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}:\text{CBr}\cdot\text{CO}_2\text{H} \rightarrow \text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , since intermediate compounds have been isolated. By exposure of ethyl aconitate to bromine vapour for 2—3 weeks, it is converted into ethyl  $\alpha\beta$ -dibromotricarballylate, which on distillation yields the lactone ester of *bromohydroxytricarballylic acid*, b. p.  $205^\circ/10$  mm., and on hydrolysis with barium hydroxide, sodium carbonate, or methyl-alcoholic potassium hydroxide gives aconitic acid. When treated with cold alcoholic sodium ethoxide, the ethyl dibromo-ester yields ethyl  $\alpha$ -bromo-aconitate, which on hydrolysis gives rise to aconitic acid.

The tendency of the dibromides to regenerate the parent acids depends on the mobility of the acids produced. Glutaconic acid itself is the most mobile and can only be isolated in one form, and the labile form of the ester has a very transitory existence. Introduction of substituents in either the  $\alpha$ - or  $\beta$ -positions decreases the mobility. Thus the normal form of  $\alpha$ -methylglutaconic acid was converted into  $\alpha\beta$ -dibromo- $\alpha$ -(or  $-\gamma$ )-methylglutaric acid, m. p.

178° (decomp.), by the action of bromine vapour; the acid yields normal  $\alpha$ -methylglutaconic acid when hydrolysed. Similarly, normal  $\beta$ -methylglutaconic acid was transformed into  $\alpha\beta$ -dibromo- $\beta$ -methylglutaconic acid, m. p. 142°, from which only the labile form of  $\beta$ -methylglutaconic acid is obtained by hydrolysis.

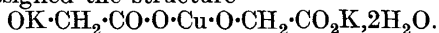
The tendency to reduction is suppressed by introducing two substituents, either in the  $\alpha\beta$ - or  $\alpha\gamma$ -positions.  $\alpha\beta$ -Dimethylglutaconic acid, when exposed to bromine vapour, yields  $\alpha$ -bromo- $\alpha\beta$ (or  $-\beta\gamma$ )-dimethylglutaric acid, m. p. 115° (decomp.), whereas the corresponding  $\alpha\gamma$ -dimethylglutaconic acid gives  $\alpha\beta$ -dibromo- $\alpha\gamma$ -dimethylglutaric acid, m. p. 134°; both bromo-acids are converted by the action of alkalis into hydroxylation products, and not into glutaconic acids.

The reaction is confined to glutaconic acids and is not shown by static unsaturated acids of the  $\alpha\beta$ - and  $\beta\gamma$ -type. Thus, vinylacetic acid can be converted into crotonic acid and cyclohexylideneacetic acid into cyclohexeneacetic acid, but when their dibromides are treated with dilute alkalis the unsaturated acids are not regenerated.

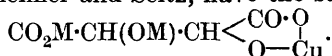
In all these cases, the replacement of the halogen by hydrogen in presence of aqueous alkali hydroxide results in the formation of alkali hypobromite in solution. Reduction was carried out in alcoholic solution of sodium ethoxide. Under these conditions, ethyl bromoaconitate might yield ethyl ethylaconitate and sodium hypobromite or ethyl aconitate and ethyl hypobromite. That the latter course is the more probable has been shown by conducting an experiment in presence of ethyl malonate, which by oxidation consequent on reduction of the bromoaconitate gives ethyl ethanetetra-carboxylate.

C. J. S.

**Metallic Hydroxy-acid Complexes. III. Constitution of Cuprimalates and Analogous Compounds.** I. W. WARK (*J. Chem. Soc.*, 1924, 125, 2004—2009).—The isomeric change from cupric malate to cuprimalic acid is regarded as merely due to the wandering of a hydrogen atom resulting in a structure in which the copper atom replaces one atom of hydrogen in an alcoholic hydroxyl group and one atom in a carboxyl group. This idea is extended to the structure of certain alkaline complexes containing copper. In disagreement with the view of Pickering, the constitution of potassium cupricitrate,  $(C_6H_4O_7)_2K_6Cu, 6H_2O$ , is considered to be  $(CO_2K \cdot CH_2)_2C(OK) \cdot CO \cdot O \cdot Cu \cdot O \cdot C(CH_2 \cdot CO_2K)_2 \cdot CO_2K$ , in which the potassium atom *b* imparts alkalinity to the compound. Similarly, to the alkaline cupriglycollate described by Pickering (T., 1911, 99, 1347) is assigned the structure



The alkali derivatives of tartaric acid of the type  $M_2CuC_4H_2O_6$ , obtained by Bullnheimer and Seitz, have the structure



A second type of complex, in which the copper atom replaces the hydrogen atom in two hydroxyl groups, is exemplified in the

derivatives of monobasic monohydroxy-acids such as lactic and salicylic acids. C. J. S.

**Rotatory Dispersion of Tartaric Acid.** T. M. LOWRY and P. C. AUSTIN.—(See ii, 714.)

**Condensation of Acetoacetic Esters with Malonic Esters.** H. GAULT and H. KLEES (*Compt. rend.*, 1924, **179**, 600—601).—A preliminary note. Ethyl  $\alpha$ -chloroacetoacetate and ethyl sodiomalonate do not interact until heated; then, after several hours on the steam-bath, ethyl acetate and ethyl ethane- $\alpha\alpha\beta$ -tricarboxylate are formed. Reaction takes place with ethyl  $\alpha$ -bromoacetoacetate in the cold; the oily product contains a little (1—3%) ethyl ethane- $\alpha\alpha\beta$ -tricarboxylate, ethyl malonate (53%), and ethyl diacetyl-fumarate (?), m. p. 123°. Ethyl sodioacetoacetate and ethyl bromomalonate yield a little ethyl malonate and ethyl ethane-tetracarboxylate, together with a *liquid*, b. p. 224—230°/10 mm., in the formation of which 2 mols. of ethyl acetoacetate and 1 mol. of ethyl malonate have taken part. W. A. S.

**Biological Oxidation. III. The Oxide of the SH-Group and Oxidation by Means of Ethyl Peroxide.** A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1924, **149**, 188—190).—Using a new preparation of thioglycollic acid the author has been unable to repeat his previous observations (this vol., i, 708) regarding the structure of the intermediate oxide formed by the acid, and the further possibility of the intermediate compound being a hydroperoxide is also dismissed. Ethyl peroxide in the presence of iron and oxygen at 37° oxidises  $\alpha$ -hydroxy-acids, formic, acetic, and glycerophosphoric acids, whilst mono- and di-hydric alcohols, aldehydes, glycerol, acetone, mono- and di-carboxylic acids, and  $\beta$ -hydroxy-acids are not oxidised. J. P.

**Functional Derivatives of  $\alpha$ -Sulphobutyric Acid and the Rotatory Power of their Active Components.** H. J. BACKER and J. H. DE BOER (*Rec. trav. chim.*, 1924, **43**, 420—433; cf. this vol., i, 708; also Backer, A., 1921, i, 855).—*Aniline butyranilide- $\alpha$ -sulphonate*, m. p. 253—256°, obtained by the action of excess of aniline on aniline sulphobutyrate, reacts with barium hydroxide or carbonate, yielding *barium butyranilide- $\alpha$ -sulphonate*. The latter, when treated with copper, cobalt, or nickel sulphate, yields the corresponding metallic salt of the butyranilide-sulphonic acid. *p-Toluidine butyro-p-toluidide- $\alpha$ -sulphonate*, m. p. 245—250°, *p-anisidine butyro-p-anisidide- $\alpha$ -sulphonate*, m. p. 242°, and *p-phenetidine butyro-p-phenetidide- $\alpha$ -sulphonate*, m. p. 261—262°, were prepared by heating the corresponding acid sulphobutyrate with excess of the base already present. On heating *o*-phenylenediamine sulphobutyrate, *benziminazole-2-propylsulphonic acid* is formed, of which the *barium* and *cobalt* salts are described. 3:4-Diaminotoluene sulphobutyrate similarly yields *methylbenziminazole-2-propylsulphonic acid*. Resolution of butyranilide- $\alpha$ -sulphonic and benziminazole-2-propylsulphonic acids into their optical isomerides was effected by means of their *strychnine* salts; in addition, the

active *barium*, *copper*, *cobalt*, and *nickel* salts of the former acid and the *barium* and *cobalt* salts of the latter were obtained. Variation in molecular rotation with wave-length is shown diagrammatically for both aqueous and alcoholic solutions of copper and cobalt butyranilide- $\alpha$ -sulphonate; the curves exhibit some marked abnormalities.

H. J. E.

**Preparation of Acetone from Acetic Acid.** I. M. MASHINO (*J. Chem. Ind. Japan*, 1924, 27, 804—809).—Acetone is obtained when a mixture of acetic acid vapour and nitrogen is passed over heated granulated calcium oxide at 260—550°. The optimum temperature is 400—500°. The yield (about 54%) of acetone is best when acetic acid is passed at the rate of 7—10 g. per hour at 450°, but is only slightly decreased by passing the acid at the rate of 16 g. per hour at 550°.

K. K.

**Catalytic Reduction of Oximes in the Presence of Colloidal Palladium.** W. GULEWITSCH [with B. SSEMENOWITSCH, S. KAPLANSKY, and L. BRONDE] (*Ber.*, 1924, 57, [B], 1645—1653).—Ethyl  $\beta$ -aminobutyrate is not formed by the catalytic hydrogenation of ethyl  $\beta$ -oximinobutyrate in aqueous-alcoholic solution in the presence of colloidal palladium; the observed absorption of hydrogen is due to fission of the oxime and reduction of the liberated hydroxylamine to ammonia. Acetoxime and methyl ethyl ketoxime could not be reduced under similar conditions, although the potential activity of the catalyst remained unaltered. Benzaldoxime, on the other hand, yields a mixture of mono- and di-benzylamine, ammonia, and benzaldehyde (cf. Paal and Gerum, *A.*, 1909, i, 381; Rosenmund and Pfankuch, this vol., i, 34); di-benzylamine is readily characterised by its *nitrate*, m. p. 194°. Benzophenoneoxime gives diphenylmethylaniline, but acetophenoneoxime and dibenzylketoxime could not be reduced. Acetaldoxime and propaldoxime are reduced exclusively to the corresponding tertiary amines. Reduction takes place only at the commencement of the experiment; subsequently, when the reaction appears to proceed more slowly, the oxime probably becomes hydrolysed and the liberated hydroxylamine is converted into ammonia. The production of the tertiary amine is not due to elimination of ammonia from preformed, primary amine.

H. W.

**Diacetone [Di-isopropylidene] Compounds of Arabinose and Galactose.** O. SVANBERG and S. W. BERGMAN (*Arkiv Kemi, Min., Geol.*, 1924, 9, 1—16).—The monoacetone derivatives of arabinose and galactose are not formed by hydrolysis of the diacetone compounds. The action of sulphuric acid on an acetone solution of arabinose yields diacetonearabinose [arabinose diisopropylidene ether] (yield 92—93%), m. p. 41—42°, b. p. 85—87°/1 mm., 90—91°/2 mm.,  $[\alpha]_{\text{D}}^{25}$  yellow +5.5°  $\pm$  0.2 in water (cf. Fischer, *A.*, 1895, i, 437), which is quantitatively hydrolysed by 0.5% hydrochloric acid (but not by 0.1—0.2% acid) to arabinose. It was found that  $\alpha$ -galactose was not acted on by acetone and sulphuric acid, but  $\beta$ -galactose dissolved, and was converted into its diiso-

xx\*



propylidene derivative, b. p.  $126^{\circ}/1$  mm.,  $[\alpha]_{D}^{18}$  yellow  $-46^{\circ}$  in water (cf. Freudenberg and Hixon, A., 1923, i, 1179). On hydrolysis, it behaved like diacetonearabinose. Diacetonegalactose on oxidation with potassium permanganate gave a positive, but diacetoneglucose a negative phloroglucinol test; it may be concluded that in the former case the OH in position 6 is unsubstituted, so that oxidation to a glycuronic acid derivative occurs (cf. Karrer and Hurwitz, A., 1921, i, 767; Irvine and Patterson, T., 1922, 121, 2146). F. M. H.

**Examination of Photosynthetic Sugars by the Methylation Method.** J. C. IRVINE and G. V. FRANCIS (*Ind. Eng. Chem.*, 1924, 16, 1019—1020).—A sample of syrup prepared by photosynthesis from formaldehyde was found to contain no polysaccharides of the type,  $C_6H_{10}O_5$ , or ketoses, but to have an apparent methoxyl content of 9—12%. Part of the reducing power to Fehling's solution was due to substances other than sugars. The syrup was purified by drying at  $80^{\circ}$  under a pressure of 0.2 mm. of mercury and was then subjected to methylation, whereby a fraction was obtained with a methoxyl content of 54.5% and a molecular weight of 232. After hydrolysis, the composition of the product closely corresponded with tetramethylhexose. It is deduced that the original proportion of hexoside present could not exceed 10%. The bulk of the syrup (to the extent of at least 80%) consists of non-sugar compounds which contain hydroxyl groups. C. I.

**The Glucose of Sucrose.** H. COLIN and A. CHAUDUN (*Bull. Soc. Chim. biol.*, 1924, 6, 625—630).—Polarimetric measurements show that the dextrose produced in the inversion of sucrose has at first a higher rotatory power than ordinary dextrose, but rapidly attains the normal value; it is therefore probably first split off from the sucrose molecule as  $\alpha$ -glucose. C. R. H.

**Preparation of  $\beta$ -Methylglucoside.** H. H. SCHLUBACH and K. MAURER (*Ber.*, 1924, 57, [B], 1686—1687).— $\beta$ -Methylglucoside is the primary product of the methylation of dextrose by Haworth's method (T., 1915, 107, 8), but its isolation from the product of the reaction is rendered difficult by the presence of sodium methyl sulphate. Separation may be readily effected if the dry product is acetylated with acetic anhydride and pyridine and the mixture poured into ice-water. Sodium methyl sulphate passes into solution, whereas tetra-acetyl- $\beta$ -methylglucoside is precipitated in the homogeneous condition and is subsequently hydrolysed to  $\beta$ -methylglucoside, the yield being about 40%. H. W.

**Inversion of Sucrose and Determination of Hydrion Concentration.** M. DUBOUX.—(See ii, 842.)

**Apparent Concentration of the Hydrogen Ion in Solutions containing Sucrose.** T. W. J. TAYLOR and R. F. BOMFORD (*J. Chem. Soc.*, 1924, 125, 2016—2017).—By means of the hydrogen electrode method, the apparent concentration of the hydrogen ion in solutions of sucrose undergoing inversion with hydrochloric

acid in presence of sodium chloride has been determined. The *E.M.F.* slowly falls to a constant value about 1% smaller than the initial value of the cadmium cells employed, and hence the apparent hydrogen-ion concentration increases by about 7% during the inversion.

C. J. S.

**Mutarotation Lag in Sucrose Inversion.** S. W. PENNYCUICK (*J. Chem. Soc.*, 1924, 125, 2049—2063).—It is deduced mathematically that the lag in mutarotation when sucrose is inverted in presence of acids is not inappreciable. The method adopted for following the inversion before mutarotational equilibrium is established consists in chilling a portion of the solution to 0°, when inversion is practically stopped, and determining the rotation at this temperature. To determine the rotation after equilibrium, inversion is arrested in a portion of the reaction mixture by addition of sodium hydroxide, after which it is cooled to 0° and a reading taken. It is shown that after a brief interval of time the lag becomes strictly proportional to the concentration of the remaining sucrose, and that the graphs of  $\log(\lambda_t - \lambda_\infty)$ , with and without lag, respectively, against  $t$ , become strictly parallel, both having the slope  $k_1$ , the inversion constant.

The usual method of following the inversion while the lag is present gives the correct value of  $k_1$  if certain precautions are observed, but the curve  $\log(\lambda_t - \lambda_\infty)$  with lag against time does not extrapolate to  $\log(\lambda_0 - \lambda_\infty)$  at  $t=0$ , but to  $\log\{\lambda_0 - \lambda_\infty + A(R+S)\}$ , where  $R+S$  is the total lag constant under the given conditions,  $k_1$  being given by  $1/t \log[\lambda_0 - \lambda_\infty + A(R+S)]/(\lambda_t - \lambda_\infty)$ . The short-interval formula also gives the correct value of  $k_1$  (whether the lag is appreciable or not), provided it is not applied at the initial stages of the inversion.

C. J. S.

**Action of Ultra-violet Radiations on Solutions of Sucrose.** P. BEYERSDORFER and W. HESS (*Ber.*, 1924, 57, [B], 1708—1711).—The photochemical decomposition of  $M/8$ ,  $M/2$ , and  $2M$  solutions of sucrose in water has been investigated at 20°, 70°, and 100°, the course of the change being followed by observations of the optical rotation, acidity, and reducing power of the solutions. Reaction is scarcely appreciable at 20°, but the rate increases first slowly and then rapidly with increasing temperature. The photochemical degradation of sucrose is almost completely inhibited by the presence of chlorophyll or, to a less extent, of green-PLX. Manganese chloride, potassium chloride, potassium bromide, and potassium iodide have little influence on the change, which, however, scarcely occurs in the presence of sodium acetate; this result is not surprising, since the latter salt is known to prevent inversion of sucrose. The sucrose molecule is so stable towards the action of light of short wave-length that the union of its component parts by an oxygen atom appears improbable. On the other hand, lævulose is considerably more rapidly decomposed than dextrose. The products of the decomposition of sucrose are carbon monoxide, carbon dioxide, hydrogen, methane, organic acids, aldehydes, ketones, and alcohols, together with condensation products of the

type of dextrin and caramel. A crystal of sucrose when exposed to ultra-violet rays at  $70^{\circ}$  becomes coated on the exposed surface with a brown layer of caramel. The prolonged exposure of sucrose solutions to ultra-violet rays appears to yield sensibly the same products as are obtained by the dry distillation of sugar. H. W.

**Variation of the Optical Activity of Sucrose on Heating.** M. A. RAKUSIN and A. N. NESMEJANOV (*Z. Unter. Nahr. Genussm.*, 1924, **48**, 151—152).—Commercial sucrose, m. p.  $178-183^{\circ}$ ,  $[\alpha]_D +65.33^{\circ}$ , was caramelised by heating first to a temperature above the melting point and then maintaining at a lower temperature for varying lengths of time. Experiments were carried out at  $160^{\circ}$  to  $190^{\circ}$  for periods up to 4 hours. In all cases decrease of the rotatory power was observed varying with the temperature and duration of the experiment. After heating at  $180^{\circ}$  for 30 mins., the sugar was rendered optically inactive; after 2 hours at  $150^{\circ}$  the rotatory power was  $[\alpha]_D +13.2^{\circ}$ , and after 4 hours at  $140^{\circ}$ ,  $[\alpha]_D +21.0^{\circ}$ . G. S. W.

**Trihexosan.** A. PICTET and R. SALZMANN (*Helv. Chim. Acta*, 1924, **7**, 934—935).—The trihexosan obtained as the ultimate product of depolymerisation of starch by heat is hydrolysed by emulsin to dextrose and a dihexosan, m. p.  $209-210^{\circ}$  (decomp.),  $[\alpha]_D +133.2^{\circ}$ , which may be identical with the product of Pringsheim and Wolfsohn (this vol., i, 714). At present, it seems that the trihexosan is a  $\beta$ -glucosyldihexosan. W. E. E.

**A Hexahexosan Obtained from Starch.** A. PICTET and P. STRICKER (*Helv. Chim. Acta*, 1924, **7**, 932—933).—Potato starch is heated at  $200^{\circ}$  with glycerol (Pictet and Jahn, A., 1922, i, 987) until the red coloration given with iodine is at its brightest, whereby a *hexahexosan*, decomp. about  $225^{\circ}$ , is isolated as a white, amorphous powder; it does not reduce Fehling's solution. When heated with acetic anhydride and sodium acetate it gives the trihexosan nona-acetate described by Pictet and Jahn (*loc. cit.*). W. E. E.

**Hydrolysis of Starch by Salts. III. Hydrolysis by Inorganic Catalysts (Artificial Oxydases).** W. BIEDERMANN and C. JERNAKOV (*Biochem. Z.*, 1924, **149**, 309—328).—The hydrolysis of starch and the amyloses by salts of the heavy metals such as iron, copper, and manganese in the presence of hydrogen peroxide, and the typical "salt hydrolysis" shown by the chlorides and bromides of the alkali and alkaline-earth metals, suggest a parallelism between such hydrolytic actions and the oxydase- or peroxydase-like action of the salts towards guaiacum and other oxydase reagents. Manganese chloride may act on guaiacum and on starch in the absence of hydrogen peroxide and its action is therefore analogous to that of the alkali metals. J. P.

**Polysaccharides. XXVIII. Reserve Cellulose (Lichenin).** P. KARRER and M. STAUB (*Helv. Chim. Acta*, 1924, **7**, 928—929).—Although one of the preparations examined contained only 0.0055%

of phosphorus, it is certain that lichenin contains that element; the small proportion may be due to the action of large amounts of boiling water used to purify the lichenin. The ash of lichenin amounted to 0.9—1%, and contained much calcium, a little magnesium and iron, and only traces of silicic acid. When lichenin is quickly distilled at 12 mm., *l*-glucosan is obtained. W. E. E.

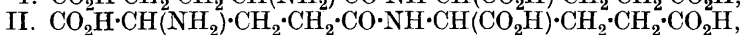
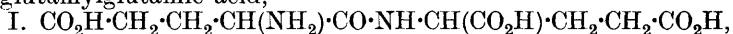
**Proposed Definition of "Cellulose."** P. KLASON (*Papier-Fabr.*, 1924, 22, 373—377).—Two reagents are proposed for the complete removal of lignin from wood under conditions such that the cellulose residue remains constant in weight even after excessively prolonged digestion. They are both made up with 80 g. of sodium hydrogen sulphite per litre, but the weaker one contains 200 c.c. and the stronger 500 c.c. of *N*-hydrochloric acid per litre. The wood is digested continuously at 98°, the liquor being siphoned off and renewed every 4 days, until the residue is substantially constant in weight and free from lignin. With the weaker acid, spruce wood in chips or rasped yields 54% of cellulose after 9—12 days' digestion, but with the stronger acid, the yield from rasped wood is about 7% lower, whereas that from chipped wood is only 1.5% lower. Hence it is suggested that spruce wood contains two types of cellulose, one resistant to the stronger acid and corresponding with crystalline cellulose and the other resistant only to the weaker acid and corresponding with amorphous cellulose. In the natural condition, the crystalline cellulose protects the amorphous, but when the cells are ruptured by rasping this protection ceases. The degree of protection of the less resistant cellulose by the more resistant varies according to the species, and this protection is less complete in beech wood than in spruce wood. Cotton cellulose also resists the weaker acid, but breaks down, yielding only 90.5% residue with the stronger acid. The use of the weaker acid under the above conditions is suggested as the basis of an analytical definition of "cellulose." [Cf. *B.*, 1924, 976.] J. F. B.

**Preparation of Cellulose Acetates.** A. CAILLE (*Chim. et Ind.*, 1924, 12, 441—448).—A suitable mixture for the acetylation of 100 g. of cotton consists of 600 g. of 44.8% acetic anhydride with 15 g. of sulphuric acid. Avoiding rapid rises of temperature, the cotton goes smoothly into solution in about 6 hours with a maximum temperature of 38°. Higher temperatures yield products of low viscosity; smaller quantities of sulphuric acid involve prolonged periods of acetylation and inferior esterification. During the primary acetylation, the proportions of combined acetic and sulphuric acids increase steadily until the product, precipitated at the stage when the cotton fibre is entirely dissolved, contains 66—67% of acetic acid and 0.97% of sulphuric acid. These products are mixed acetic-sulphuric acid esters, and the secondary modification, induced by the introduction of 20 g. of water to the acetylated mixture, consists of an acid hydrolysis of the sulphuric acid ester. The stability of the ultimate cellulose acetate depends on the elimination, as completely as possible, of the combined sulphuric

acid groups. This may be promoted by a secondary hydrolysis of the precipitated solid by digestion with 0.25% sulphuric acid at 75°. The acid function of the sulphuric acid ester is capable of neutralisation by mineral bases yielding ester salts, so that products washed with calcareous water are far more stable than those washed with distilled water.

J. F. B.

**Constitution of the Anhydrides of Glutamic Acid.** A. BLANCHETIÈRE (*Bull. Soc. chim.*, 1924, [iv], **35**, 1317—1325).—The results of biuret tests on the *tricyclopeptide* from glutamic acid (A., 1923, i, 12) are sometimes positive and sometimes negative. This is explained if the *tricyclopeptide* gives rise to the two forms of glutamylglutamic acid,



which are theoretically possible. Actually, when the *tricyclopeptide* is hydrolysed with sodium or barium hydroxide, a crystalline glutamylglutamic acid is obtained together with a gum which is thought to be the second form of the acid. According to the results of the biuret reaction, the crystalline form has the structure I.

W. E. E.

**Formaldehyde Compounds of Simple Amino-acids.** H. KRAUSE (*Z. physiol. Chem.*, 1924, **139**, 216—218).—Polemical (cf. Krause, A., 1919, i, 67; Bergmann, Jacobsohn, and Schotte, this vol., i, 19).

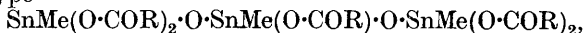
C. R. H.

**Carbamide and Guanidine Derivatives of Aliphatic Sulphonic Acids.** II. R. ANDREASCH (*Monatsh.*, 1924, **45**, 1—7).—The action of potassium sulphite on certain bromoacyl-carbamides and on chloroacetamide is described.

In completion of earlier work (A., 1923, i, 546), the *barium* salt (+2H<sub>2</sub>O) of sulphoacetylcarbamide is described.  $\alpha$ -Bromopropionylcarbamide was converted by aqueous-alcoholic potassium sulphite into the *potassium* salt (+1½H<sub>2</sub>O) of  $\alpha$ -sulphopropionylcarbamide. Interaction of ethyl bromopropionate and thiocarbamide in alcoholic solution formed the *hydrobromide* of methylthiohydantoin. The corresponding hydrochloric acid solution was oxidised with potassium chlorate at 50—60° to the potassium salt of  $\alpha$ -sulphopropionylcarbamide. Aqueous methylthiohydantoin hydrobromide treated with bromine at 60° followed by barium carbonate gives barium  $\alpha$ -sulphopropionate, doubtless formed by hydrolysis of the expected sulphonate of propionylcarbamide. By heating phenylcarbamide with bromopropionyl bromide at 135—155°,  $\alpha$ -bromopropionylphenylcarbamide, m. p. 162°, was obtained. Its interaction with potassium sulphite gave the *potassium* salt (+H<sub>2</sub>O) of  $\alpha$ -sulphopropionylphenylcarbamide. By heating  $\alpha$ -bromoisovaleryl chloride and ethylcarbamide, there was obtained  $\alpha$ -bromoisovalerylethylcarbamide, m. p. 110° (cf. D.R.-P. 185962). Potassium sulphite replaced the bromine by hydrogen, giving ethylisovalerylethylcarbamide, m. p. 120°. Similarly,  $\alpha$ -bromo- $\alpha$ -ethylbutyrylcarbamide gave  $\alpha$ -ethylbutyrylcarbamide, m. p. 203°.

With potassium sulphite, the halogen in halogen derivatives of acid amides is readily replaced by  $\text{HSO}_3$ . Thus chloroacetamide yields the *potassium* salt of sulphoacetamide. *Sodium* and *ammonium* salts are prepared analogously. F. M. H.

**Derivatives of Methylstannonic Acid. II.** H. LAMBOURNE (*J. Chem. Soc.*, 1924, 125, 2013—2015).—Penta-acyl derivatives of the type



have been obtained by the action of dichloroacetic, propionic, *n*-butyric, and isobutyric acids on methylstannonic acid, R being  $\text{CHCl}_2$ , Et, Pr <sup>$\alpha$</sup> , or Pr <sup>$\beta$</sup> , respectively. The *pentadichloroacetyl* compound has m. p. 235—240° (decomp.). The *pentapropionyl* compound melts at 156—157°, solidifies again at 160°, and remelts at about 240°. The *pentabutyryl* compound and *pentaisobutyryl* compound have m. p. 105° and 194°, respectively.

The propionyl, butyryl, and isobutyryl penta-acyl derivatives when hydrolysed with alcohol yield hexa-acyl derivatives, regarded as having a cyclic structure.

The *hexapropionyl* compound partly melts at about 246° (decomp.), and is completely hydrolysed to methylstannonic acid on repeated boiling with alcohol. The *hexabutyryl* and *hexaisobutyryl* compounds have m. p. 180° and about 260°, respectively.

C. J. S.

**Magnesium Acetylenyl Bromide.** J. SALKIND and A. ROSENFELD (*Ber.*, 1924, 57, [B], 1690—1692).—Magnesium acetylenyl bromide,  $\text{CH}\equiv\text{C}\cdot\text{MgBr}$ , is almost the sole product of the action of acetylene on magnesium and bromobenzene in the presence of ether if the boiling solution is continuously saturated with the gas during the whole course of the reaction. It is converted by acetophenone into  $\gamma$ -phenyl- $\Delta^{\alpha}$ -butinen- $\gamma$ -ol,



an almost colourless liquid which cannot be distilled (the *copper* derivative is described) together with smaller amounts of the  $\beta\epsilon$ -diphenyl- $\Delta\gamma$ -hexinene- $\beta\epsilon$ -diols.

H. W.

**Stereoisomeric Forms of Decahydronaphthalene (Decalene).** F. EISENLOHR and R. POLENSKE (*Ber.*, 1924, 57, [B], 1639—1644).—*cis*-Decahydronaphthalene, b. p. 193°/768 mm.,  $d_4^{20 \text{ vac.}}$  0.8953,  $n_D^{20}$  1.47817, is prepared by the action of a solution of sodium in absolute alcohol at 200° on *cis*- $\beta$ -decahydronaphthalene-semicarbazone, m. p. 183°. Particularly if the alcohol used contains a trace of water, the hydrocarbon is accompanied by a considerable proportion of *cis*-decahydro- $\beta$ -naphthol, which is transformed by potassium hydrogen sulphate at 200° into *cis*-octahydronaphthalene, b. p. 194°/771 mm.,  $d_4^{20 \text{ vac.}}$  0.9090,  $n_D^{20}$  1.49124. The unsaturated hydrocarbon is smoothly hydrogenated in ethereal solution in the presence of spongy platinum to *cis*-decahydronaphthalene, the physical constants of which agree with those of the product described above. *trans*- $\beta$ -Decahydronaphthalenesemi-

carbazone (cf. Häckel, this vol., i, 32) is converted similarly by sodium ethoxide solution at  $210^{\circ}$  into a mixture of *trans*-decahydro- $\beta$ -naphthol and *trans*-decahydronaphthalene, b. p.  $185^{\circ}/756$  mm.,  $d_4^{20}$  vac. 0.8823,  $n_D^{20}$  1.47218. The hydrocarbon having almost identical physical constants is also prepared by the hydrogenation of *trans*-octahydronaphthalene, b. p.  $189^{\circ}/768$  mm.,  $d_4^{20}$  vac. 0.9009,  $n_D^{20}$  1.48504, which is derived from *trans*-decahydro- $\beta$ -naphthol, m. p.  $75^{\circ}$  (cf. Häckel, *loc. cit.*), by the action of potassium hydrogen sulphate. The optical constants of the authors' *cis*-decahydronaphthalene agree closely with those of the specimens prepared by Häckel (*loc. cit.*) and Willstätter and Seitz (this vol., i, 628). This is not the case with the *trans*-derivatives. It appears, therefore, that the product of the hydrogenation of naphthalene in the presence of nickel contains some component other than *trans*-decahydronaphthalene which tends to accumulate in the fractions of lowest boiling point. H. W.

**Internal Structure of Crystallised Carbon and Benzene.** J. BECKENKAMP.—(See ii, 754.)

**Mechanism of Substitution Reactions in the Aromatic Nucleus.** E. DE B. BARNETT and J. W. COOK (*Rec. trav. chim.*, 1924, 43, 262—265).—The possibility is considered of the formation of *cis* and *trans* geometrically isomeric unstable additive compounds in substitution reactions in the aromatic nucleus. The facts that *p*-chlorobromobenzene is almost the sole product in the bromination of chlorobenzene, no *p*-dibromobenzene being formed, and that bromonitrobenzene is alone produced in the nitration of bromobenzene, are explained by assuming that the intermediate additive compound has the *trans* configuration in each case. The type of isomerism here assumed is analogous to the isomerism of the esters of  $\Delta^{2:5}$ -dihydroterephthalic acids established by Baeyer. In the anthracene series, but not in the benzene series, several such additive compounds, for instance, the esters of nitrodihydroanthranol, have been isolated. J. K.

**Replaceability of the Halogen Atom in Chloro- and Bromo-4-nitro-2-cyanobenzene.** H. P. BAUDET (*Rec. trav. chim.*, 1924, 43, 707—726).—The reactivity of the halogen atom in these compounds is studied and compared with that of the halogen in chloro- and bromo-2:4-dinitrobenzenes and in chloro- and bromo-2-nitro-4-cyanobenzenes. In this way, the influence of the cyano group on the reactivity of the adjacent halogen atom is estimated. The reactivity of the chlorine in chloro-4-nitro-2-cyanobenzene is demonstrated by its direct replacement to give the following compounds: 4-nitro-2-cyanoanisole; 4-nitro-2-cyanophenetole; 4-nitro-2-cyanodiphenyl ether, m. p.  $129^{\circ}$  (by the action of phenol and sodium ethoxide); *p*-nitro-2-cyanoaniline, m. p.  $209^{\circ}$ ; 4-nitro-2-cyanomethylaniline, m. p.  $187^{\circ}$ , which gives with concentrated nitric acid 4:6-dinitro-2-cyanophenylmethylnitroamine, m. p.  $100^{\circ}$ ; 4-nitro-2-cyanoethylaniline, m. p.  $144^{\circ}$ , which gives 4:6-dinitro-2-cyanophenylethylnitroamine, m. p.  $89^{\circ}$ ; 4-nitro-2-cyanodimethyl-

*aniline*, m. p.  $110^{\circ}$ ; 4-nitro-2-cyanodiphenylamine, m. p.  $172^{\circ}$  (by the action of aniline); 4-nitro-2-cyanophenyl-*m*-tolylamine, m. p.  $142^{\circ}$ ; 4-nitro-2-cyanophenyl-*p*-tolylamine, m. p.  $218^{\circ}$ ; 4-nitro-4'-amino-2-cyanodiphenylamine, m. p.  $204^{\circ}$  (by the action of phenylhydrazine); 4-nitro-2-cyanophenylhydrazine (by the action of hydrazine hydrate), giving benzaldehyde-4-nitro-2-cyanophenylhydrazone, m. p.  $206^{\circ}$ ; 4-nitro-2-cyanohydrazobenzene, m. p.  $236^{\circ}$ . Aniline, phenylhydrazine, and the toluidines react more readily with chloro-4-nitro-2-cyanobenzene than with chloro-2-nitro-4-cyanobenzene. With chloro-4-nitro-2-cyanobenzene, *p*-toluidine reacts more readily than *o*-toluidine, but less readily than *m*-toluidine. Methylaniline has no action on chloro-4-nitro-2-cyanobenzene. 4-Nitro-2-cyanophenylhydrazine has no action on acetone, whereas *p*-nitrophenylhydrazine readily reacts. Measurements of the velocity constants of the reaction between sodium methoxide or ethoxide and chloro- or bromo-4-nitro-2-cyanobenzene in absolute alcohol are given. Chlorine is more readily replaced than bromine and the velocity constant for sodium methoxide is smaller than that for sodium ethoxide. When the 2-nitro group of chloro-2 : 4-dinitrobenzene is replaced by a cyano group, the velocities of the actions of both sodium methoxide and ethoxide are decreased. Interchange of the cyano and nitro groups of the halogeno-4-nitro-2-cyanobenzenes reduces the velocity constants to about one-nineteenth. The velocity of the reaction of *p*-chloronitrobenzene with sodium methoxide is about  $1/7500$  of the velocity of the reaction of chloro-4-nitro-2-cyanobenzene with the same substance. In 90% alcohol, the velocity of the action of sodium methoxide on the halogeno-4-nitro-2-cyanobenzenes is greater than in absolute alcohol; the increase is greater for the chloro compound than for the bromo compound. On the other hand, with sodium ethoxide in 90% alcohol, *k* is smaller and the decrease is greater for the chloro compound than for the bromo compound. Measurements of *k* are given for the action of sodium methoxide on chloro-2 : 4-dinitrobenzene in mixtures of methyl alcohol and water. As the proportion of water in the medium is increased, a maximum in the value of *k* is reached; this occurs the sooner the higher the temperature.

W. E. E.

**Monochlorotrinitrobenzenes and the Replacement of their Substituents.** P. G. VAN DE VLIET (*Rec. trav. chim.*, 1924, 43, 606—635).—Chloro-3 : 4 : 5-trinitrobenzene, m. p.  $168^{\circ}$ , is obtained by the action of a mixture of nitric oxide and nitrogen peroxide at  $0^{\circ}$  on 4-chloro-2 : 6-dinitroaniline (from 1 : 4-dichloro-3 : 5-dinitrobenzene and alcoholic ammonia) mixed with concentrated nitric acid.

Chloro-2 : 3 : 5-trinitrobenzene is obtained from aceto-*m*-nitroanilide by nitrating with fuming nitric acid (*d* 1.52) in the presence of sulphuric acid and hydrolysing the 2 : 3-dinitroacetanilide separated from the resulting mixture of three isomerides; the dinitroaniline is diazotised, converted by cuprous chloride into chloro-2 : 3-dinitrobenzene, and nitrated in the presence of fuming



sulphuric acid. The semi-solid product is separated into an oil and chloro-2 : 3 : 5-trinitrobenzene, m. p. 105—106°. Its structure is confirmed by conversion into chloro-3 : 5-dinitroaniline.

Chloro-2 : 3 : 4-trinitrobenzene, m. p. 68°, is prepared from the oil resulting from the above nitration, and its structure is confirmed by its conversion into a chlorodinitroaniline which yields chloro-2 : 4-dinitrobenzene.

Chloro-2 : 3 : 6-trinitrobenzene is not formed in the nitration of chloro-2 : 3-dinitrobenzene, and seven other methods of preparing this isomeride were tried unsuccessfully.

Den Hollander (A., 1920, i, 538) claims to have prepared 1 : 2-dichloro-3 : 6-dinitrobenzene (m. p. 60°). His experiments were repeated, starting from a mixture of 2 : 3- and 2 : 5-dinitroacetanilide. After hydrolysis, the 2 : 5-dinitroaniline (m. p. 138°) was dissolved in concentrated hydrochloric acid and treated with potassium chlorate. The mixture of chlorodinitroanilines thus obtained was diazotised and the diazo compounds were treated with cuprous chloride solution. 1 : 4-Dichloro-2 : 5-dinitrobenzene was isolated, and 1 : 4 : 6-trichloro-2 : 5-dinitrobenzene (m. p. 60°) was obtained from the mother liquor (A., 1921, i, 549).

To study the behaviour of the chlorotrinitrobenzenes towards sodium methoxide, the reaction mixture is poured into water and this is tested for chlorine and nitrite ions. In this way, it is shown that, in the following compounds, only the groups mentioned are replaced by methoxyl: chloro-2 : 4 : 6-trinitrobenzene, chloro; chloro-3 : 4 : 5-trinitrobenzene, 4-nitro; chloro-3 : 4 : 6-trinitrobenzene, chloro and 3-nitro; chloro-2 : 3 : 5-trinitrobenzene, 2-nitro; chloro-2 : 3 : 4-trinitrobenzene, chloro and 3-nitro. In the action of sodium methoxide on 1 : 3-dichloro-2 : 4-dinitrobenzene, it is the 3- and not the 1-chlorine atom which is replaced.

Owing to the considerable velocities developed in the reactions between sodium methoxide and the chlorotrinitrobenzenes all quantitative experiments were carried out at 0°. In the cases of the 1 : 2 : 4 : 6-, 1 : 3 : 4 : 6-, and 1 : 2 : 3 : 5-isomerides, the velocities were too great to be determined. For the 1 : 3 : 4 : 5-isomeride,  $k=7.5$  (approx.), and for the 1 : 2 : 3 : 4-isomeride,  $k=10.7$  (approx.), the constant being calculated from the formula  $dx/dt=k(a-x)^2$ .

Den Hollander's rules (*loc. cit.*) for the action of sodium methoxide on chloronitro derivatives of benzene prove to be of very limited application, and the following empirical conclusion is drawn. When sodium methoxide reacts with chloronitrobenzene derivatives, the substituents which are *meta* with respect to a nitro group tend to be inactive, whilst those that are *ortho* or *para* with respect to a nitro group tend to be replaced. It is concluded that the introduction of a nitro group into a chloronitro derivative of benzene causes a much greater increase in the reactivity of the substituents than does the introduction of a chlorine atom.

W. E. E.

**Mononitration of *p*-Chlorotoluene.** H. H. HODGSON and P. ANDERSON (*J. Chem. Soc.*, 1924, 125, 2195—2196).—4-Chloro-2-nitrotoluene and 4-chloro-3-nitrotoluene, obtained on nitrating

*p*-chlorotoluene under various conditions (or by the Sandmeyer reaction from the corresponding nitrotoluidines), are quantitatively converted into 4-chloro-*o*-toluidine (I) and 3-amino-*p*-tolyl mercaptan (II), respectively, by boiling with sodium di- or tri-sulphide in alcoholic solution. The quantities of I and II in the reduction product are found: (a) by titration of each after separation by steam distillation; (b) by diazotisation, when II is converted into the insoluble diazosulphide,  $C_7H_6\begin{smallmatrix} N \\ | \\ S \end{smallmatrix}_2$ , whilst diazotised I is coupled with  $\beta$ -naphthol and the azo compound weighed. The figures obtained by this method of analysis agree very closely with those calculated by interpolation and extrapolation of Holleman's cryoscopic data (A., 1909, i, 18). A. C.

**Ammonium as a Reducing Agent.** H. H. SCHLUBACH and H. MIEDEL (*Ber.*, 1924, 57, [B], 1682—1686).—A solution of sodium in liquid ammonia is added gradually to a solution of ammonium chloride in the same solvent in which the substance to be reduced is at least partly dissolved at  $-80^\circ$  to  $-50^\circ$ . If the compound under investigation is not sufficiently soluble in liquid ammonia, benzene or ether may be added. In general, reduction appears to be due to the direct addition of nascent hydrogen without preliminary formation of an intermediate additive compound with the sodium. The action is highly selective and appears to resemble most closely that of sodium and alcohol. Probably owing to the low temperature of the reactions, the formation of by-products is largely avoided.

Phenylbutylene is smoothly hydrogenated to phenylbutane, whereas cinnamic acid and stilbene remain unchanged. Benzophenone is converted directly into diphenylmethane; the intermediate production of benzhydrol could not be established. On the other hand, Michler's ketone, didiphenyl ketone, benzil, benzoin, and deoxybenzoin are unaffected. Acetophenone could not be reduced, whereas  $\beta$ -phenylethyl methyl ketone readily yields  $\alpha$ -phenylbutan- $\gamma$ -ol. The latter substance is also obtained with rather greater difficulty from styryl methyl ketone. Less favourable results were obtained with 1:3-dimethyl- $\Delta^6$ -cyclohexen-5-one and methylheptenone. Benzene is unaffected, whereas pyridine is converted into piperidine. Nitrobenzene is transformed into aniline. H. W.

**Synthesis of Diaryl Compounds by means of the Diazo Reaction.** M. GOMBERG and W. E. BACHMANN (*J. Amer. Chem. Soc.*, 1924, 46, 2339—2343).—In the formation of diaryl compounds by Bamberger's method (A., 1896, i, 299) the isolation of the unstable explosive diazonium oxides (or diazo anhydrides) is unnecessary. Both symmetrical and unsymmetrical diaryl compounds may be obtained by diazotising the amine in the usual manner, adding the hydrocarbon, and slowly adding to the cooled, well-stirred mixture a 15 to 25% sodium hydroxide solution until the mixture contains about 1 to 2% of free alkali. Equally good

results were obtained by adding benzenediazonium chloride to a well-stirred mixture of benzene and sodium hydroxide solution, the solution at the end containing 2% of free alkali. It is suggested that the normal sodium diazotate is first produced and that this undergoes partial hydrolysis:  $2\text{RN}_2\cdot\text{ONa} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{RN}_2\cdot\text{OH} + 2\text{NaOH}$ ;  $2\text{RN}_2\cdot\text{OH} \rightleftharpoons \text{RN}_2\cdot\text{O}\cdot\text{N}_2\text{R} + \text{H}_2\text{O}$ . With benzene and benzenediazonium chloride, in addition to diphenyl, *p*-phenyldiphenyl and more complex products are produced by the diazo compound coupling with the diaryl compound first formed (cf. Gerngross and Dunkel, this vol., i, 720).

The following compounds have been prepared by this method (the figures in brackets denote yields in % of theory): From aniline, diphenyl (22%), phenylthiophen (11%), *p*-cyanodiphenyl (10%), *o*- and *p*-bromodiphenyl, methyl diphenyl-4-carboxylate, *p*-nitrodiphenyl, and phenylpyridine. From *p*-bromoaniline, *p*-bromodiphenyl (40–46%), *p*-bromophenylthiophen, m. p.  $100^\circ$  (20%); from *m*-bromoaniline, *m*-bromodiphenyl, b. p.  $299\text{--}301^\circ$  (28%); from *p*-chloroaniline, *p*-chlorodiphenyl (41%), *p*-chlorophenylthiophen, m. p.  $83^\circ$  (24%); from *m*-chloroaniline, *m*-chlorodiphenyl, b. p.  $284\text{--}285^\circ$  (27%); from *p*-nitroaniline, *p*-nitrodiphenyl (30%), *p*-nitrophenylthiophen, m. p.  $137\text{--}138^\circ$  (23%); from *m*-nitroaniline, *m*-nitrodiphenyl (18%); from *o*-nitroaniline, *o*-nitrodiphenyl; from *p*-cyanoaniline, *p*-cyanodiphenyl (15%); from *m*-cyanoaniline, *m*-cyanodiphenyl, m. p.  $49^\circ$  (19%), *m*-cyanophenylthiophen, m. p.  $53\text{--}54^\circ$  (15%); from *p*-aminodiphenyl, *p*-phenyldiphenyl; and from ethyl *p*-aminobenzoate, ethyl diphenyl-4-carboxylate (12%).

R. B.

**Action of Nitric Acid on  $\alpha\alpha$ -Diphenylethylene and  $\alpha\alpha$ -Di-*p*-tolylethylene. II.** R. ANSCHÜTZ and A. HILBERT (*Ber.*, 1924, 57, [B], 1697–1700; cf. Anschütz and Hilbert, A., 1921, i, 783; Konovalov and Jatzewitsch, A., 1905, i, 763).— $\beta$ -Nitro- $\alpha\alpha$ -diphenylethyl alcohol is converted by reduction with granulated zinc and glacial acetic acid into  $\beta$ -amino- $\alpha\alpha$ -diphenylethyl alcohol, m. p.  $110^\circ$ , whereas stannous chloride transforms it into benzophenone and methylamine.  $\beta$ -Nitro- $\alpha$ -ethoxy- $\alpha\alpha$ -diphenylethane, m. p.  $91\text{--}92^\circ$  (cf. Konovalov and Jatzewitsch, *loc. cit.*), and  $\beta$ -nitro- $\alpha$ -methoxy- $\alpha\alpha$ -diphenylethane, m. p.  $139^\circ$ , are described. Di-*p*-tolylethylene, b. p.  $163\text{--}165^\circ/13\text{ mm.}$ , m. p.  $61^\circ$ , is prepared by the action of magnesium *p*-tolyl bromide on ethyl acetate and subsequent distillation of the product. It is converted by bromine in carbon disulphide solution into  $\beta$ -bromo- $\alpha\alpha$ -di-*p*-tolylethylene, m. p.  $67^\circ$ , and is reduced by sodium and alcohol to  $\alpha\alpha$ -di-*p*-tolylethane, b. p.  $155\text{--}157^\circ/12\text{ mm.}$  The hydrocarbons are converted by nitric acid in glacial acetic acid solution into  $\beta$ -nitro- $\alpha\alpha$ -di-*p*-tolylethylene, m. p.  $116^\circ$ , which is oxidised by chromic acid to di-*p*-tolyl ketone. *p*-Nitro- $\alpha$ -ethoxy- $\alpha\alpha$ -di-*p*-tolylethane, prepared by the action of sodium ethoxide on  $\beta$ -nitro- $\alpha\alpha$ -di-*p*-tolylethylene, has m. p.  $95^\circ$ .

H. W.

**Partition of Silver Nitrate between Aniline and Water.** A. FRUMKIN and R. KULVARSKAJA.—(See ii, 757.)

**Action of Aromatic Amines on Semicarbazide Hydrochloride.** H. MAZOUREWITCH (*Bull. Soc. chim.*, 1924, [iv], 35, 1183—1186).—The *s*-diphenylcarbamide formed as a by-product in the action of aniline on the semicarbazidesemicarbazones of mesityl oxide and 3-methyl-5-ethyl- $\Delta^2$ -cyclohexenone (this vol., i, 969) probably results from the decomposition of the semicarbazidesemicarbazones, since it is now shown that the action of boiling aromatic amines on semicarbazide hydrochloride yields the corresponding substituted carbamide, the suggested mechanism of the reaction being as follows:  $R \cdot NH_2 + NH_2 \cdot NH \cdot CO \cdot NH_2 = NH_2 \cdot NH \cdot CO \cdot NHR + NH_3$ ;  $NH_2 \cdot NH \cdot CO \cdot NHR + NH_2 R = (NHR)_2 CO + (NH_2)_2$ . Thus aniline and semicarbazide hydrochloride yield *s*-diphenylcarbamide, m. p. 233—235° (decomp.); similarly, *o*-toluidine yields *s*-di-*o*-tolylcarbamide, m. p. 237—239° (decomp.); *p*-toluidine, *s*-di-*p*-tolylcarbamide, m. p. 248—253° (decomp.); 3-*o*-xylylidine, *s*-di-*o*-xylylcarbamide, m. p. 242° (decomp.), and benzylamine, *s*-dibenzylcarbamide, m. p. 168°. With *p*-aminoacetophenone and *p*-bromoaniline, the reaction is more complicated and definite products have not been isolated. R. B.

**Velocity of Benzylation of certain Amines.** D. H. PEACOCK (*J. Chem. Soc.*, 1924, 125, 1975—1980).—Aniline and other amines have been benzylated by means of benzyl chloride and *p*-nitrobenzyl chloride and the reaction velocity constants determined from the expression used by Menschutkin (cf. A., 1890, 1366; 1900, 335) and also from an amended expression which takes into account the action of amine on the hydrochloride formed. Both equations give similar results for the initial stages, but that of Menschutkin agrees better with the later stages in spite of the above consideration. The following values were found for  $k_{35}$ ,  $k_{45}$ , and  $E$  (the energy of activation): Aniline-benzyl chloride, 0.00157, 0.00315, 13454 cal.; aniline-*p*-nitrobenzyl chloride, 0.000588, 0.00125, 14678 cal.; *p*-toluidine-benzyl chloride, 0.00217, 0.00495, 16050 cal.; *p*-toluidine-*p*-nitrobenzyl chloride, 0.00137, 0.00252, 11860 cal. The value  $E$  is calculated from  $\log k_1/k_2 = E/R(1/T_2 - 1/T_1)$ . The value of the velocity coefficients changes with the concentration of the reactants and particularly of the amine. Values of  $k$  are given for the reaction of 9 bases with benzyl chloride in alcohol at 40°. The following benzylated amines and their benzoyl (A) and *p*-toluenesulphonyl (B) derivatives were isolated: Benzyl-*o*-chloroaniline, m. p. 44°, (A) m. p. 111°; benzyl-*p*-chloroaniline, m. p. 45°, (A) m. p. 138°; benzyl-2 : 5-dichloroaniline, m. p. 47°, (A) m. p. 69°; benzylaniline, (A) m. p. 105°, (B) m. p. 133°; benzyl-*o*-toluidine, (A) m. p. 65°; benzyl-*p*-toluidine, (A) m. p. 127°, (B) m. p. 126°. A. C.

**Chlorine or Bromine Derivatives obtained by the Aid of Mixtures of Hydrogen Peroxide and the Corresponding Halogen Acids.** A. LEULIER (*Bull. Soc. chim.*, 1924, [iv], 35, 1325—1330).—A mixture of hydrogen peroxide and hydrochloric or hydrobromic acid is a satisfactory source of nascent halogen for the preparation of aromatic bromo or chloro derivatives.

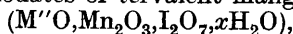
The following compounds were prepared in this way: *p*-Chloro-acetanilide (poor yield), 3 : 5-dichloro-*o*-nitroaniline, 2 : 6-dichloro-*p*-nitroaniline (74% yield), a chloro-2 : 4-dinitroaniline (m. p. 131—132°), 5-chloroaceto-*o*-toluidide (poor yield), 3-chloro-5-nitro-*o*-toluidine, chloroaceto-*p*-phenetidide (m. p. 123—124°), 5-bromoaceto-*o*-toluidide, 3-bromo-5-nitro-*o*-toluidine. Brominations proceed more satisfactorily than chlorinations. W. E. E.

**Magnesium Anilide.** A. TERENTIEFF (*Bull. Soc. chim.*, 1924, [iv], 35, 1164—1168).—In the absence of air, magnesium reacts with aniline vapour at 370—380° under atmospheric pressure, yielding magnesium anilide,  $(\text{NHPh})_2\text{Mg}$ , a light yellow powder. The product is unstable in air and rapidly blackens; its composition was accordingly calculated from the amounts of aniline consumed and of hydrogen liberated out of contact with air. Magnesium anilide is violently decomposed by water with regeneration of aniline (cf. Meunier, A., 1903, i, 544); alcohol vapour at 100—110° causes a similar decomposition, yielding aniline. With ethyl acetate vapour at 200°, acetanilide is produced (cf. Bodroux, A., 1904, i, 662; 1905, i, 585). In a current of dry air at 100°, profound oxidation takes place, but a small quantity of azobenzene was the only product isolated; the reaction with oxygen is explosive. Carbon dioxide at 180° yields magnesium phenylcarbamate,  $(\text{NHPh}\cdot\text{CO}_2)_2\text{Mg}$  (cf. Houben, A., 1904, i, 1104; 1909, i, 921), which on heating at 250—270° is decomposed into magnesium oxide, carbon dioxide, and *s*-diphenylcarbamide. R. B.

**New Types of Ter- and Quadri-valent Compounds of Manganese.** F. OLSSON (*Arkiv Kem., Min., Geol.*, 1924, 9, No. 10, 5—9).—When solutions of chlorides of organic bases in absolute alcohol, saturated with hydrogen chloride, are mixed with manganese trichloride solution obtained by reduction of potassium permanganate in alcoholic solution by means of hydrogen chloride (cf. Meyer and Best, A., 1900, ii, 77), double salts with chlorides of quaternary ammonium bases,  $2\text{RCl}\cdot\text{MnCl}_3$  (R=an organic base), are obtained. The formation of these compounds is probably determined by their low solubility in alcohol. Such pentachloromanganates are green and are free from solvent in the form of alcohol of crystallisation. The compounds prepared were:  $(\text{NMe}_4)_2\text{MnCl}_5$ ;  $(\text{NEt}_4)_2\text{MnCl}_5$ ;  $(\text{NPr}_4)_2\text{MnCl}_5$ ;  $(\text{NPhMe}_3)_2\text{MnCl}_5$ ;  $(\text{NPhEt}_3)_2\text{MnCl}_5$ ;  $(\text{NPhMe}_2\text{Et})_2\text{MnCl}_5$ ;  $(\text{NPhMeEt}_2)_2\text{MnCl}_5$ ;  $(\text{NHMe}_3\text{Et})_2\text{MnCl}_5$ ;  $(\text{NMe}\cdot\text{C}_{10}\text{H}_8\text{Me})_2\text{MnCl}_5$ ;  $(\text{NEt}\cdot\text{C}_{10}\text{H}_8\text{Me})_2\text{MnCl}_5$ ;  $(\text{NMe}_3\cdot\text{C}_6\text{H}_4\text{Me})_2\text{MnCl}_5$ ;  $(\text{NPhMeEtPr})_2\text{MnCl}_5$ . When the compound  $\text{NEt}_4\cdot\text{MnO}_4$ , obtained from silver permanganate and tetraethylammonium chloride, is reduced by acetic acid and dry hydrogen chloride is passed through the solution, the reddish-brown compound,  $\text{NEt}_4\cdot\text{MnCl}_4\cdot 2\text{C}_2\text{H}_4\text{O}_2$ , gradually separates.

The double iodates,  $\text{K}(\text{Rb}, \text{Cs}, \text{NH}_4)_2\text{Mn}(\text{IO}_3)_5$ , prepared by the action of the alkali iodates on the compound  $\text{Mn}(\text{OAc})_3\cdot 2\text{H}_2\text{O}, \text{HIO}_3$ , crystallise in yellow or yellowish-brown, doubly-refracting, cube-like octahedra, and are more stable in the air and towards the usual reagents than the double chlorides.

The following periodates of tervalent manganese,



prepared by Price's method (A., 1903, ii, 652), form red crystals, but turn brown at 110°, with loss of their water of crystallisation:  $M=H_2$ ,  $x=5$ ;  $M=Na_2$ ,  $x=3$ ;  $M=K_2$ ,  $x=2$ ;  $M=Sr$ ,  $x=3$ ;  $M=Mg$ ,  $x=3$ ;  $M=(CH_6N_3)_2$ ,  $x=8$ ;  $M=Ag_2$ ,  $x=0$ ;  $M=Cd$ ,  $x=4$ ;  $M=Zn$ ,  $x=4$ ;  $M=Cu$ ,  $x=3$ ;  $M=Pb$ ,  $x=3$ .

The compound  $Mn(CHBzAc)_3$ , prepared from benzoylacetone and manganese acetate, forms microscopic, stellar aggregates of green prisms, m. p. 168.5°.

By the action of manganese tetrachloride, prepared by Weinland and Dinkelacker's method (A., 1909, ii, 48), on different chlorides at the temperature of solid carbon dioxide, the following double chlorides are obtained as black crystals:  $(NMe_4)_2MnCl_6$ ;  $(NPhMe_3)_2MnCl_6$ ;  $(NMe_3 \cdot C_6H_4Me)_2MnCl_6$ ;  $(NPhMe_2Et)_2MnCl_6$ ;  $(NPhMeEt_2)_2MnCl_6$ . Double iodates of quadrivalent manganese having the formulæ  $Rb_2Mn(IO_3)_6$  and  $Cs_2Mn(IO_3)_6$  are obtainable by the action of iodic acid and alkali iodate on manganese dioxide suspended in water (cf. Berg, A., 1899, ii, 426). The corresponding barium salt, described by Berg, is obtainable more readily by dissolving manganese triacetate, barium iodate, and iodic acid in 10% nitric acid.

Periodates of quadrivalent manganese ( $M''O, 2MnO_2, I_2O_7, xH_2O$ ) may be obtained as crystalline powders by the interaction of manganic acetate, 10% nitric acid, and periodates. The following were prepared:  $M=H_2$ ,  $x=5$ ;  $M=Na_2$ ,  $x=2$ ;  $M=K_2$ ,  $x=1.5$ ;  $M=Ca$ ,  $x=4$ ;  $M=Sr$ ,  $x=4$ ;  $M=Mg$ ,  $x=3$ ;  $M=Ag_2$ ,  $x=2$ ;  $M=(CH_6N_3)_2$ ,  $x=10$ ;  $M=Cd$ ,  $x=5$ ;  $M=Zn$ ,  $x=3.5$ ;  $M=Cu$ ,  $x=4$ ;  $M=Pb$ ,  $x=2$ ; also  $Al_2O_3, 4MnO_2, 2I_2O_7, 10H_2O$ . T. H. P.

**Quinquevalent Chromium.** F. OLSSON (*Arkiv Kem., Min., Geol.*, 1924, 9, No. 10, 10—12).—The addition to a solution of chromium oxychloride of chlorides of organic bases dissolved in concentrated acetic acid saturated with hydrogen chloride (cf. Weinland and Fiederer, A., 1907, i, 549; ii, 31) yields double chlorides of the form  $RCl, CrOCl_3$ ; variation of the proportions of the reagents within wide limits is without influence on the composition of the resulting compounds, which form reddish- or yellowish-brown, rhombic tablets and are moderately stable in dry air. Such are:  $NMe_4CrOCl_4$ ;  $NEt_4CrOCl_4$ ;  $NPr_4CrOCl_4$ ;  $NPhMe_3CrOCl_4$ ;  $NPhEt_3CrOCl_4$ ;  $NPhMe_2EtCrOCl_4$ ;  $NPhMeEt_2CrOCl_4$ ;  $NMe(C_{10}H_8Me) \cdot CrOCl_4$ ;  $NEt(C_{10}H_8Me) \cdot CrOCl_4$ ;  $NMe_3(C_6H_4Me) \cdot CrOCl_4$ ;  $NPhMeEtPrCrOCl_4$ .

Addition of an aqueous solution of the compound  $4CrO_3, Cr_2O_3$  to excess of a solution of potassium fluoride in 40% hydrofluoric acid at 0° yields the compound  $KF, CrO_2F, H_2O$  as a yellowish-brown precipitate. T. H. P.

**Stereochemistry of Saturated Tervalent Nitrogen. VI. Attempts to Prepare Optically Active Compounds of Tervalent Nitrogen.** J. MEISENHEIMER, L. ANGERMANN, O. FINN, and E. VIEWEG (*Ber.*, 1924, 57, [B], 1744—1759).—Although the

existence of an asymmetric, saturated, tervalent nitrogen atom has frequently been assumed in order to account for the formation of stereoisomeric compounds containing this atom, no substance of this class has hitherto been resolved into optically active components. With this end in view, a large number of tertiary amines, particularly such as contain the acetyl and phenacyl groups, which appear to exert a favourable influence on the resolution of sulphonium compounds, have been examined with entirely negative results. It is therefore concluded that saturated, tervalent nitrogen, unless present in a particular manner in a polycyclic ring system, seldom if ever causes the phenomenon of stereoisomerism; this conclusion is in harmony with the observations of Pope and his co-workers (T., 1904, **85**, 1330; 1907, **91**, 458; 1910, **97**, 2199). The attribution of the non-resolvability of these compounds to the presence of the three radicals attached to the nitrogen atom in the same plane as the nitrogen atom involves difficulties in other directions, so that it is assumed that this is only a mean position around which the atoms in ammonia and the amines constantly oscillate. Stabilisation occurs only when the fourth co-ordination position of the nitrogen atom is occupied by a positively charged hydrogen atom or an alkyl residue (ammonium compounds), an oxygen atom (amine oxides), or a complex metallic residue (ammines). According to Werner's theory, a close analogy exists between the amines and the ions of sulphonium salts,  $[\text{Sabc}]\text{X}$ . Since, however, the former are non-resolvable whereas the latter have been resolved, this analogy cannot be fully maintained. It appears more probable that the central sulphur atom is co-ordinatively quadrivalent and that when sulphonium salts become ionised the tetrahedral disposition of the radicals is maintained by the immediate substitution of water for halogen: 
$$\left[ \begin{array}{c} \text{Me} \text{S} \text{Me} \\ \text{Me} \text{Cl} \end{array} \right] \xrightarrow[\text{in water}]{\text{solution}} \left[ \begin{array}{c} \text{Me} \text{S} \text{Me} \\ \text{Me} \text{Aq} \end{array} \right] \text{Cl}.$$

1-Methyl-1 : 2 : 3 : 4-tetrahydroquinoline d- $\pi$ -bromocamphorsulphonate,  $\text{C}_{10}\text{H}_{12}\text{N}\cdot\text{C}_{10}\text{H}_{15}\text{O}_4\text{BrS}$ , prepared from its components in ethyl acetate, has m. p.  $141^\circ$  (decomp.),  $[\text{M}]_{\text{D}} + 276^\circ$  in ethyl alcohol; the corresponding monohydrate has m. p.  $137^\circ$ . Diethylaniline gives a d- $\pi$ -bromocamphorsulphonate, m. p.  $222-223^\circ$ ,  $[\text{M}]_{\text{D}} + 272^\circ$  in alcohol. Ethylaniline gave with a somewhat old specimen of the acid mainly ethylaniline d- $\pi$ -bromocamphorsulphonate, m. p.  $146.5-148^\circ$  (monohydrate, m. p. about  $80^\circ$ ), together with smaller amounts of a salt,  $\text{C}_8\text{H}_{11}\text{N}\cdot\text{C}_{16}\text{H}_{10}\text{O}_4\text{BrS}$ , m. p.  $195-196^\circ$ , which is probably derived from d-isobromocamphorsulphonic acid (cf. Kipping, T., 1905, **87**, 635). Ethylpropylaniline d- $\pi$ -bromocamphorsulphonate has m. p.  $137-138^\circ$ .

Acetonylethylethylamine,  $\text{C}_6\text{H}_{13}\text{ON}$ , an unstable liquid, b. p.  $44-45/15$  mm., prepared from methylethylamine and chloroacetone in ethereal solution, yields a picrate, m. p. indefinite,  $80-85^\circ$ , and a d- $\alpha$ -bromocamphor- $\pi$ -sulphonate, m. p.  $115-122^\circ$ ,  $[\text{M}]_{\text{D}} + 275^\circ$ . Phenacylmethylethylamine, b. p.  $130-131/11$  mm., the picrate, m. p.  $116-118^\circ$  after previous softening, and the d-bromocamphorsulphonate, m. p.  $141-142^\circ$  after softening at  $137^\circ$ ,  $[\text{M}]_{\text{D}}$

+276°, are described. Methylaniline and chloroacetone give a mixture of 1:3-dimethylindole, b. p. 119—120°/7 mm. (*picrate*, m. p. 141—143°), much unchanged methylaniline, and *acetonylmethylaniline*, b. p. 135—136°/8 mm.; the latter substance yields a crystalline *picrate*, but its salts with optically active acids could not be caused to crystallise. 1-Acetonyl-1:2:3:4-tetrahydroquinoline, b. p. 178°/17 mm., m. p. 39—41°, gives a d-bromocamphorsulphonate, m. p. (indefinite) 110—116°,  $[M]_D +265^\circ$ . 1-Phenacyl-1:2:3:4-tetrahydroquinoline, m. p. 101—103°, and its d-bromocamphorsulphonate, m. p. (indefinite) 110—135°, are described; the base recovered from the salt was optically inactive. Acetonylmethyleyclohexylamine, b. p. 106°/11 mm., does not yield a crystalline bromocamphorsulphonate; the *picrate* has m. p. 162—163° after previous softening. The amine absorbs oxygen when dissolved in ether and becomes converted into benzoylmethyleyclohexylamine, m. p. 130—135°.

N-Phenyl-N-p-tolylanthranilic acid, m. p. 173°, prepared from phenylanthranilic acid, p-iodotoluene, copper powder, and potassium carbonate in the presence of nitrobenzene at 200—215°, is readily purified through the sparingly soluble, tetrahydrated sodium salt; it could not be resolved by means of the *strychnine* salt, m. p. 184—185°, or *quinine* salt (+C<sub>6</sub>H<sub>6</sub>), m. p. 154—164°; the cinchonine, brucine, and morphine salts do not crystallise satisfactorily. Phenyl- $\alpha$ -naphthylanthranilic acid, m. p. 226°, could not be resolved by means of its *brucine* salt (+1.5H<sub>2</sub>O), m. p. 237°, or *morphine* salt (+4H<sub>2</sub>O), m. p. 174° (decomp.) after softening at 155°.

H. W.

**Derivatives of Diphenylamine.** E. PAPASOGLI (*Atti R. Accad. Lincei*, 1924, [v], 33, ii, 106—110).—p-Bromo-p'-nitrodiphenylamine, C<sub>6</sub>H<sub>4</sub>Br·NH·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>, prepared by treating p-nitrodiphenylamine with a mixture of sulphuric acid, bromine, and pyridine (or quinoline) in acetic acid solution, forms orange-yellow crystals, m. p. 162°. When subjected in acetic acid solution to a current of nitrous anhydride, it is converted into the required nitrosoamine, C<sub>6</sub>H<sub>4</sub>Br·N(NO)·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>, m. p. 151°, which yields p-bromo-p'-nitrodiphenylamine when treated with hydroxylamine hydrochloride in alcoholic solution.

T. H. P.

**Derivatives of ac-Tetrahydro- $\beta$ -naphthylamine.** A. WINDAUS [with O. DALMER, H. SCHREITERER, R. HUPE, and H. KÖCHER] (*Ber.*, 1924, 57, [B], 1731—1739).—2-Amino-7-hydroxynaphthalene is reduced by sodium and amyl alcohol to a mixture of 2-amino-7-hydroxy-1:2:3:4-tetrahydronaphthalene, m. p. 168.5°, and 2-amino-7-hydroxy-5:6:7:8-tetrahydronaphthalene, which can be separated from one another, since only the former is soluble in sodium hydroxide solution; it yields a hydrochloride, m. p. 166.5°, a *picrate*, m. p. 205° after softening, and a dibenzoyl derivative, m. p. 174° after softening; 2-acetamido-7-hydroxy-1:2:3:4-tetrahydronaphthalene has m. p. 195°. The base is converted by bromine in glacial acetic acid solution into 6:8-dibromo-2-amino-7-hydroxy-1:2:3:4-tetrahydronaphthalene, m. p. 251° (decomp.),



after darkening at  $215^{\circ}$  (*hydrobromide*, m. p.  $234^{\circ}$ ; *diacetyl* derivative, m. p.  $187^{\circ}$ ). The action of nitric acid on a solution of 2-amino-7-hydroxy-1:2:3:4-tetrahydronaphthalene in glacial acetic acid leads to the almost immediate separation of the *nitrate* of nitro-2-amino-7-hydroxy-1:2:3:4-tetrahydronaphthalene; the corresponding free *base*, m. p.  $236^{\circ}$  (decomp.), its *hydrochloride*, decomp.  $260$ — $310^{\circ}$ , and *diacetyl* derivative, m. p.  $178^{\circ}$ , are described. The filtrates from the *nitrate* described above gradually deposit the *nitrate* of 6:8-dinitro-2-amino-7-hydroxy-1:2:3:4-tetrahydronaphthalene; the free *base*, m. p.  $243^{\circ}$  (decomp.), the *hydrochloride*, decomp.  $220$ — $290^{\circ}$ , and the *diacetyl* derivative, m. p.  $193^{\circ}$  (decomp.), are described. The portion of the product of the reduction of 2-amino-7-hydroxynaphthalene which does not dissolve in sodium hydroxide (see above) is separated by light petroleum into 2-amino-7-hydroxy-5:6:7:8-tetrahydronaphthalene, m. p.  $141.5^{\circ}$ , b. p.  $200$ — $210^{\circ}/12.5$  mm. (*hydrochloride*, m. p.  $236^{\circ}$ ; *picrate*, m. p.  $181^{\circ}$ ), and ar-2-aminodihydronaphthalene, b. p.  $150$ — $155^{\circ}/14$  mm., m. p.  $53^{\circ}$  (*picrate*, m. p.  $194^{\circ}$  [decomp.]; *di-bromo* compound,  $C_{10}H_{11}NBr_2$ , m. p.  $62^{\circ}$ ); the *picrate* of ar-2-amino-tetrahydronaphthalene has m. p.  $204^{\circ}$  (decomp.).

2-Amino-7-methoxynaphthalene, m. p.  $143^{\circ}$  (*hydrochloride*, m. p.  $222$ — $223^{\circ}$  [decomp.]; *picrate*, decomp.  $165^{\circ}$ ; *acetyl* derivative, m. p.  $156^{\circ}$ ), is prepared by the action of ammonium sulphite and ammonia on 2-hydroxy-7-methoxynaphthalene at  $150$ — $160^{\circ}$ . It is reduced by sodium and boiling amyl alcohol to a mixture of the corresponding tetrahydro derivatives, which is separated into its components by treatment of its ethereal solution with carbon dioxide, whereby 2-amino-7-methoxy-1:2:3:4-tetrahydronaphthalene is precipitated as the *carbonate* (? *carbamate*); the free *base*, a colourless liquid, *hydrochloride*, m. p.  $213^{\circ}$ , *picrate*, decomp. about  $212^{\circ}$  after softening, and *picrolonate*, decomp. about  $252^{\circ}$ , are described. The *base* is converted by hydriodic acid into 2-amino-7-hydroxy-1:2:3:4-tetrahydronaphthalene. The physical constants of the *hydrochloride*, m. p.  $225^{\circ}$ , *picrate*, m. p.  $183^{\circ}$  (decomp.), and *acetyl* derivative, m. p.  $93^{\circ}$ , of 2-amino-7-methoxy-5:6:7:8-tetrahydronaphthalene, are given with reserve as the complete freedom of the *base* from the isomeric 1:2:3:4-tetrahydro compound is not established. 2-Hydroxy-7-methoxy-1:2:3:4-tetrahydronaphthalene, prepared by the catalytic hydrogenation of 2-hydroxy-7-methoxynaphthalene in the presence of spongy palladium, has m. p.  $71^{\circ}$ .

2:7-Diaminonaphthalene (*dipicrate*, m. p.  $210^{\circ}$ ; *diacetyl* derivative, m. p.  $261^{\circ}$ ; *dibenzoyl* derivative, m. p.  $267^{\circ}$ ) is reduced by sodium and boiling amyl alcohol to 2:7-diamino-1:2:3:4-tetrahydronaphthalene, b. p.  $162^{\circ}/20$  mm., m. p. about  $60^{\circ}$  (*hydrochloride*, m. p. about  $360^{\circ}$  [decomp.]; *diacetyl* derivative, m. p.  $203^{\circ}$ ; *dibenzoyl* compound, m. p.  $255^{\circ}$ ). It is transformed by nitrous acid into 2-amino-7-hydroxy-1:2:3:4-tetrahydronaphthalene.

The following derivatives of 2:6-dihydroxynaphthalene are described: the *monomethyl ether*, m. p.  $136$ — $137^{\circ}$ ; 2-amino-

6-methoxynaphthalene, m. p. 139—140° (hydrochloride, m. p. 181°; acetyl derivative, m. p. 159—160°). 2:6-Diaminonaphthalene, m. p. 216—217°, is smoothly reduced to 2:6-diamino-1:2:3:4-tetrahydronaphthalene, m. p. 61°; the hydrochloride, diacetyl derivative, m. p. 240°, and dibenzoyl compound, m. p. 258°, are described. H. W.

**Nitrophenyl Ethers and their Halogen Substitution Products.** O. MATTER (D.R.-P. 386618; from *Chem. Zentr.*, 1924, i, 2632).—Nitrophenyl ethers are prepared by heating mono- or poly-halogenated nitrohydrocarbons with monohydric alcohols and feebly basic metal hydroxides, carbonates, or hydrogen carbonates, with or without the addition of catalysts. For example, *p*-chloronitrobenzene yields *p*-nitroanisole on heating at 175—185° with sodium carbonate and diluted methyl alcohol; at 200—210° with sodium carbonate, ethyl alcohol, and copper powder, *p*-nitrophenetole is formed. With slight variations in the conditions 3:4-dichloronitrobenzene yields 2-chloro-4-nitroanisole, m. p. 95°, and 2:5-dichloronitrobenzene yields 4-chloro-2-nitroanisole, m. p. 95°, and 4-chloro-2-nitrophenetole, m. p. 61—62°. F. A. M.

**Solubility and Partition Measurements of Picric Acid in Solutions of Salts.** E. SCHREINER (*Z. anorg. Chem.*, 1924, 138, 311—321).—By means of measurements of conductivity and catalytic power, the value  $K_0=0.31$  at 25° is found for the dissociation constant of picric acid in water on the basis of Bjerrum's theory (A., 1919, ii, 9); a closely agreeing value is given by *E.M.F.* measurements. The solubility of picric acid in water at 25° is  $c_0=0.0575$  mol. per litre, and its solubility has been measured in aqueous solutions of sodium chloride, barium chloride, and magnesium sulphate. The partition of picric acid between benzene and aqueous solutions of the above-mentioned salts has also been studied, and the hydrogen-ion concentration calculated in each case. The experimental results together with those of Rothmund and Drucker (A., 1904, ii, 391) are used to calculate the partition and solubility constants on the basis of Bjerrum's theory, and satisfactorily constant values are obtained. W. H.-R.

**Steric Hindrance in the Migration of Acyl from Nitrogen to Oxygen.** L. C. RAIFORD and C. M. WOOLFOLK (*J. Amer. Chem. Soc.*, 1924, 46, 2246—2255).—The migration of the acetyl group from nitrogen to oxygen when an *o*-acetamidophenol is benzoylated by the Schotten-Baumann method (A., 1923, i, 326) is not inhibited by the presence of bromine atoms ortho to the amino and hydroxyl groups, although in the case of 2:5:6-tribromo-3-acetamido-*p*-cresol either benzoylation was incomplete or migration was only partial.

2:3:5-Tribromo-*p*-cresol, m. p. 99°, on treatment with sodium nitrite and glacial acetic acid, is converted into 2:5-dibromo-3-nitro-*p*-cresol (or 5:6-dibromo-3-nitro-*p*-cresol), m. p. 123°, which is reduced by Raiford's method (A., 1911, i, 993) to the corresponding 2:5(or 5:6)-dibromo-3-amino-*p*-cresol, m. p. 122°.

Acetic anhydride and sodium acetate convert the base into 2 : 5 (or 5 : 6)-*dibromo-3-acetamido-p-tolyl acetate*, needles, hydrolysed by 10% aqueous sodium hydroxide to 2 : 5(or 5 : 6)-*dibromo-3-acetamido-p-cresol*, m. p. 158°, which with benzoyl chloride and sodium hydroxide gives, in 77% yield, 2 : 5(or 5 : 6)-*dibromo-3-benzoylamido-p-tolyl acetate*, m. p. 232°, hydrolysed by methyl-alcoholic sodium hydroxide to 2 : 5(or 5 : 6)-*dibromo-3-benzoylamido-p-cresol*, m. p. 154° (decomp.). The latter compound is identical with that obtained by benzoylating 2 : 5(or 5 : 6)-*dibromo-3-amino-p-cresol* by Ransom's method (A., i, 1900, 218) and on acetylation is converted into the benzoylamido-*p-tolyl acetate*.

Acetylation of 2 : 5 : 6-*tribromo-3-amino-p-cresol* with sodium acetate and acetic anhydride gives in 92% yield slightly impure 2 : 5 : 6-*tribromo-3-acetamido-p-tolyl acetate*, m. p. 171°, which on hydrolysis with 1% sodium hydroxide yields 2 : 5 : 6-*tribromo-3-acetamido-p-cresol*, m. p. 189°. Benzoyl chloride and sodium hydroxide convert this into 2 : 5 : 6-*tribromo-3-benzoylamido-p-tolyl acetate*, m. p. 177° (blackening) (yield 72%), the structure of which follows from its hydrolysis with aqueous alcoholic sodium hydroxide to 2 : 5 : 6-*tribromo-3-benzoylamido-p-cresol*, m. p. 195°, identical with the product obtained by benzoylating 2 : 5 : 6-*tribromo-3-amino-p-cresol* by Ransom's method. Acetic anhydride and sodium acetate convert the benzoylamido-*p-cresol* into the *p-tolyl acetate*, m. p. 195°.

Tetrabromo-*o-cresol*, m. p. 204°, on treatment with sodium nitrite and acetic acid, gives in addition to the 4 : 5 : 6-*tribromo-3-nitro-o-cresol*, m. p. 159°, the isomeric 3 : 4 : 6-*tribromo-5-nitro-o-cresol*, m. p. 177° (decomp.), obtained by Zincke and Klostermann (A., 1907, i, 322). On reduction by Raiford's method, the 4 : 5 : 6-*tribromo derivative* gives, in 74% yield, the *hydrochloride* of 4 : 5 : 6-*tribromo-3-amino-o-cresol*; the free base has m. p. 167°. Acetylation of the base by the usual method gives, in 86% yield, 4 : 5 : 6-*tribromo-3-acetamido-o-tolyl acetate*, m. p. 146°, which on hydrolysis with aqueous alcoholic alkali gives an 82% yield of 4 : 5 : 6-*tribromo-3-acetamido-o-cresol*, m. p. 186°. Benzoylation converts the last into 4 : 5 : 6-*tribromo-3-benzoylamido-o-tolyl acetate*, m. p. 234°, the structure of which is established by its synthesis by benzoylation of 4 : 5 : 6-*tribromo-3-amino-o-cresol* by Ransom's method, followed by acetylation of the 4 : 5 : 6-*tribromo-3-benzoylamido-o-cresol*, m. p. 133°, with sodium acetate and acetic anhydride. R. B.

**Influence of Weight of Acyl in the Migration from Nitrogen to Oxygen. II.** L. C. RAIFORD and J. R. COUTURE (*J. Amer. Chem. Soc.*, 1924, 46, 2305—2318).—In continuation of their previous work on the migration of acetyl from nitrogen to oxygen in benzoylation by the Schotten-Baumann method (A., 1920, i, 156; 1922, i, 931; 1923, i, 326, 925), the authors have repeated the work of Auwers and Eisenlohr on acetylbenzoyl derivatives of 3-amino-*p-cresol*. Two different mixed diacyl derivatives were obtained, each of which gave a mixture of mono-*N*-acylated derivatives on hydrolysis. A study of the acylation of 5-bromo-3-amino-*p-cresol*

and 4 : 6-dibromo-*o*-aminophenol shows that an increase in the weight of the aliphatic acyl radical hinders its displacement by benzoyl. The introduction of a nitro group into the benzoyl radical in the meta- or para-position greatly weakens the power of the radical to displace other groups from nitrogen in acylated *o*-aminophenols. The effect is greatest when the nitro group is in the para-position, but the introduction of a chlorine atom in the para-position does not diminish the power of the benzoyl group to displace other acyl groups. Neither relative weight nor relative acidity of the acyl radicals is the sole determining factor in the migration, and rearrangement may occur in both directions either in acylation or in hydrolysis. With two acyl groups of the same weight, one aromatic and one aliphatic, there is little tendency for replacement in acylation, but migration may occur during hydrolysis.

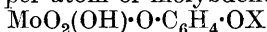
3-Acetamido-*p*-cresol, m. p. 158°, on benzoylation, yields 3-acetamido-*p*-tolyl benzoate, m. p. 147°; the isomeric 3-benzamido-*p*-tolyl acetate melts at 135°. 4 : 6-Dibromo-*o*-propionamidophenyl propionate, m. p. 162°, obtained on heating the hydrochloride of the base with sodium propionate and excess of propionic anhydride [the tripropionyl derivative,  $C_3H_5O \cdot OC_6H_2Br_2 \cdot N(C_3H_5O)_2$ , m. p. 153°, is obtained with a large excess of anhydride], on hydrolysis with dilute alkali yields 4 : 6-dibromo-*o*-propionamidophenol, m. p. 88°, which on benzoylation gives in 99.4% a propionylbenzoyl derivative, m. p. 182°, identical with that obtained by the action of propionic anhydride on 4 : 6-dibromo-*o*-benzoylamidophenol, and yielding on hydrolysis a mixture of the *N*-benzoyl and *N*-propionyl compounds. 4 : 6-Dibromo-*o*-*n*-hexoamidophenyl hexoate, m. p. 111°, obtained by the action of *n*-hexoyl chloride on the phenol in pyridine, on hydrolysis yields 4 : 6-dibromo-*o*-hexoamidophenol, m. p. 70–71°, converted quantitatively by benzoyl chloride into 4 : 6-dibromo-*o*-hexoamidophenyl benzoate, m. p. 137°, hydrolysed to a mixture of *N*-benzoyl and *N*-hexoyl-4 : 6-dibromo-*o*-aminophenol. The isomeric 4 : 6-dibromo-*o*-benzoylamidophenyl hexoate, m. p. 137°, also yields a mixture of the two *N*-acyl derivatives on hydrolysis. Similarly, 4 : 6-dibromo-*o*-acetamidophenyl hexoate, m. p. 120°, obtained by the action of hexoyl chloride on *o*-acetamidophenol, and 4 : 6-dibromo-*o*-hexoamidophenyl acetate, m. p. 133°, similarly prepared from *o*-hexoamidophenol, both yield on hydrolysis a mixture of the two acylamidophenols. Acetylation of 5-bromo-3-amino-*p*-cresol with excess of acetic anhydride in pyridine gives a triacetyl derivative, m. p. 109°,  $OAc \cdot C_6H_2Br(Me) \cdot NAc_2$ . The diacetyl derivative obtained with acetyl chloride yields on hydrolysis the *N*-acetyl derivative, which with *p*-nitrobenzoyl chloride in pyridine is quantitatively converted into 5-bromo-3-acetamido-*p*-tolyl *p*-nitrobenzoate, m. p. 206°, identical with the product obtained by the action of acetyl chloride on 5-bromo-3-*p*-nitrobenzoylamido-*p*-cresol, m. p. 190°, and yielding *p*-nitrobenzoic acid and the acetamidophenol on hydrolysis. *p*-Nitrobenzoyl chloride and 4 : 6-dibromo-*o*-benzoylamidophenol, and benzoyl chloride and 4 : 6-dibromo-*p*-nitrobenzoylamidophenol, m. p. 214°, obtained by hydrolysis of the diacyl compound, yield the same benzoylnitrobenzoyl derivative, m. p.

246°, which on hydrolysis yields *p*-nitrobenzoic acid and the benzoylamidophenol. Similarly, the same *acetyl-m-nitrobenzoyl* compound, m. p. 190°, was obtained by the action of *m*-nitrobenzoyl chloride on 5-bromo-3-acetamido-*p*-cresol and of acetyl chloride on 5-bromo-3-*m-nitrobenzoylamido-p-cresol*, m. p. 190°, the diacyl compound on hydrolysis yielding both possible acylaminophenols. 5-Bromo-3-*p-chlorobenzoylamido-p-cresol*, m. p. 166°, from hydrolysis of the diacyl derivative, with acetyl chloride, and 5-bromo-3-acetamido-*p*-cresol with *p*-chlorobenzoyl chloride, yield the same diacyl derivative, which on hydrolysis yields the *N-p-chlorobenzoyl* derivative, but no *p*-chlorobenzoic acid. Similarly, 4 : 6-dibromo-2-*p-chlorobenzoylamidophenol*, m. p. 209—210°, and *p*-nitrobenzoyl chloride yield a *p-chlorobenzoyl-p-nitrobenzoyl* derivative, m. p. 276°, identical with that obtained from 4 : 6-dibromo-2-*p-nitrobenzoylamidophenol* and *p-chlorobenzoyl* chloride. On hydrolysis, this yields only *p*-nitrobenzoic acid and the *N-p-chlorobenzoyl* derivative, m. p. 209—210°. R. B.

**Nitration of Derivatives of *p*- and *m*-Aminophenols.** F. REVERDIN (*Bull. Soc. chim.*, 1924, [iv], 35, 1168—1183).—A general survey of researches on the nitration of derivatives of *p*-aminophenol (A., 1905, i, 51, 430; 1906, i, 165, 748; 1907, i, 37, 695; 1909, i, 377, 913; 1910, i, 470; 1911, i, 37, 776; 1912, i, 182, 963; 1913, i, 850; 1922, i, 537; 1923, i, 320, 714; this vol., i, 727) and *m*-aminophenol (A., 1914, i, 166, 831, 954; 1915, i, 60, 524, 878; 1916, i, 141, 645). R. B.

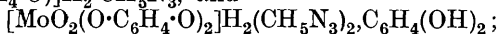
**Action of Formic Acid on Phenols and Propenyl Phenolic Ethers.** L. S. GLITCH (Bull. Soc. chim., 1924, [iv], 35, 1160—1164).—Phenolic ethers containing a propenyl side-chain are converted by boiling with 90% formic acid into their dimeric forms, which are thus readily obtained pure (cf. Semmler, A., 1908, i, 664). Anethole is converted in this way into dianethole, m. p. 133·5—134° (cf. Orndorff, A., 1898, i, 129), *isoeugenol* into *diisoeugenol*, methyl-*isoeugenol* into *dimethyldiisoeugenol*, m. p. 105·5—106° (cf. Széki, A., 1906, i, 660; Ciamician and Silber, A., 1909, i, 306), *isosafrole* into *diisosafrole*, m. p. 145—145·5°, whilst the isomeric allyl compounds, methylchavicol, eugenol, methyleugenol, and safrole, are unchanged. The crude *dimethyldiisoeugenol* melts at 89°, but no compound m. p. 96° could be isolated in the recrystallisations. R. B.

**Pyrocatechol Compounds of Sexa- and Quinque-valent Molybdenum.** R. WEINLAND and P. HUTHMANN (*Arch. Pharm.*, 1924, 262, 329—343; cf. A., 1920, i, 40).—Among the compounds of pyrocatechol and molybdic acid are many containing one or two pyrocatechol residues per atom of molybdenum, viz.,

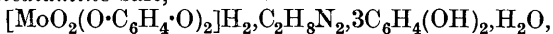


and  $\text{MoO}_2(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OX})_2$ , (where X = NH<sub>4</sub> or an organic basic radical). It is possible to obtain a number of products containing a higher proportion of pyrocatechol, but it is now shown that in these only two pyrocatechol residues are attached to the molybdenum,

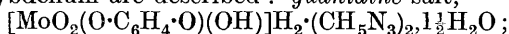
forming a complex anion, the rest of the pyrocatechol being probably attached to the cation by a secondary valency. If the compounds with organic bases having more than two pyrocatechol residues per atom of molybdenum are recrystallised, they readily lose some of their pyrocatechol and finally a compound is obtained containing never less than two pyrocatechol residues. Ethylenediamine forms such a compound, containing five pyrocatechol residues, and three of these may be readily removed as above. Pyrocatechol compounds of quinquevalent molybdenum are all prepared from the green salt,  $\text{MoOCl}_3 \cdot 2\text{NH}_4\text{Cl}$ . As this gives a hydroxide,  $\text{MoO}(\text{OH})_3$ , it was expected that it would yield compounds with three pyrocatechol residues per atom of molybdenum, but none was obtained with more than two. The following new substances are described: *barium monoppyrocatecholumolybdate*,  $[\text{MoO}_3(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O})]_2\text{H}_2\text{Ba} \cdot 3\text{H}_2\text{O}$ , prepared from the corresponding ammonium salt; the *mono-* and *di-guanidine* salts (which, like the other members of this series, may be prepared by the interaction of either ammonium molybdate or the trioxide  $\text{MoO}_3$ , pyrocatechol, and the appropriate base or its salts),  $[\text{MoO}_3(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O})]\text{H}_2 \cdot \text{CH}_5\text{N}_3$ , and



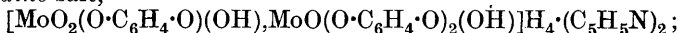
the *ethylenediamine* salt,



the *piperidine* salts,  $2[\text{MoO}_3(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O})]\text{H}_2 \cdot \text{C}_5\text{H}_{11}\text{N} \cdot 3\text{H}_2\text{O}$  and  $[\text{MoO}_2(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O})_2]\text{H}_2(\text{NH}_3) \cdot (\text{C}_5\text{H}_{11}\text{N}) \cdot 2\text{H}_2\text{O}$ ; the *piperazine* salts,  $[\text{MoO}_2(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O})_2]\text{H}_2 \cdot \text{C}_4\text{H}_{10}\text{N}_2$  (and its mono- and di-hydrates) and  $[\text{MoO}_3(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O}) \cdot \text{MoO}_2(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O})_2]\text{H}_4 \cdot \text{C}_4\text{H}_{10}\text{N}_2 \cdot 2\text{H}_2\text{O}$  (and the corresponding tetrahydrate). The following derivatives of quinquevalent molybdenum are described: *guanidine* salt,



*pyridine* salt,



*piperazine* salt,  $[\text{MoO}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O})_2(\text{OH})]\text{H}_2 \cdot \text{C}_4\text{H}_{10}\text{N}_2 \cdot \text{H}_2\text{O}$ . B. F.

### Preparation of Potassium Guaiacolsulphonate ("Thiocol").

A. DECIO (*Boll. Chim. farm.*, 1924, **63**, 529—530).—Guaiacolsulphonic acid, prepared by the action of sulphuric acid on guaiacol, is converted, together with the excess of sulphuric acid, into calcium salt by neutralisation with calcium carbonate. Treatment of the mixed calcium salts with potassium carbonate converts the calcium guaiacolsulphonate into the corresponding potassium salt, the calcium carbonate formed and the calcium sulphate being then removed by filtration. [Cf. *B.*, 1924, 964.] T. H. P.

### Electrolytic Introduction of Alkyl Groups. J. M. NELSON

and A. M. COLLINS (*J. Amer. Chem. Soc.*, 1924, **46**, 2256—2267).—In the electrolysis of a mixture of benzaldehyde and ethyl iodide, saturated with tetraethylammonium iodide,  $\alpha$ -phenylpropyl ethyl ether,  $\text{CHPhEt} \cdot \text{OEt}$ , b. p. 85—90°/15 mm., having a characteristic, pleasant odour, is obtained. It is oxidised to propiophenone by potassium dichromate and sulphuric acid. The introduction of the two ethyl groups is analogous to the reduction of benzalde-

hyde to benzyl alcohol and to its conversion into  $\alpha$ -phenylpropyl alcohol by the Grignard reaction. The introduction of alkyl groups appears to take place with difficulty and other reactions occur simultaneously. Part of the benzaldehyde undergoes reduction to *as*-diphenylethylene glycol, *s*-diphenylethylene glycol (hydrobenzoin), and stilbene, which, together with ethylene, a benzoate resembling ethyl benzoate, an iodide (giving with dimethylaniline a substance, m. p.  $152^{\circ}$ ) similar to, but not identical with, benzyl iodide, and a residual tar, are all formed at the cathode. Hydrobenzoin is always formed even when benzoic acid and water are excluded and the electrolysis is conducted in an atmosphere of nitrogen, and its formation may possibly take place as indicated:  $2\text{CHPhO} + 2\text{EtI} + 2e \rightarrow [\text{CHPh(OH)}]_2 + 2\text{C}_2\text{H}_4 + 2\text{I}^-$ , a reaction which is analogous to the reducing action of magnesium ethyl bromide (cf. Hess and Rheinboldt, A., 1921, i, 777). The yield of  $\alpha$ -phenylpropyl ethyl ether is not affected by the presence of traces of benzoic acid, nor by the absence of a diaphragm.

Preliminary experiments with benzaldehyde and methyl iodide indicate that a similar reaction obtains in this case, an *ether* which on oxidation yields acetophenone, and is probably  $\alpha$ -phenylethyl methyl ether, being obtained. Attempts to introduce methyl groups into benzonitrile, propionitrile, and acetone by this method were unsuccessful, methane being formed practically in quantitative yield, calculated on the current consumption. R. B.

**Utilisation of Cassia Oil for the Synthesis of Cinnamyl Alcohol.** A. J. HILL and E. H. NASON (*J. Amer. Chem. Soc.*, 1924, 46, 2236—2246).—The sodium hydrogen sulphite method of separating cinnamaldehyde from cassia oil is unsuitable for large-scale working (cf. Heusler, A., 1891, 1052; Tiemann, A., 1898, i, 247), but 85.7% of the theoretical yield can be separated as cinnamylidene diacetate by treatment of the oil with acetic anhydride in the presence of a few drops of sulphuric acid. The diacetate is readily hydrolysed to the aldehyde by heating with 10% sulphuric acid (yield 96%). On reduction of the diacetate with iron (8.3 mols.) and 50% acetic acid, yields of cinnamyl acetate up to 63.7% of theory (cf. Barbier and Leser, A., 1905, i, 653) are obtained in 12 hours. Large amounts of acetic acid retard the reduction. Copper sulphate inhibits the reduction, whilst nickel sulphate promotes the formation of phenylpropyl alcohol. With aluminium amalgam, reduction is incomplete; zinc-copper and zinc-nickel couples in alcoholic solution give hydrocinnamoin and other glycols (cf. Thiele, A., 1899, i, 616). Reduction with zinc and acetic acid gives similar results, cinnamyl acetate never being obtained when zinc is used. Cinnamyl acetate can also be obtained by reduction of cinnamaldehyde or cassia oil by the same method, the yield in the latter case being 77% of theory. Hydrolysis of the acetate with 5% alcoholic sodium hydroxide gives 96% of the theoretical yield of cinnamyl alcohol (*p*-nitrobenzoate, m. p.  $78^{\circ}$ ), which is separated from any phenylpropyl alcohol by treatment with calcium chloride, with which the cinnamyl alcohol

forms an additive compound. Cinnamaldehyde is best determined by precipitation of the phenylhydrazone in glacial acetic acid.

R. B.

**Molecular Transformations. XIV. Action of Acetyl Chloride on 4:4':4'':4'''-Tetrabromobenzopinacone. Contribution to the Problem of Affinity.** P. J. MONTAGNE (*Rec. trav. chim.*, 1924, **43**, 636—642; cf. *Ber.*, 1918, **51**, 1479).—The action of acetyl chloride on 4:4':4'':4'''-tetrabromobenzopinacone simultaneously follows two courses. The main reaction results in the formation of 4:4':4'':4'''-tetrabromobenzopinacol, whilst the side reaction gives 4:4'-dibromobenzhydrol. This is explained by assuming that in acetyl chloride solution two forms of the tetrabromobenzopinacone are present in mutual equilibrium. The difference between the forms lies in the distribution of affinity between the atoms of the molecule. Which of the two changes, intramolecular transformation or decomposition, a particular molecule undergoes is determined by the relative intensities of its main and subsidiary valencies. According to this theory, in the pinacone-pinacol transformation, the elimination of water and the migration of the bromophenyl group take place simultaneously.

W. E. E.

**2-Hydroxy-5-methoxycyclohexylcarbinol.** L. HELFER (*Helv. Chim. Acta*, 1924, **7**, 950—956).—*p*-Hydroxyanisole is hydrogenated in the presence of reduced nickel to 4-methoxycyclohexanol, b. p. 204—205° (acetyl derivative, b. p. 102—103°/12 mm.). Oxidation by potassium dichromate and sulphuric acid leads to 4-methoxycyclohexanone (b. p. 200—201°/760 mm., 72°/9 mm.; semicarbazone, m. p. 178°), which gives, with sodium ethoxide and isoamyl formate, 4-methoxy-2-hydroxymethylencyclohexanone (b. p. 108—110°/10 mm.). Sodium and alcohol reduce this to 6-hydroxy-3-methoxycyclohexylcarbinol, b. p. 172—174°/13 mm. 2-Hydroxymethylene-4-methylcyclohexanone gives with semicarbazide a cyclic semicarbazone,  $\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{C}=\text{N} \\ | \qquad \qquad | \\ \text{CHMe}\cdot\text{CH}_2\cdot\text{C}\cdot\text{CH} \end{array} > \text{N}\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 161°. It is

reduced in the same way as the corresponding methoxy compound (above) to 2-hydroxy-5-methylcyclohexylcarbinol, m. p. 70°. The action of formaldehyde on *p*-hydroxyanisole in the presence of calcium hydroxide gives 2-hydroxy-5-methoxybenzyl alcohol (m. p. 81°) and a little 2-hydroxy-5-methoxy-*m*-xylylene glycol, m. p. 127°.

W. E. E.

**Effect of Sulphur on the Colour of certain Phthaleins.** H. S. HOLT and E. E. REID (*J. Amer. Chem. Soc.*, 1924, **46**, 2333—2337).—By condensing *p*-hydroxybenzoyl-*o*-benzoic acid with *o*-hydroxyphenyl thio-ethers in the presence of zinc chloride (cf. Orndorff and Murray, A., 1917, **i**, 339), a series of derivatives of phenolphthalein containing the alkylthiol (or alkylsulphone) group ortho to hydroxyl has been obtained. The products form oximes, acetates, and benzoates, but the acetates could not be crystallised or the benzoates purified. The introduction of the methylthiol



group changes the colour of the phenolphthalein in alkaline solution to purple, but the auxochrome effect diminishes with increasing weight of the alkyl group. The phenylthiol group has practically no effect and the methylsulphone group none. The  $p_H$  value of the indicator is only slightly affected. Similar products were obtained by condensing *p*-hydroxybenzoyl-*o*-benzoic acid with phenyl mercaptan, *o*-nitrophenyl mercaptan, *p*-nitrophenyl methyl sulphide, and *o*-nitrophenyl methyl sulphide, but were not purified.

The following thio-ethers were obtained by diazotisation of the corresponding *o*-amino derivative: *o*-hydroxyphenyl methyl sulphide, b. p.  $105^\circ/22$  mm.,  $d_{25}^{25}$  1.168; *o*-hydroxyphenyl amyl sulphide, b. p.  $125^\circ/10$  mm.,  $d_{25}^{25}$  1.061; phenyl *o*-hydroxyphenyl sulphide, m. p.  $44^\circ$ , and *o*-hydroxyphenylmethylsulphone, m. p. above  $220^\circ$ . The

following ethers of 3-thiolphenolphthalein (annexed formula) have been obtained: methyl,  $p_H$  8.4–10, oxime, m. p.  $189^\circ$  (decomp.); amyl,  $p_H$  8.6–9.8, oxime, m. p.  $175$ – $176^\circ$  (decomp.); phenyl,  $p_H$  9.0–10, oxime, m. p.  $190^\circ$  (decomp.). 4 : 4' - Dihydroxydiphenylphthalide-3-methylsulphone has  $p_H$  9.6, oxime, m. p.  $165$ – $167^\circ$  (decomp.). Fusion of phthalic anhydride (1 mol.) with *o*-hydroxyphenyl methyl sulphide (2 mols.) and zinc chloride at  $180^\circ$  yields a salmon-coloured hydroxymethylthiolanthraquinone, m. p.  $188^\circ$  (decomp.).

R. B.

**Diacylamides. I.** K. BRUNNER, W. SEEGER, and S. DITTRICH (*Monatsh.*, 1924, **45**, 69–86; cf. Brunner, A., 1915, i, 1007; Miller, A., 1916, i, 203; Wolchowe, A., 1916, i, 844).—Diacylamides react with secondary hydrazines and aromatic amines to give substituted hydrazidines and amidines, respectively, in addition to acetylated derivatives, thus resembling nitriles. Diacetamide and *as*-phenylmethylhydrazine (equivalent quantities) were digested in 10% acetic acid at  $100^\circ$  for 24 hours; the fraction, b. p.  $160$ – $185^\circ/13$ – $17$  mm., was freed from much acetylated hydrazine by crystallisation and the residue converted by ethereal oxalic acid into the oxalate of acetophenylmethylhydrazidine, m. p.  $129$ – $130^\circ$ . Treatment with barium hydroxide gave the base,



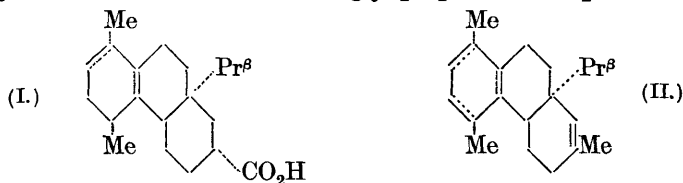
m. p.  $83$ – $84^\circ$  (yield 7%); picrate, m. p.  $158$ – $159^\circ$ ; dibenzoyl derivative, m. p.  $148$ – $149^\circ$ ; methiodide, m. p.  $210^\circ$  (decomp.).

Dibenzamide and aniline do not condense in presence of sodium (cf. Walther, A., 1894, i, 503; Lottermoser, A., 1897, i, 38), but by heating equivalent amounts of the amide and aniline hydrochloride at  $140$ – $145^\circ$  benzphenylamidine, m. p.  $113.5^\circ$ , is formed in 10% yield, together with benzanilide and benzamide from a by-reaction, and benzoic acid. The hydrochloride, m. p.  $224^\circ$ , and chloroplatinate are described. The reaction does not depend on the formation of benzonitrile, which does not react with aniline hydrochloride at so low a temperature. Dibenzamide does not react similarly with dimethylaniline hydrochloride, but with

diphenylaniline hydrochloride at  $170^\circ$  it gives benzdiphenylamidine,  $\text{CPh}(\text{:NH})\cdot\text{NPh}_2$ , m. p.  $112^\circ$ . F. M. H.

### Higher Terpene Compounds. XXIII. *d*-Pimaric Acid.

L. RUZICKA and F. BALAS (*Helv. Chim. Acta*, 1924, 7, 875—885; cf. A., 1923, i, 818).—When *d*-pimaric acid is dehydrogenated by means of sulphur, it gives a dimethylphenanthrene,  $\text{C}_{16}\text{H}_{14}$ ; it loses not only a carboxyl group, but also three other carbon atoms, which are taken to represent a tertiary isopropyl group. Together with the evidence of molecular refraction, this result leads to the conclusion that *d*-pimaric acid is probably a dimethylisopropyl-decahydrophenanthrenecarboxylic acid. When dehydrogenated by means of sulphur, ethyl *d*-pimarate gives the same product as the acid itself. In order to locate the carboxyl group, ethyl *d*-pimarate is reduced to *d*-pimarol,  $\text{C}_{20}\text{H}_{32}\text{O}$ , b. p.  $166\text{—}168^\circ/0.1\text{ mm.}$ ,  $d_4^{15}$  1.0114,  $n_D^{15}$  1.5357, from which, by elimination of water, methyl-*d*-pimarol,  $\text{C}_{20}\text{H}_{30}$ , b. p.  $140\text{—}145^\circ/0.3\text{ mm.}$ ,  $d_4^{25}$  0.9587,  $n_D^{25}$  1.5301, is obtained. Dehydrogenation of this compound by means of sulphur gives a new trimethylphenanthrene,  $\text{C}_{17}\text{H}_{16}$ , m. p.  $81^\circ$  (*picrate*, m. p.  $115^\circ$ ; *quinone*, m. p.  $154^\circ$ ; *quinoxaline*, m. p.  $154^\circ$ ), in which the methyl group derived from the carboxyl group of *d*-pimaric acid is still present. Hence this methyl group, and therefore the original carboxyl group, cannot be tertiary. This result is also to be expected from the difficulty with which *d*-pimaric acid is esterified. The trimethylphenanthrene from methyl-*d*-pimarol oxidises to a quinone of the same number of carbon atoms, therefore in *d*-pimaric acid positions 9 and 10 of the phenanthrene nucleus are vacant. The subjoined formula I is accordingly proposed for *d*-pimaric acid.



When *d*-pimaric acid is converted into methyl-*d*-pimarol, a third double bond, adjacent to the carboxyl group, is produced. But methyl-*d*-pimarol is highly unsaturated, and it follows that the two double bonds of *d*-pimaric acid cannot be in the same ring as the carboxyl group. On the other hand, dehydrogenation with nickel and palladium introduces only one more double bond into methyl-*d*-pimarol, forming *dehydromethyl-d-pimarol*,  $\text{C}_{20}\text{H}_{28}$ , b. p.  $185\text{—}195^\circ/12\text{ mm.}$ ,  $d_4^{14}$  0.9771,  $n_D^{15}$  1.5404 (formula II). This is explained if the double bonds of *d*-pimaric acid are as shown in I; the tertiary isopropyl group common to the two rings prevents their dehydrogenation. That there is probably no double bond adjacent to the carboxyl group of *d*-pimaric acid follows from the fact that the Bouveault reduction of simple  $\alpha\beta$ -unsaturated esters always leads to a saturated product. When *d*-pimaric acid is distilled in a vacuum, *d*-pimarol,  $\text{C}_{19}\text{H}_{28}$ , b. p.  $182\text{—}184^\circ/12\text{ mm.}$ ,  $[\alpha]_D^{25} +109^\circ$ ,  $d_4^{25}$  0.9693,  $n_D^{25}$  1.5349, is obtained. This compound contains

three double bonds, and the fact that it is unsaturated supports the former conclusion that the two double bonds of *d*-pimaric acid are not in the same ring as the carboxyl group. The partial dehydrogenation of *d*-pimaric gives *dehydro-d-pimaric*,  $C_{18}H_{26}$ , b. p. 203–212°/12 mm.,  $d_4^{25}$  0.9863,  $n_D^{15}$  1.5505, which is notably less unsaturated than *d*-pimaric. This is further support for the structure of *d*-pimaric acid given, since *dehydro-d-pimaric*, like its higher homologue, II, contains a benzene nucleus. *d-Pimaric*, obtained by heating *d*-pimaric acid at 310°, has b. p. 184–186°/12 mm.,  $[\alpha]_D^{20} + 30.1^\circ$  in 4% chloroform solution,  $d_4^{23}$  0.9717,  $n_D^{23}$  1.5406. W. E. E.

**Derivatives of Hexamethylenetetramine.** GEHE u. Co. A.-G., and H. RUNNE (D.R.-P. 386691; from *Chem. Zentr.*, 1924, i, 2612).—By combining aryloxyacetic acids with hexamethylenetetramine, the bitter taste of the acids is neutralised, the salts having a slightly sweet after-taste; they are useful as internal or external antiseptics. The following salts, prepared in the usual way, are described: *phenoxyacetate*, sinters about 177°; *p-tolyloxyacetate*, sintering about 194°; *guaiacolglycollate*, sintering about 130°; *salicyloxyacetate* (1 mol. acid + 2 mols. base), sintering about 86°; *acid salicyloxyacetate* (1 mol. acid + 1 mol. base) crystallises slowly and is more hygroscopic than the neutral salt. F. A. M.

**Halogenated Anhydrides of o-Hydrocoumaric Acid [Melilotic Acid].** CHEMISCHE WERKE GRENZACH A.-G. (D.R.-P. 386619; from *Chem. Zentr.*, 1924, i, 2633).—Halogenated coumarins or halogenated *o*-coumaric acids are treated with reducing agents and the resulting halogenated *o*-hydrocoumaric acids converted into the anhydrides by heating. 3:5-*Dichlorocoumarin*, m. p. 157° (from 3:5-dichlorosalicylaldehyde) on reduction with sodium amalgam in aqueous suspension yields 3:5-*dichloromelilotic acid*, m. p. 122°, which on heating at 210° gives the *anhydride*, m. p. 107°, b. p. 204°/25 mm. 5-*Chlorocoumarin* (from 5-chlorosalicylaldehyde), m. p. 165°, is reduced by sodium amalgam to 5-chloromelilotic acid, m. p. 142°, giving the *anhydride*, m. p. 109°, b. p. 192°/20 mm. The anhydrides are of value against intestinal parasites. F. A. M.

**Elemic Acid from Manila Elemi Resin.** H. LIEB and D. SCHWARZL (*Monatsh.*, 1924, 45, 51–61).—To  $\alpha$ -elemic acid from *Canarium commune* is assigned the formula  $C_{27}H_{42}O_3$  (contrast Tschirch and Cremer, A., 1902, i, 812; Buri, A., 1878, ii, 439); it is transformed by light into a resin which is regarded as identical with Tschirch and Cremer's  $\beta$ -acid.

$\alpha$ -Elemic acid, m. p. 215°, is a monocarboxylic acid;  $[\alpha]_D^{20} - 24.48^\circ$  in alcohol. There are described: *potassium* salt (+5H<sub>2</sub>O), becoming anhydrous at 115°, hydrolysed by water; *sodium* salt (+5H<sub>2</sub>O); amorphous *silver* salt, which with methyl iodide gives the *mono-methyl* ester (gummy). Tschirch and Cremer's preparation of an acetyl and benzoyl derivative could not be repeated.

Oxidation of  $\alpha$ -elemic acid with chromic oxide in acetic acid gave a monocarboxylic acid,  $C_{27}H_{40}O_3$ , m. p. 274°,  $[\alpha]_D^{23} - 67.13^\circ$

in chloroform; *sodium* salt ( $+7\text{H}_2\text{O}$ ). Although attempts to prepare a crystalline oxime, semicarbazone, or hydrazone were unsuccessful, it is regarded as a ketonic acid, and the name "elemonic acid" is suggested for it;  $\alpha$ -elemic acid must then contain a secondary alcoholic group, and for it is suggested the name "elemolic acid." Both readily take up bromine, whilst subsequent elimination of hydrogen bromide leaves an amorphous residue.

Oxidation of  $\alpha$ -elemic acid with nitric acid gave an amorphous acid,  $\text{C}_{21}\text{H}_{25}\text{O}_{10}\text{N}_3$  (cf. Tschirch and Cremer, *loc. cit.*), decomp.  $175^\circ$ ; *silver* salt,  $\text{C}_{21}\text{H}_{23}\text{O}_{10}\text{N}_3\text{Ag}_2$ . [Cf. *B.*, 1924, 952.]

F. M. H.

### Ring-chain Tautomerism. X. Inhibited Tautomerism.

F. DICKENS, L. HORTON, and J. F. THORPE (*J. Chem. Soc.*, 1924, 125, 1830—1840).—From cyclohexanone cyanohydrin (Higson and Thorpe, *T.*, 1906, 89, 1455) and ethyl sodiocyanoacetate, *ethyl 1-cyanocyclohexane-1-cyanoacetate*, m. p.  $54^\circ$ , b. p.  $210\text{--}212^\circ/22\text{ mm.}$ , is obtained. When hydrolysed, it affords 1-carboxycyclohexane-1-acetic acid. The sodium derivative of the ester decomposes when its solution is evaporated, yielding 1-cyanocyclohexane-1-acetonitrile, m. p.  $84^\circ$ , and *sodium 1-cyanocyclohexane-1-cyanoacetate*, m. p.  $145\text{--}149^\circ$  (*silver* and *aniline* salt [m. p.  $98^\circ$ ] also described). When a solution of this sodium salt (which is the main product when a small excess of sodium is used in the hydrolysis) is acidified and the oily precipitate first formed redissolved in an excess of hydrochloric acid, 1-carbamylcyclohexane-1-cyanoacetic acid, m. p.  $90^\circ$  (decomp.  $100^\circ$ ), crystallises (*sodium* salt, m. p.  $105\text{--}108^\circ$ ). When heated at  $72\text{--}74^\circ$  this acid affords ammonium 1-carboxycyclohexane-1-acetate, together with the *imide* of  $\alpha$ -carbamyl-1-carboxycyclohexane-1-acetic acid, m. p.  $152^\circ$  (decomp.); when it is treated with acetic acid, the *imide* of 1-carboxycyclohexane-1-cyanoacetic acid, m. p.  $123\text{--}124^\circ$ , is obtained, and this, when boiled with aqueous potassium hydroxide, affords  $\alpha$ -carbamyl-1-carboxycyclohexane-1-acetic acid, m. p.  $126^\circ$ , which is converted at its melting point into the *imide* of 1-carboxycyclohexane-1-acetic acid, m. p.  $145^\circ$  (this is also obtained by interaction of 1-carboxycyclohexane-1-acetic anhydride and carbamide). When 1-cyanocyclohexane-1-acetonitrile is dissolved in concentrated sulphuric acid, it is converted into 1-carbamylcyclohexane-1-acetamide, m. p.  $201^\circ$ .

When the sodium compound of ethyl  $\alpha\beta$ -dicyano- $\beta\beta$ -dimethylpropionate (Higson and Thorpe, *loc. cit.*) is treated with water it affords a mixture of (i) *as*-dimethylsuccinonitrile, m. p.  $68^\circ$  (this is best prepared by boiling the solution and is not a liquid as stated by Hell and Lothberg [*A.*, 1889, 959]); (ii) the *imide* of  $\alpha$ -cyano- $\beta\beta$ -dimethylsuccinic acid, m. p.  $116^\circ$ , and (iii)  $\beta$ -carbamyl- $\alpha$ -cyano- $\beta\beta$ -dimethylpropionic acid, m. p.  $142^\circ$ . The first is converted by cold concentrated sulphuric acid into *as*-dimethylsuccinamide, m. p.  $153^\circ$ , and (iii) is converted into (ii) by hot acetic acid.

cycloHeptanone cyanohydrin condenses with ethyl sodiocyanoacetate to give *ethyl 1-cyanocycloheptane-1-cyanoacetate*, b. p.

201°/13 mm., the sodium compound of which, when treated with water and the solution evaporated to dryness, yields the corresponding sodium salt. The free acid cannot be obtained; a solution of the sodium salt yields when acidified solely the *imide* of 1-carboxycycloheptane-1-cyanoacetic acid, m. p. 130°. The sodium salt is accompanied by some 1-cyanocycloheptane-1-acetonitrile, m. p. 58°. When ethyl 1-cyanocycloheptane-1-cyanoacetate is dissolved in concentrated sulphuric acid and the diluted solution boiled, the *imide* of 1-carboxycycloheptane-1-acetic acid, m. p. 116°, is formed, together with a little 1-carboxycycloheptane-1-acetic acid, m. p. 153°.

The parent compounds of all three series are  $\beta\beta$ -disubstituted  $\alpha\beta$ -dicyanopropionic acids; the mechanism of the various reactions is discussed on the lines indicated by the title of the paper, the effect of the different modes of  $\beta\beta$ -substitution on the proximity of the other groups being kept in view.

W. A. S.

**Isomeric Esters of *p*-Ethoxybenzoylacrylic Acid.** G. P. RICE (*J. Amer. Chem. Soc.*, 1924, **46**, 2319—2326).—In view of the difference between the isomeric esters of benzoylacrylic acid (A., 1923, i, 218) and of *p*-methoxybenzoylacrylic acid (this vol., i, 287), the isomeric methyl and ethyl esters of *p*-ethoxybenzoylacrylic acid have been investigated. The stable yellow esters, like those of *p*-methoxybenzoylacrylic acid, are isomerised on exposure to sunlight in benzene solution, and the reverse change is effected in benzene solution containing a crystal of iodine. The methyl ester of the ethoxy compound, unlike that of the methoxy compound, is not polymerised on exposure to sunlight in the solid state, isomerisation alone taking place, and since the methoxy ester has the higher m. p., the physical state of the substance does not appear to be the sole determinant of polymerisation or isomerisation. *p*-Ethoxybenzoylacrylic acid itself does not polymerise on exposure to light. Both yellow and colourless esters are partly hydrolysed by dilute sodium carbonate and cold concentrated hydrochloric acid, yielding *p*-ethoxybenzoylacrylic acid, boiling dilute hydrochloric acid yielding also  $\alpha$ -hydroxy- $\beta$ -*p*-ethoxybenzoylpropionic acid. The colourless esters are first transformed into the yellow esters by hydrochloric acid. With semicarbazide, the esters of the *p*-ethoxy-acid behave like those of the *p*-methoxy-acid. The colourless esters yield an additive compound and its semicarbazone; the yellow esters yield, in addition, two isomeric semicarbazones. This reaction establishes the isomerism of the colourless ethyl ester, which could only be obtained liquid. *p*-Ethoxybenzoylacrylic acid itself yields a semicarbazone.

*Methyl p*-ethoxybenzoylpropionate, m. p. 53°, is converted by Kohler and Engelbrecht's method (A., 1919, i, 330) into *methyl p*-ethoxybenzoylacrylate, yellow needles, m. p. 81·5°; the colourless *isomeride*, m. p. 53°, can be obtained by direct esterification of *p*-ethoxybenzoylacrylic acid, yellow needles, m. p. 141—142° (*semicarbazone*,  $C_{13}H_{15}O_4N_3$ , m. p. 212° [decomp.]), obtained in 62% yield from maleic anhydride and phenetole by the Friedel-Crafts

reaction. *Ethyl p-ethoxybenzoylpropionate*, m. p.  $51^{\circ}$ , similarly yields *ethyl p-ethoxybenzoylacrylate*, yellow needles, m. p.  $54^{\circ}$ ; colourless *isomeride*, an oil. On bromination in chloroform, methyl *p-ethoxybenzoylacrylate* yields a *dibromo* compound,  $C_{13}H_{14}O_4Br_2$ , m. p.  $92^{\circ}$ , the ethyl ester similarly yielding the *dibromo* derivative,  $C_{14}H_{16}O_4Br_2$ , m. p.  $81^{\circ}$ . Bromination of *p-ethoxybenzoylacrylic acid* in acetic acid yields  $\alpha\beta$ -*dibromo- $\beta$ -p-ethoxybenzoylpropionic acid*, m. p.  $151^{\circ}$ . Hydrolysis of the esters of *p-ethoxybenzoylacrylic acid* with hydrochloric acid yields  $\alpha$ -*hydroxy- $\beta$ -p-ethoxybenzoylpropionic acid*, m. p.  $132^{\circ}$ . Colourless methyl *p-ethoxybenzoylacrylate* with 2 mols. of semicarbazide hydrochloride in methyl alcohol in the presence of sodium acetate yields *methyl  $\alpha$ -semicarbazido- $\beta$ -p-ethoxybenzoylpropionate*, m. p.  $169^{\circ}$ , together with the *semicarbazone* of the semicarbazide, m. p.  $176^{\circ}$  (decomp.). The yellow ester, on similar treatment, yields in addition to these two substances, the two isomeric *methyl p-ethoxybenzoylacrylate semicarbazones*, yellow, m. p.  $173^{\circ}$ , colourless, m. p.  $149^{\circ}$ . Similarly, colourless ethyl *p-ethoxybenzoylacrylate* yields *ethyl  $\alpha$ -semicarbazido- $\beta$ -p-ethoxybenzoylpropionate*, m. p.  $154^{\circ}$ , and its *semicarbazone*, m. p.  $183^{\circ}$  (decomp.), whilst the yellow *isomeride* yields in addition the two isomeric *ethyl p-ethoxybenzoylacrylate semicarbazones*, plates, m. p.  $155^{\circ}$ , and yellow needles, m. p.  $140^{\circ}$ .

R. B.

**Terephthalic Acid Derivatives.** M. T. BOGERT and P. S. NISSON (*Proc. Nat. Acad. Sci.*, 1924, **10**, 426—433; cf. A., 1920, i, 65).—*p*-Dihydroxyisopropylbenzene (*loc. cit.*) shows little or no physiological activity and has none of the properties of a local anæsthetic. Methyl terephthalate and magnesium ethyl iodide yield, not the expected pinacone, but *p-di( $\alpha$ -ethylpropenyl)benzene*, b. p.  $149$ — $151^{\circ}/20$  mm., in 46% yield. When magnesium *n*-butyl bromide is used, a gum, containing some unsaturated hydrocarbon, is obtained. Magnesium aryl halides, but not the alkyl derivatives, interact with terephthaloyl chloride to produce compounds of the type  $COR \cdot C_6H_4 \cdot COR$ ; thus, magnesium phenyl bromide affords *p*-dibenzoylbenzene. Methyl aminoterephthalate (cf. Kaufmann and Weissel, A., 1912, i, 863) interacts with ethyl iodide at  $100^{\circ}$  to give *methyl ethylaminoterephthalate*, m. p.  $83.5^{\circ}$ , and with ethyl sulphate at  $150^{\circ}$  to give *methyl diethylaminoterephthalate*, b. p.  $191$ — $192^{\circ}/20$  mm. When methyl aminoterephthalate is treated with magnesium methyl or ethyl bromide, or magnesium *n*-butyl bromide, only gummy products are obtained. Methyl dimethylaminoterephthalate (Kaufmann and Weissel, *loc. cit.*) and magnesium methyl iodide afford no pinacone, but 2 : 5-diisopropenyl-dimethylaniline, m. p.  $62$ — $63^{\circ}$ ; 2 : 5-diisopropenyldiethylaniline (?), b. p.  $195$ — $197^{\circ}/18$  mm., was similarly obtained. Methyl aminoterephthalate yields, however, with magnesium phenyl bromide, a glycol (pinacone), viz., 2 : 5-di(hydroxydiphenylmethyl)aniline, m. p.  $202^{\circ}$ ; the dimethylamino and diethylamino esters similarly afforded 2 : 5-di(hydroxydiphenylmethyl)dimethylaniline, m. p.  $185^{\circ}$ , and 2 : 5-di(hydroxydiphenylmethyl)diethylaniline, m. p.  $179^{\circ}$ , re-

spectively. These compounds are sparingly soluble and valueless pharmacologically. W. A. S.

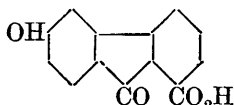
**Synthesis of 3:5-Dihydroxycinnamic Acid.** Y. ASAHINA and T. MATSUZAKI (*J. Pharm. Soc. Japan*, 1924, No. 509, 527—539).—3:5-Dihydroxybenzoic acid is prepared by heating a mixture of 100 g. of benzoic acid, 100 g. of phosphoric oxide, and 300 g. of fuming sulphuric acid (50%  $\text{SO}_3$ ) at 280—300° for 10 hours, followed by fusion with potassium hydroxide (cf. Barth and Senhofer, *Annalen*, 1871, 159, 217). The acid is changed into 3:5-dimethoxybenzaldehyde, through  $(\text{OMe})_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{NHP}$ ,  $(\text{OMe})_2\text{C}_6\text{H}_3\cdot\text{CCl}\cdot\text{NPh}$ , and  $(\text{OMe})_2\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{NPh}$ . By applying Perkin's reaction to the aldehyde, 3:5-dimethoxycinnamic acid, m. p. 174°, is produced. On heating with hydrogen iodide, bromide, or other reagents, it gives no dihydroxy compound. When  $(\text{OMe})_2\text{C}_6\text{H}_3\cdot\text{CCl}\cdot\text{NPh}$  is treated with zinc chloride, hydrogen chloride, and ether, a *chloro-3:5-dimethoxybenzaldehyde*, m. p. 129°, is obtained; *oxime*, m. p. 125°. When Perkin's reaction is applied to crude 3:5-diacetoxybenzaldehyde and the resulting acid is hydrolysed with sodium carbonate, 3:5-dihydroxycinnamic acid,  $\text{C}_9\text{H}_8\text{O}_4\cdot 0.5\text{H}_2\text{O}$ , m. p. 244—245° (decomp.), is formed. It gives the above dimethyl derivative, m. p. 174°, by treatment with methyl sulphate. K. K.

**Anthraquinonecarboxylic Acids.** E. DE B. BARNETT, J. W. COOK, and H. H. GRAINGER (*Ber.*, 1924, 57, [B], 1775—1781).—Anthraquinone-1-carboxylic acid is reduced by zinc and fuming hydrochloric acid in the presence of glacial acetic acid to a mixture of 10-anthrone-1-carboxylic acid,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{CH} \\ \text{CH}_2 \end{smallmatrix}\rangle\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$ , m. p. 252°, and the lactone of 9:10-dihydro-9-anthranol-1-carboxylic acid (I), m. p. 277—278° after darkening at 264°; the latter compound is converted by boiling alcoholic potassium hydroxide solution into anthracene-1-carboxylic acid. The action of nitric acid (*d* 1.5) and glacial acetic acid on anthracene-1-carboxylic acid yields primarily the *acetate* of a nitro-dihydroanthranol-1-carboxylic acid, m. p. 172° (decomp.), which is converted by pyridine into 9(? 10)-nitroanthracene-1-carboxylic acid, decomp. 249°. Anthracene-1-carboxylic acid is readily brominated in boiling glacial acetic acid to 9(? 10)-bromoanthracene-1-carboxylic acid, m. p. 281—282° (decomp.), but bromination does not proceed beyond this stage when excess of halogen is used. The action of bromine on anthracene-1-carboxylic acid in the presence of pyridine yields *anthracyl-10-pyridinium bromide-1-carboxylate*,  $\text{C}_6\text{H}_3\langle\begin{smallmatrix} \text{CH} \\ \text{C}(\text{NC}_5\text{H}_5\text{Br}) \end{smallmatrix}\rangle\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}\cdot 1.5\text{H}_2\text{O}$ . Phenyl anthracene-1-carboxylate, m. p. 207—209°, is converted by bromine (2 g.-mol.) into the ester of the monobromo-acid, but by a large excess of bromine into a mixture of the esters of the mono- and dibromo-acids. Anthracene-2-carboxylic acid, conveniently obtained

by the reduction of 9-anthrone-2-carboxylic acid with zinc dust and ammonia, resembles the isomeric acid in its behaviour during nitration, yielding initially an additive product which is transformed by pyridine into a mixture of isomeric nitroanthracene-carboxylic acids which has not been separated into its components. On the other hand, it is transformed by bromine into a *dibromo-anthracene-2-carboxylic acid*, m. p.  $335^{\circ}$  (decomp.). 9-Anthrone-2-carboxylic acid is converted by acetic anhydride and pyridine into its *acetyl* derivative, m. p.  $253-255^{\circ}$  (decomp.), which is transformed by nitration and subsequent acetylation of the product into *10-nitro-9-acetoxyanthracene-2-carboxylic acid*, m. p.  $228^{\circ}$  (decomp.), after previous softening. H. W.

**2 : 4-Dihydroxybenzoyl-o-benzoic Acid and some of its Derivatives.** W. R. ORNDORFF and E. KLINE [with C. V. SHAPIRO] (*J. Amer. Chem. Soc.*, 1924, **46**, 2276-2291).—2 : 4-Dihydroxybenzoyl-o-benzoic acid, m. p.  $208-209^{\circ}$  (decomp.), is obtained in 68% yield by heating phthalic anhydride with resorcinol at  $126^{\circ}$ , the use of boric acid (Fischer and Bollmann, A., 1922, i, 936) being unnecessary. The acid is also obtained (in 89.5% yield) by decomposition of fluorescein with sodium hydroxide, whilst on heating above its melting point the acid is converted into fluorescein, phthalic anhydride, and water. The  $\gamma$ -fluorescein described by Liebig (A., 1912, i, 376) was not obtained, but the reactions prove that the formation of fluorescein takes place in two stages, the intermediate product being 2 : 4-dihydroxybenzoyl-o-benzoic acid, which is colourless when pure, and melts to a red liquid. Contrary to Baeyer's statement, well-crystallised *ammonium*, *sodium*, *potassium*, *silver*, *barium*, *calcium*, *zinc* (m. p.  $80-90^{\circ}$ ), and *lead* salts have been prepared, to which the ketonic structure,  $(\text{OH})_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{M}$ , is assigned, the lactone structure,  $(\text{OH})_2\text{C}_6\text{H}_3\cdot\underset{\text{O}-\text{CO}}{\text{C}(\text{OH})\cdot\text{C}_6\text{H}_4}$ , being attributed to the free

acid (cf. Orndorff and Kelley, A., 1922, i, 833). On heating with acetic anhydride and sodium acetate, the acid is converted into a colourless *triacetate*,  $\text{C}_{14}\text{H}_7\text{O}_5\text{Ac}_3$ , m. p.  $134-135^{\circ}$ , and not a diacetate as stated by Liebig (*loc. cit.*), which is readily hydrolysed by alcoholic sodium hydroxide, yielding the dihydroxy-acid and a small quantity of a reddish-brown substance probably identical with the orange *anhydride*,  $\text{C}_{14}\text{H}_8\text{O}_4$ , m. p. above  $350^{\circ}$ , obtained by the action of thionyl chloride on either the crude yellow or the pure dihydroxy-acid. The orange anhydride gives a deep red solution in sodium hydroxide which does not yield the dihydroxy-acid on boiling. The anhydride appears to give an acetate with acetic anhydride. The annexed formula is suggested for this anhydride. By treatment with excess of acetic anhydride the dihydroxy-acid yields the *anhydride* of the monoacetate described by Fischer and Bollmann (*loc. cit.*),  $\text{C}_{14}\text{H}_7\text{O}_4\text{Ac}$ , m. p.  $135-136^{\circ}$  (from glacial acetic acid), which when crystallised from dilute acetic acid yields Fischer and Bollmann's



*yy\**



monoacetate, m. p. 161—162°. Dilute ethyl and methyl alcohol similarly convert the anhydride into the *ethyl* ester, m. p. 62—66°, and *methyl* ester, m. p. 110°, respectively. This anhydride has the structure  $\text{OAc} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} - \text{CO} \\ \text{CO} - \text{C}_6\text{H}_4 \end{smallmatrix}$ . The monoacetate itself could not

be obtained by acetylation with acetic anhydride, whilst with acetyl chloride the crude yellow dihydroxy-acid yields the *diacetate* of 2 : 4-dihydroxybenzoyl-*o*-benzoic anhydride, m. p. above 350°, together with a small quantity of an isomeric substance,  $(\text{C}_{14}\text{H}_8\text{O}_2)_2\text{Ac}_2\text{O}$ , which does not melt below 300°. The diacetate dissolves in sodium hydroxide, giving a deep purple solution, from which, on boiling, the orange anhydride,  $\text{C}_{14}\text{H}_8\text{O}_4$ , described above, together with a little dihydroxy-acid, is precipitated, and not the anhydride,  $(\text{C}_{14}\text{H}_9\text{O}_4)_2\text{O}$ , as stated by Graebe. The pure dihydroxy-acid on similar treatment yields a colourless *substance*,  $(\text{C}_{14}\text{H}_7\text{O}_4\text{Ac})_2$ , m. p. 291—293° (decomp.), practically insoluble in sodium hydroxide and yielding on boiling the dihydroxy-acid with only a small amount of the orange anhydride. Esterification of the dihydroxy-acid in the presence of sulphuric acid yields the *ethyl* ester, m. p. 133—134° (cf. Tambor, A., 1910, i, 558), and *methyl* ester, m. p. 191—192°. 2 : 4-Dihydroxybenzoyl-*o*-benzoic acid yields a *phenylhydrazone*,  $\text{C}_{20}\text{H}_{14}\text{O}_3\text{N}_2$  (+EtOH, lost at 130°), m. p. 260—261°, whilst on bromination in glacial acetic acid 3 : 5-dibromo-2 : 4-dihydroxybenzoyl-*o*-benzoic acid, m. p. 224° (decomp.; cf. Heller, A., 1895, i, 235; Meyer, A., 1897, i, 69), is obtained, which on heating above its m. p. is converted into eosin and phthalic anhydride, and on heating with resorcinol and zinc chloride at 160—180° yields *as*-dibromofluorescein. Dry ammonia converts the dibromo-acid into the unstable *triammonium* salt,  $\text{C}_{14}\text{H}_8\text{Br}_2\text{O}_5 + 3 \cdot 5\text{NH}_3$ , which loses 2 mols. of ammonia in a vacuum and the remaining 1.5 mols. in a current of air at 85°. The dibromo-acid forms a *triacetate*,  $\text{C}_{14}\text{H}_5\text{Br}_2\text{O}_5\text{Ac}_3$ , m. p. 179—182°, and the *anhydride* of a monoacetate,  $\text{C}_{14}\text{H}_5\text{Br}_2\text{O}_4\text{Ac}$ , m. p. 200—201° (decomp.). On heating with acetyl chloride, the dibromo-acid yields 3 : 5-dibromo-2 : 4-diacetoxybenzoyl-*o*-benzoic anhydride, m. p. 218°.

R. B.

**Bile Acids. XI.** M. SCHENCK (*Z. physiol. Chem.*, 1924, **139**, 39—51).—The triketotricarboxylic acid,  $\text{C}_{24}\text{H}_{32}\text{O}_9$ , obtained by oxidation of *isobilianic* acid (this vol., i, 179) is termed *bilisoidanic acid*; it reacts with hydroxylamine to form an amorphous monoxide. On reduction with zinc and acetic acid, dichloromono-deoxybilianic acid (Pregl, A., 1903, i, 318) gives a small yield of deoxybilianic acid; this establishes the position of the chlorine atoms in the former substance.

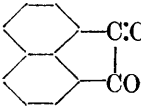
E. S.

**Compounds of Piperonal and Acetic Anhydride.** W. P. JORISSEN and P. A. A. VAN DER BEEK (*Rec. trav. chim.*, 1924, **43**, 586—590).—The fusion curve of piperonal and acetic anhydride up to 60 mol. % of the latter shows no sign of a compound. When the compounds are heated together at 100° for 24 hours in presence of a trace of hydrobromic acid or phosphorus trichloride (cf.

Blanksma, A., 1910, i, 680) a fusion curve is obtained which shows that, besides a 1 : 1 molecular compound, there also exists a labile compound of 2 mols. of piperonal and 1 mol. of acetic anhydride.

W. E. E.

**Reaction of Aldehydes. III.** R. DE FAZI (*Gazzetta*, 1924, 54, 658—667; cf. A., 1921, i, 568).—With piperonal, cuminaldehyde, *m*-tolualdehyde, cinnamaldehyde, *p*-dimethylaminobenzaldehyde, and furfuraldehyde, fluorene yields unsaturated condensation products which give various colorations with concentrated sulphuric acid, but on reduction form compounds giving no such coloration. Acenaphthene does not yield condensation products with these cyclic aldehydes under the conditions employed by the author, but acenaphthenone reacts with such aldehydes in presence of sodium hydroxide, the resulting compounds giving violet-red colorations with concentrated sulphuric acid. These compounds cannot, however, be formed when acenaphthene and cyclic aldehydes are placed in contact with sulphuric acid, since such conditions lead neither to the formation of acenaphthenone nor, if the latter is added, to the formation of either condensation products or coloration. The results obtained with indones (A., 1921, ii, 357) show that, with some organic compounds containing closed nuclei, the same coloration with sulphuric acid may be determined by the presence of the cyclostatic group  $-\text{CO}\cdot\text{CH}\cdot\text{CH}-$  as by  $-\text{CH}_2\cdot\text{CH}\cdot\text{CH}-$ .

  $\text{C}\cdot\text{CH}\cdot\text{C}_6\text{H}_5 < \begin{smallmatrix} \text{O} \\ \diagup \diagdown \end{smallmatrix} > \text{CH}_2$  Piperonylideneacenaphthenone (annexed formula) forms canary-yellow needles, m. p. 159—160°; 4-hydroxy-3-methoxybenzylideneacenaphthenone,  $\text{C}_{20}\text{H}_{14}\text{O}_3$ , from acenaphthenone and vanillin, m. p. 149—150°; *p*-methoxybenzylideneacenaphthenone,  $\text{C}_{20}\text{H}_{14}\text{O}_2$ , from anisaldehyde, canary-yellow needles, m. p. 97—98°; cinnamylideneacenaphthenone,  $\text{C}_{21}\text{H}_{14}\text{O}$ , yellow needles, m. p. 167—168°; *p*-dimethylaminobenzylideneacenaphthenone, garnet-red, stellar aggregates of needles, m. p. 158—160°, and furfurylideneacenaphthenone,  $\text{C}_{17}\text{H}_{10}\text{O}_2$ , golden-yellow prisms, m. p. 142—143°.

T. H. P.

**The Systems, Aldehydes—Organic Acids and Ketones—Organic Acids.** M. PASSERINI (*Gazzetta*, 1924, 54, 672—682).—The suggestion that, in the reaction of a carbylamine with an aldehyde or ketone in presence of an organic acid, the aldehyde or ketone first forms with the organic acid a labile additive compound (cf. A., 1922, i, 731) is verified by : (1) the electrical conductivities of mixtures of acetone with acetic acid, a minimum value being shown by the mixture containing the components in about molecular proportions; (2) the results of thermal analysis of the three systems formed by benzoic acid with *m*-nitrobenzaldehyde, piperonal, and benzil, respectively. These conclusions are in accord with those of Kendall and Brakeley (A., 1922, ii, 126).

T. H. P.

**Carbylamines. XI. Reaction of Phenylcarbylamine with Anil Derivatives of Aromatic *o*-Hydroxyaldehydes.** M. PASSERINI (*Gazzetta*, 1924, 54, 667—671).—In the formation of dianil

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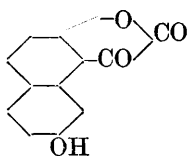
derivatives by the interaction of aromatic hydroxy compounds with carbylamines (cf. this vol., i, 57, 751 and succeeding abstract), either the carbylamine may act in its dimeric form,  $(\text{NR}:\text{C})_2$ , or there may be two distinct stages, the anil derivative of the hydroxy-aldehyde being formed first. The former of these interpretations is excluded by the observation that benzeneazophenylcarbylamine, which reacts in the same way as phenylcarbylamine with  $\beta$ -naphthol, has the simple molecular weight in freezing benzene. That the second explanation is the true one is shown by the formation of the dianil derivative of 2-hydroxy-1-naphthylglyoxal from phenylcarbylamine and the anil derivative of 2-hydroxy-1-naphthaldehyde, and by that of the dianil derivative of *o*-hydroxyphenylglyoxal from salicylideneaniline and phenylcarbylamine; benzylideneaniline does not, however, react with phenylcarbylamine under the conditions used.

The reaction between phenylcarbylamine and naphthols or phenol is evidently determined by the presence of the hydroxyl group, which imparts special properties to the methinic group in the ortho position; the same influence is probably exerted by the hydroxyl group of the anil derivatives of the hydroxyaldehydes.

T. H. P.

**Carbylamines. X. Reaction of Aromatic Carbylamines with Naphthols and with Phenols.** M. PASSERINI (*Gazzetta*, 1924, 54, 633—640).—The action of phenylcarbylamine on various hydroxy derivatives of benzene and naphthalene has been investigated (cf. this vol., i, 57, 751). With 2:7-dihydroxynaphthalene, the reaction is similar to that occurring with  $\beta$ -naphthol, 2 mols. of the carbylamine and 1 mol. of the hydroxy compound interacting; no tetra-anil is obtained. Phenol, thymol, and resorcinol also react with phenylcarbylamine, but the products formed are syrupy, and only in the first case could a small amount of the dianil be separated. The reaction proceeds well with  $\beta$ -naphthol and benzeneazophenylcarbylamine.

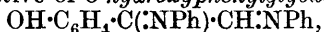
The dianil derivative of 2:7-dihydroxy-1-naphthylglyoxal,  $\text{C}_{10}\text{H}_5(\text{OH})_2\cdot\text{C}(\text{NPh})\cdot\text{CH}\cdot\text{NPh}$ , obtained from 2:7-dihydroxynaphthalene and phenylcarbylamine, forms pale yellow needles, m. p. 174—176°, and its dibenzoyl derivative,  $\text{C}_{38}\text{H}_{26}\text{O}_4\text{N}_2$ , orange-red crystals, m. p. 154—156° (decomp.). Phenylhydrazine converts the dianil into 2:7-dihydroxy-1-naphthylglyoxal diphenylhydrazone,  $\text{C}_{10}\text{H}_5(\text{OH})_2\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$ , m. p. 220° (decomp.), and, when boiled with potassium hydroxide solution, the anil yields the lactone of 2:7-dihydroxy-1-naphthylglyoxylic acid (annexed formula), which has a distinctly acid reaction and forms lustrous, yellow crystals, decomp. 280—282°; 2:7-dihydroxynaphthalene-1-carboxylic acid, obtained by oxidising this lactone with hydrogen peroxide in acetic acid solution, has m. p. 275°.



The dibenzeneazoanil derivative of 2-hydroxy-1-naphthylglyoxal,  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{C}(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NPh})\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$ , forms minute, dark-

red crystals, m. p.  $263^{\circ}$ , and is converted by phenylhydrazine into 2-hydroxy-1-naphthylglyoxal diphenylhydrazone (cf. this vol., i, 57).

The *dianil* derivative of *o*-hydroxyphenylglyoxal,



obtained from phenol and phenylcarbylamine, yellow needles, m. p.  $150$ — $152^{\circ}$ , yields *o*-hydroxyphenylglyoxal diphenylhydrazone when treated with phenylhydrazine.

T. H. P.

**Catalytic Reduction of Oximes in the Presence of Colloidal Palladium.** W. GULEWITSCH.—(See i, 1285.)

**Magnesium Acetylenyl Bromide.** J. SALKIND and A. ROSENFELD.—(See i, 1291.)

**Electrolytic Reduction of Piperitone.** A. R. PENFOLD and F. R. MORRISON (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 215—217).—An almost quantitative yield of isomenthone is obtained by the electrolytic reduction of piperitone. [Cf. *B.*, 1924, 926.]

W. T. K. B.

**Phenacyl Mercaptan and Related Substances.** B. GROTH (*Arkiv Kem., Min., Geol.*, 1924, **9**, No. 1, 1—63).—The preparation of phenacylmercaptan by several methods is described; a number of its derivatives and certain phenacylthiocarbonates were also prepared.

The interaction of phenacyl bromide and sodium hydrogen sulphide solution at  $15^{\circ}$  gives only 13% of the theoretical yield of phenacyl mercaptan, together with diphenacyl sulphide. Phenacyl bromide with Bender's salt in aqueous alcohol at  $0^{\circ}$  gives *S*-phenacyl *O*-ethyl thiocarbonate,  $\text{C}_{11}\text{H}_{12}\text{O}_3\text{S}$ , b. p.  $152^{\circ}/1.6$  mm.,  $175$ — $176^{\circ}/3$  mm.,  $d_4^{15}$  1.1948,  $n_D^{15}$  1.554; *semicarbazone*, m. p.  $142$ — $143^{\circ}$ ; with potassium xanthate it gives *S*-phenacyl *O*-ethyl dithiocarbonate, m. p.  $32^{\circ}$  (*phenylhydrazone*, m. p.  $64^{\circ}$ ); with potassium trithiocarbonate it gives phenacyl trithiocarbonate,  $(\text{COPh}\cdot\text{CH}_2\cdot\text{S})_2\text{CS}$  (yield 90%), obtained in two forms, m. p.  $103$ — $104^{\circ}$  and m. p.  $110^{\circ}$ ; *bisphenylhydrazone*, m. p.  $139$ — $140^{\circ}$ , after keeping, m. p.  $146$ — $147^{\circ}$ . Alkaline hydrolysis of these thiocarbonates, under varying conditions, gave no phenacyl mercaptan, showing the sulphur atom to be loosely attached to the phenacyl group. Boiling 20% nitric acid with the third ester gave benzoic acid and at  $60$ — $70^{\circ}$  gave *SS*-diphenacyl dithiocarbonate, m. p.  $98^{\circ}$ ; *bisphenylhydrazone*, m. p.  $162^{\circ}$  (decomp.).

Phenacyl bromide reacts with potassium carbothiolonglycollate solution at  $0^{\circ}$ , forming phenacyl trithiocarbonate and phenacyl-carbothiolonglycollic acid,  $\text{COPh}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $107^{\circ}$ , which is precipitated by acidification of the filtrate; it forms acid sodium and potassium salts; calcium (+4 $\text{H}_2\text{O}$ ), strontium (+5 $\text{H}_2\text{O}$ ), barium (+2 $\text{H}_2\text{O}$ ), cupric, lead, magnesium, and zinc salts; methyl ester, m. p.  $76^{\circ}$ ; ethyl ester, m. p.  $51^{\circ}$ ; phenylhydrazone, m. p.  $119$ — $120^{\circ}$ . Hydrolysis with acetic acid gave a good yield of phenacyl mercaptan. Hydrolysis with sodium carbonate gave diphenacyl disulphide, and acetophenone or phenacyl trithiocarbonate according to the conditions; alcoholic potassium hydroxide gave potassium

carbothiolonglycollate (cf. Ahlqvist, A., 1919, i, 435). Oxidation of phenacylcarbothiolonglycollic acid with neutral permanganate gives *phenacylcarbothiolglycollic acid*,  $\text{COPh}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CO}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $77^\circ$  (yield 80%); acid *sodium* salt; *barium* salt ( $+3\text{H}_2\text{O}$ ); *phenylhydrazone*, m. p.  $136\text{--}137^\circ$ . By the action of water or weak acid, this also gave phenacyl mercaptan, yield 68%.

Potassium dithiocarbaminoacetate (cf. Körner, A., 1908, i, 509) with phenacyl bromide forms *phenacyldithiocarbaminoacetic acid*,  $\text{COPh}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $103^\circ$  (yield 88%); *sodium* salt ( $+2\text{H}_2\text{O}$  and  $+7\text{H}_2\text{O}$ ). With alkali, it gives a 54% yield of phenacyl mercaptan. By (a) heating at  $119^\circ$ , (b) steam distillation, or, best, (c) action of acetic acid on the sodium salt solution at  $95\text{--}100^\circ$ , water is eliminated, forming 2-thion-4-phenylthiazoline-3-acetic acid,  $\text{PhC}\cdot\text{CH}\cdot\text{S}\cdot\text{CS}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ; *sodium* salt ( $+3\frac{1}{2}\text{H}_2\text{O}$ ); *barium* salt ( $+2\text{H}_2\text{O}$  and  $+7\text{H}_2\text{O}$ ); *methyl* ester, m. p.  $115\text{--}116^\circ$ ; *ethyl* ester, m. p.  $72\text{--}73^\circ$ .

By decomposition of sodium phenacylcarbothiolonglycollate with acetic acid at  $80\text{--}95^\circ$ , *phenacyl mercaptan*,  $\text{COPh}\cdot\text{CH}_2\cdot\text{SH}$ , m. p.  $23\text{--}24^\circ$ , b. p.  $103^\circ/1\cdot5\text{ mm.}$ ,  $116\text{--}118^\circ/4\text{ mm.}$ ,  $140\text{--}142^\circ/16\text{--}18\text{ mm.}$ ,  $n_D^{20} 1\cdot594$ ,  $d_4^{25} 1\cdot1713$ , is obtained in 70% yield; *semicarbazone*, m. p.  $164\text{--}165^\circ$ ; *phenylhydrazone*, m. p.  $90\text{--}91^\circ$ ; *oxime*, m. p.  $70^\circ$ . It behaves as a pseudo-acid and its *sodium* salt may have the structure  $\text{S}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{ONa}$ , but only one benzoyl derivative

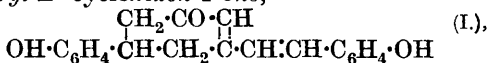
could be obtained. *Phenacyl thiobenzoate*, m. p.  $84\text{--}85^\circ$ , was also synthesised from potassium thiobenzoate and phenacyl bromide; *phenylhydrazone*, m. p.  $108^\circ$ . Reduction of the mercaptan by Clemmensen's method gives ethylbenzene. With alcoholic lead acetate, it gives *lead phenacyl sulphide* (gradual decomp.). With phenacyl bromide and sodium ethoxide, *diphenacyl sulphide*, m. p.  $77^\circ$ , is formed. The mercaptan has a simple molecule and does not polymerise, alone or with zinc; condensation products are formed by the action of calcium chloride. Alcoholic hydrochloric acid converts it into 2 : 5-diphenyl-1 : 4-dithiine, m. p.  $118^\circ$ . This, or phenacyl mercaptan with ethyl mercaptan in presence of hydrochloric acid, gives a condensation product, m. p.  $161^\circ$ , either 2 : 5-diethylmercapto-2 : 5-diphenyl-1 : 4-dithiane or 3 : 6-diethylmercapto-2 : 5-diphenyl-1 : 4-dithiane. Similarly, phenacyl and benzyl mercaptans interact, forming a compound,  $\text{C}_{30}\text{H}_{28}\text{S}_4$ , m. p.  $216\text{--}217^\circ$  (on rapid heating) or  $206\text{--}207^\circ$  (slow heating). The properties of phenacyl mercaptan are compared with those of hydroxyketones.

In the above experiments, the yield of mercaptan was ascertained by oxidising its solution with iodine in the presence of potassium iodide to *diphenacyl disulphide*, m. p.  $81^\circ$  (yield 90%); *bisphenylhydrazone*, m. p.  $150^\circ$ . When potassium acts on alcoholic diphenacyl disulphide, ether precipitates the *dipotassium* salt, from which acid liberates a *dienol* form, m. p.  $168\text{--}170^\circ$  (or  $135^\circ$  on rapid heating); the *dibenzoyl* derivative, m. p.  $168^\circ$ , is hydrolysed to benzoic acid and is regarded as bis- $\beta$ -hydroxystyryl  $\alpha\alpha'$ -disulphide. The action of potassium on alcoholic diphenacyl disulphide gives, after 2 weeks,

*diphenacyl*, m. p. 144—145°. The disulphide is more unstable than the mercaptan, sulphur being readily removed by the action of alkali, whilst silver nitrate precipitates silver sulphide. F. M. H.

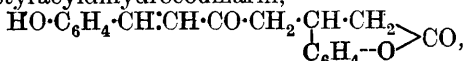
**Isomerism of the Styryl Alkyl Ketones. I. Isomerism of 2-Hydroxystyryl Methyl Ketone.** A. MCGOOKIN and I. M. HEILBRON (*J. Chem. Soc.*, 1924, 125, 2099—2105).—The yellow 2-hydroxystyryl methyl ketone prepared according to Harries (A., 1892, 169) does not condense with gentisaldehyde, but is converted into the colourless isomeride, m. p. 139°, described by Tiemann and Kees (A., 1885, 1074). Protocatechualdehyde, *p*-hydroxybenzaldehyde, or vanillin also brings about the conversion. Vanillin gives a nearly theoretical yield of pure substance. Exposure of an alcoholic solution of the yellow form to the light of a quartz mercury lamp causes complete isomerisation. The colourless isomeride condenses with salicylaldehyde to form 2 : 2'-dihydroxydistyryl ketone, yellow needles, m. p. 159°; Decker and Felsler (A., 1908, i, 906) found m. p. 168°. On methylation, 2-methoxystyryl methyl ketone is formed, m. p. 50°, identical with that prepared from the yellow isomeride. The sodium salt was obtained in golden-coloured crystals. An attempt to prepare the sodium salt of the yellow isomeride by treatment of the ketone with alcoholic sodium ethoxide and fractional precipitation of the crimson reaction liquid with chloroform resulted in the separation of (i) lustrous bottle-green crystals of the sodium salt of 2 : 2'-dihydroxydistyryl ketone, (ii) an orange salt, (iii) golden-yellow crystals, and (iv) a pale yellow salt, the sodium derivative of salicylaldehyde. The orange salt is probably the sodium salt of the yellow isomeride, although on dissolving in water and acidifying the solution only the colourless isomeride was obtained. The oxime, semicarbazone, and phenylhydrazone of the colourless ketone are identical with those obtained from the yellow isomeride. The isomerism is considered to be of the *cis-trans* type, the yellow isomeride being the *cis*-form. It is the more labile and tends to disrupt in presence of alkali. In all cases where isomeric styryl ketones have been obtained the isomerides have identical m. p., and one form appears to pass into the other at or just below the m. p. The colourless isomerides of 5-bromo-2-hydroxystyryl methyl ketone and 3-methoxy-4-hydroxystyryl methyl ketone were prepared from the yellow forms by methods similar to the above. The yellow form of 4 : 5-methylenedioxydistyryl methyl ketone, m. p. 107° (Haber, A., 1891, 704), on purification had m. p. 110—111°, identical with that of the colourless variety. A. C.

**Interaction of Ethyl Acetoacetate and *o*-Hydroxydistyryl Ketones.** I. M. HEILBRON and T. A. FORSTER (*J. Chem. Soc.*, 1924, 125, 2064—2068; cf. this vol., i, 413).—3-*o*-Hydroxyphenyl-5-*o*-hydroxystyryl- $\Delta^5$ -cyclohexen-1-one,



m. p. 240° (with 1 mol. of methyl alcohol), was prepared by condensing 2 : 2'-dihydroxydistyryl ketone with ethyl acetoacetate in

aqueous sodium hydroxide solution. It was accompanied by 4-*o*-hydroxystyracyldihydrocoumarin,



m. p. 235°, *methyl ether*, m. p. 130°. The hexenone gives a deep red, the coumarin only a pale yellow coloration with concentrated sulphuric acid. 3-*o*-Methoxyphenyl-5-*o*-methoxystyryl- $\Delta^5$ -cyclohexen-1-one, m. p. 128°, was obtained on methylating the corresponding dihydroxycyclohexenone. 2 : 2'-Dimethoxydistyryl ketone, m. p. 127°, condenses with sodium ethyl acetoacetate in boiling alcohol forming *ethyl* 3-*o*-methoxyphenyl-5-*o*-methoxystyryl- $\Delta^5$ -cyclohexen-1-one-2-carboxylate, m. p. 159°. The carbethoxy group could not be removed by either acid or alkali. 3-*o*-Hydroxyphenyl-5-*o*-methoxystyryl- $\Delta^5$ -cyclohexen-1-one, m. p. 172°, was similarly prepared from 2'-methoxy-2-hydroxydistyryl ketone. Its methyl ether is identical with the dimethyl ether of I. *Ethyl* 3-*o*-methoxyphenyl-5-*o*-hydroxystyryl- $\Delta^5$ -cyclohexen-1-one-2-carboxylate, m. p. 159—161°, was obtained from the alkaline filtrate of the above hexenone. 2-Acetyl-3-*o*-methoxyphenyl-5-*o*-methoxystyryl- $\Delta^5$ -cyclohexen-1-one, m. p. 174°, was prepared by condensing 2 : 2'-dimethoxydistyryl ketone with acetylacetone. On heating it with a mixture of potassium methoxide and hypiodite, the acetyl group was split off and a methyl ether obtained identical with that from I. A. C.

**Chalkones and Hydrochalkones.** V. TOGNAZZI (*Gazzetta*, 1924, 54, 697—704; cf. Bargellini, A., 1912, i, 118; 1913, i, 59, 90; 1914, i, 1074; 1915, i, 19).—When reduced by means of hydrogen in presence of platinum or palladium black, chalkones usually undergo hydrogenation at the double linking, but not at the carbonyl group, the only two known exceptions to this rule being 2 : 4 : 6-trimethoxyphenyl 3 : 4-dimethoxystyryl ketone, which yields 2 : 4 : 6 : 3' : 4'-pentamethoxy- $\alpha$ -diphenylpropane, and 4 : 6-dimethoxy-2-ethoxyphenyl 3 : 4-dimethoxystyryl ketone, which also yields the corresponding propane derivative (cf. Freudenberg, A., 1920, i, 752). Of a number of other chalkones examined by the author, only one, namely, furfurylidene-2 : 4 : 5-trimethoxyacetophenone, appears to absorb more than 2 atoms of hydrogen per molecule, but the product of the reaction was resinous and could not be purified. Certain compounds analogous to the chalkones, such as distyryl ketone, also seem to absorb, in presence of platinum black, more hydrogen than is required by the double linkings.

*p*-Methoxyphenyl *p*-methoxystyryl ketone (4 : 4'-dimethoxychalkone), prepared from anisaldehyde and *p*-methoxyacetophenone, has m. p. 100—102°, and *p*-methoxyphenyl  $\beta$ -*p*-methoxyphenylethyl ketone has m. p. 29—31°.

4'-Methoxy-3 : 4-dioxymethylenechalkone [*p*-anisyl piperonylidene-methyl ketone], from *p*-methoxyacetophenone and piperonaldehyde (cf. Scholtz and Meyer, A., 1910, i, 562), gives *p*-anisyl piperonylethyl ketone,  $\text{C}_{17}\text{H}_{16}\text{O}_4$ , m. p. 56—58°, on reduction in presence of platinum black.

*p*-Anisyl furfurylidenemethyl ketone,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_4\text{H}_3\text{O}$ , from *p*-methoxyacetophenone and furfuraldehyde, m. p.  $79-81^\circ$ , yields an oily reduction product. 2 : 4 : 5-Trimethoxyphenyl furfurylidenemethyl ketone has m. p.  $116-118^\circ$ .

2-Hydroxy-4-methoxyphenyl piperonylidenemethyl ketone (piperonalpaeonol; cf. Emilewicz and von Kostanecki, A., 1899, i, 368) gives 2-hydroxy-4-methoxyphenyl piperonylethyl ketone,  $\text{C}_{17}\text{H}_{16}\text{O}_5$ , white needles, m. p.  $85-87^\circ$ , on reduction.

2' : 4' : 5'-Trimethoxy-3 : 4-dioxymethylenechalkone has m. p.  $186-188^\circ$  (cf. Bargellini and Avrutin, A., 1911, i, 68), and 2 : 4 : 5-trimethoxyphenyl piperonylethyl ketone,  $\text{C}_{19}\text{H}_{20}\text{O}_6$ , has m. p.  $131-133^\circ$ .  
T. H. P.

**Functions of Chromophores. X. The Quinone Chromophore. II.** J. LIFSCHITZ [with J. ZIMMERMANN, H. LOURIE, and G. A. TEN BOKKEL-HUININK] (*Rec. trav. chim.*, 1924, **43**, 403—419).—All groups which contain a cross-conjugated system of unsaturated linkings may be regarded as quinonoid chromophores. This structure, rather than its diketonic nature, determines the chromophoric character of the quinone in the narrow sense; the central carbon atom is the source of the colour. This conception permits of a single explanation of the optical properties of dyes and their relationship to the quinones (cf. this vol., i, 654).

H. J. E.

**Functions of Chromophores. XI. The Quinone Chromophore. III.** J. LIFSCHITZ (*Rec. trav. chim.*, 1924, **43**, 654—670).—The views previously developed (this vol., i, 654 and preceding abstract) on the subject of the *p*-quinone chromophore are successfully applied in the discussion of the molecular compounds of quinone, the halochromism of triphenylmethane derivatives and ketones and of free radicals. The views of earlier workers in these fields are critically discussed.

W. E. E.

**Colour of the Simple Quinoneimines and their Salts. II. Some New Quinoneimines and their Stability.** B. CORDONE (*Helv. Chim. Acta*, 1924, **7**, 956—964; cf. this vol., i, 214).—Quinoneimines are particularly prone to two reactions and, according to circumstances, one of the two is generally favoured to the exclusion of the other. Hydrolysis to the corresponding quinone in presence of water is slow at the ordinary temperature, but at the boiling point the action is rapid and quantitative. The more heavily the nucleus is substituted by alkyl groups, the more rapid is the hydrolysis. The tendency to polymerise is affected by light, temperature, and the presence of acids, but chiefly by the number of substituent alkyl groups. The presence of even a single alkyl group in the nucleus of a quinoneimine will greatly lessen its tendency to polymerise, particularly if it is adjacent to the imino group. The effect of acids varies. In ether solution, and more especially in the dry state, anhydrous acids cause polymerisation. The tendency of the quinoneimine bases to "quinonise" in the presence of water is changed by acid to a tendency to polymerise.



On the other hand, homologues of benzoquinoneimines containing in the nucleus at least two alkyl groups and hence possessing relatively little tendency to polymerise are caused to "quinonise" by mineral acids in aqueous solution. The hydrochlorides undergo this change more easily than the sulphates. The picrates of the quinoneimines polymerise like the free bases, but more slowly: picric acid has no hydrolysing effect, but retards condensation. *Thymoquinone-di-imine* is obtained in ethereal solution by oxidising *p*-diaminocymene with silver oxide; the *monopicrate* exists in a yellow and a red form. In aqueous solution, the sulphate and the chloride readily form the quinone. The sulphate liberates iodine from potassium iodide. Toluquinone-2-imine, from *p*-amino-*m*-cresol, is easily isolated and may be preserved for a long time. The *monopicrate* (two forms) is more stable than the base. No other mono-salt is obtainable, but the yellow solution of the di-salt in concentrated sulphuric acid is stable. The aqueous solution of the base is stable unless heated, when the quinone is formed. Toluquinone-3-imine, from *p*-amino-*o*-cresol, is too unstable to be isolated. All the mono-salts polymerise immediately except the picrate, which exists in a yellow, amorphous form and a dense, red, crystalline form.

W. E. E.

**Colour and Constitution. IX.** F. KEHRMANN (*Helv. chim. Acta*, 1924, 7, 964—968; cf. A., 1922, ii, 333).—In view of Piccard's observation (A., 1913, i, 895) that certain quinonedi-imines, particularly the oxidation product of *p*-dimethylaminodiphenylamine, give di-salts lighter in colour than their mono-salts, the rule previously formulated must be modified to this: "If the unsaturation persists after salt formation, the addition of acids to unsaturated groupings results most frequently in a deepening of colour, even if tervalent nitrogen becomes quinquevalent. This deepening occurs regularly if the chromophore is open to the attack of the acid only at one point. When two basic groups are present, the neutralisation of the first leads to a deepening, whilst that of the second may, exceptionally, cause a lightening of the colour."

The mono-salts of the quinonedi-imines under discussion are reddish-violet, the di-salts reddish-orange; Piccard's observations on the colour of these salts are incorrect.

W. E. E.

**Derivatives of Arylamino-mercaptanaphthaquinones.** FARBWERKE VORM. MEISTER, LUCIUS, UND BRÜNING (D.R.-P. 386998; from *Chem. Zentr.*, 1924, i, 2634).—The derivatives are prepared by treating 3-chloro-2-arylamino-1:4-naphthaquinone derivatives with alkali sulphides. Thus, 3-chloro-2-anilino-1:4-naphthaquinone (from 2:3-dichloro-1:4-naphthaquinone and aniline) is boiled for a short time with sodium sulphide to give a blue solution of the sodium salt of 2-anilino-3-mercapto-1:4-naphthaquinone, from which hydrochloric acid precipitates the dark violet mercaptan, which is converted by atmospheric oxidation into benzonaphthoparathiazinequinone. On heating 2:3-dichloro-1:4-naphthaquinone with aceto-*p*-phenylenediamine, 3-chloro-2-*p*-acetamido-

*phenylamino-1:4-naphthaquinone* is obtained as red crystals, m. p.  $271^{\circ}$ ; this yields the corresponding *mercapto* compound, which is oxidised by the air to the corresponding green *p-thiazine*; this is further oxidised by hydrogen peroxide to the brownish-red *sulphoxide* of an *acetamidobenzonaphthoparathiazinequinone*.

F. A. M.

**Photochemical Behaviour of Methylantraquinones.** A. SCHAARSCHMIDT and K. KASAI (*Ber.*, 1924, 57, [B], 1671—1673).—Methylantraquinones may be arranged in the following order of decreasing sensitiveness towards light: 4-chloro-1-methylantraquinone, 2-methylantraquinone, 3-bromo-2-methylantraquinone, 1-nitro-2-methylantraquinone, 1-methylantraquinone, 3-chloro-2-methylantraquinone, 1-chloro-2-methylantraquinone, 1-chloro-2-dibromomethylantraquinone, 1:3-dimethylantraquinone. 1:3-Dimethylbenzophenone is not appreciably altered by exposure to light. Since 4-chloro-1-methylantraquinone becomes similarly altered when illuminated in an atmosphere of nitrogen or in a high vacuum, the change is considered to consist in a transformation into a coloured quinonoid modification which is not completely converted into the original form when rapidly crystallised from alcohol.

H. W.

**Tetrahydroxydimethylantraquinone.** G. FLUMIANI (*Monatsh.*, 1924, 45, 43—49).—Two compounds prepared by Brunner (*ibid.*, 1881, 2, 466) are shown to be 1:4:5:8-tetrahydroxy-2:6-dimethylantraquinone and 2:6-dimethylantracene. Brunner's starting point is now recognised as 3:6-dihydroxy-*p*-toluic acid (Schmid, A., 1911, i, 780; Herrmann, A., 1877, ii, 319; Baeyer, A., 1886, 445). By treatment with concentrated sulphuric acid at  $120$ — $130^{\circ}$ , it gives a heterogeneous solid which after many recrystallisations from ethyl benzoate yields 1:4:5:8-tetrahydroxy-2:6-dimethylantraquinone, a red powder; when heated slowly it sinters at  $200^{\circ}$  and sublimes, with slight charring, from  $260^{\circ}$ ; on rapid heating, m. p.  $290$ — $300^{\circ}$  with sublimation. Benzoic anhydride at  $130$ — $135^{\circ}$  converted it into a *dibenzoyl* derivative, white needles, m. p.  $220^{\circ}$ . Boiling acetic anhydride, with sodium acetate, formed the *tetra-acetyl* derivative, m. p.  $235$ — $236^{\circ}$  (yield 50%). Distillation of the tetrahydroxy compound with zinc dust in a current of hydrogen gave 2:6-dimethylantracene (yield 20%); m. p.  $242$ — $243^{\circ}$ , after many recrystallisations. This is oxidised by chromic acid in acetic acid solution to 2:6-dimethylantraquinone.

F. M. H.

**Formulae of Dicyclic Terpenes.** C. SLAWINSKI (*Bull. Soc. chim.*, 1924, [iv], 35, 1195—1198).—The formulae proposed for the dicyclic terpenes by Dupont (A., 1922, i, 1042) involve two new conceptions of oscillating bonds and the linking of three valencies of three separate carbon atoms with the "bridge" carbon atom, which introduce fresh complications. The author contends that his extended theory of conjugated bonds (cf. A., 1899, i, 529) is sufficient to explain the transformations of these terpenes.

R. B.

**Chemistry of Cadinene.** I. G. G. HENDERSON and A. ROBERTSON (*J. Chem. Soc.*, 1924, 125, 1992—1996).—Cadinene of greater purity than 70% could not be obtained by the repeated fractional distillation under reduced pressure of oil of cubebs. The fraction of b. p. 125—140°/12 mm. was mixed with glacial acetic acid ( $\frac{1}{3}$  vol.) and cadinene precipitated as the hydrochloride. Pure cadinene was obtained from the latter by means of anhydrous sodium acetate. Agitation of a solution of cadinene hydrochloride in glacial acetic acid with silver acetate at 70° resulted in the formation of a light yellow oil, which was steam-distilled, and a saturated compound,  $C_{15}H_{28}O_2$ , m. p. 194—195°, probably a glycol, was isolated from the residue in 2% yield. The volatile portion consisted of cadinene and an unsaturated compound,  $C_{15}H_{25}OH$ , apparently the alcohol cadinol (cf. Semmler and Jonas, A., 1915, i, 63). It formed a bromo-dibromide,  $C_{15}H_{25}OBr_3$ , an unstable, oily liquid. These hydroxy compounds were not obtained when cadinene hydrochloride was treated with silver acetate in ethereal or alcoholic solution, the sole product being cadinene. Cadinene was not hydrated by heating its acetic acid solution with 30% sulphuric acid, but yielded a brown oil the greater part of which was volatile in steam and consisted of an isomeric unsaturated hydrocarbon, termed isocadinene, b. p. 125—128°/12 mm.,  $d_4^{20}$  0.9160,  $n_D^{20}$  1.5141. The same substance was obtained on heating cadinene with glacial acetic acid at 230—235° for 24 hours. It had  $[\alpha] -1.0^\circ$ , quickly resinified in air, absorbed bromine with evolution of hydrogen bromide, and formed no solid nitrosochloride, nitrosite, or nitrosate. A sesquiterpene was isolated from the liquid left after isolating cadinene hydrochloride from oil of cade which appears very similar to one described by Lepeschkin (A., 1908, i, 278). A. C.

**Essential Oil of *Backhousia angustifolia*.** I. A. R. PENFOLD (*J. Proc. Roy. Soc. N.S. Wales*, 1923, 57, 300—312).—The oil, obtained in a yield of 1.08% by steam-distillation of the leaves and terminal branchlets, contains 75% of a hitherto undescribed phenol ( $C_{10}H_{14}O_3$ , b. p. 122—124°/10 mm.) of poor germicidal value, together with *d*- $\alpha$ -pinene,  $\beta$ -pinene, cineol, alcoholic compounds (e.g.,  $\alpha$ -terpineol), a sesquiterpene, and a stearoptene ( $C_{15}H_{16}O_5$ ; probably a lactone) of m. p. 118—119°. The phenol is an almost colourless, viscous liquid, giving a brilliant orange-red coloration with alcoholic ferric chloride. It forms a crystalline ammonium derivative,  $C_{10}H_{17}O_3N$ , m. p. 135—137°, and a purple, crystalline copper derivative,  $(C_{10}H_{12}O_3)_2Cu$ , m. p. 193—194°. Oxidation of the phenol with alkaline potassium permanganate gives potassium acetate and potassium carbonate. W. T. K. B.

**Essential Oil of *Darwinia grandiflora* and the Presence of a New Acetic Ester.** A. R. PENFOLD (*J. Proc. Roy. Soc. N.S. Wales*, 1923, 57, 237—248).—Distillation of the leaves and terminal branchlets of *Darwinia grandiflora* yields a mobile, pale yellow oil (0.35%), the main constituents of which are *d*- $\alpha$ -pinene, an unidentified terpene (b. p. 175—177°), an acetic ester ( $C_{10}H_{18}O$ ; b. p. 108—116°/10 mm.) named *darwinol acetate* and not

hitherto described, a sesquiterpene (b. p. 130—133°/10 mm.; possibly identical with eudesmene) and corresponding sesquiterpene alcohol (b. p. 134—138°/5 mm.), a stearoptene (m. p. 103—104°; probably a phenol ether), and small quantities of isovaleraldehyde, amyl alcohol, and an ester. W. T. K. B.

**Essential Oils of *Callistemon lanceolatus* and *C. viminalis*.**

A. R. PENFOLD (*J. Proc. Roy. Soc. N.S. Wales*, 1923, 57, 131—139).—The essential oil of *Callistemon lanceolatus*, obtained in a yield of 0.06—0.22%, contains cineol, dipentene, limonene, terpineol, sesquiterpene, and a small amount of phenols. *C. viminalis* appears to exist in two varieties, that from New South Wales yielding an oil (0.13—0.22%) containing *d*- $\alpha$ -pinene, cineol (about 30%), phenol (2%), sesquiterpene, and probably terpineol, whilst the oil from the Queensland variety (0.21—0.22%) contains cineol (60—80%), dipentene, limonene, terpineol, sesquiterpene, and phenol (about 0.5%). W. T. K. B.

**Germicidal Values of Commercial Eucalyptus Oils and their Pure Constituents, with Observations on the Value of Concentrated Disinfectants.** A. R. PENFOLD and R. GRANT (*J. Proc. Roy. Soc. N.S. Wales*, 1923, 57, 80—89).—The Rideal-Walker coefficients of a number of eucalyptus oils and their chemically pure constituents are tabulated. Terpenes (*e.g.*, pinene, phellandrene, limonene), sesquiterpenes, and sesquiterpene alcohols possess poor germicidal properties, whilst ketones (piperitone type), alcohols (piperitol and geraniol types), aromatic and open-chain aldehydes (cuminal, citral, and citronellal types), and phenols (*e.g.*, australol) possess well-marked germicidal properties. The effect of dilution on the coefficient of various germicidal preparations, including those with tar oils and phenol, is discussed, and it is shown that the germicidal value of a disinfectant is greater the greater the initial dispersion, provided dilution is made when the soap solution is added. W. T. K. B.

**Germicidal Values of Australian Essential Oils (exclusive of Eucalypts) and their Pure Constituents, together with those of some Essential Oil Isolates and Synthetics.** I. A. R. PENFOLD and R. GRANT (*J. Proc. Roy. Soc. N.S. Wales*, 1923, 57, 211—215; cf. preceding abstract).—The Rideal-Walker coefficients of the above are tabulated. Of the crude oils examined that from *Backhousia citriodora* has the highest coefficient (16; principal active constituent, citral) and that from *Homoranthus virgatus* the lowest (1; principal active constituent, *d*- $\alpha$ -pinene). Of the pure constituents thymol has the highest coefficient (25) and leptospermol the lowest (<1). W. T. K. B.

**Constitution of Lichenol.** A. S. PFAU (*Parfums de France*, 1924, No. 16, 137).—The compound, lichenol, m. p. 72—73°, found by Gattefossé (*Parfumerie moderne*, 1911, 4, 6) to be the chief constituent of oak moss (*Evernia prunastri*, Ach.) oil, has m. p. 73.5—74° and is identical with ethyl evernate (Pfau, this vol., i, 512).

CHEMICAL ABSTRACTS.

**Isoprene and Caoutchouc. VII. Homologues of Hydro-caoutchouc.** H. STAUDINGER and W. WIDMER (*Helv. Chim. Acta*, 1924, 7, 842—848; cf. A., 1922, i, 1043).—The hydrohalides of caoutchouc are colloids which very readily lose hydrogen halide. To explain this, however, no special hypothesis is needed (cf. Pummerer and Burkhard, A., 1923, i, 49), the hydrohalides being regarded as hydrocaoutchouc, in which the tertiary hydrogen atom is substituted by halogen. Caoutchouc hydrobromide does not react with magnesium alkyl iodide, but with zinc dimethyl and zinc diethyl, methyl- and ethyl-hydrocaoutchouc, respectively, are easily obtained. Unless the reaction mixture is well cooled, the homologue is in both cases contaminated with a saturated isomeride of caoutchouc formed by ring closure after loss of methane (or ethane) and hydrogen halide. The new homologues of hydrocaoutchouc possess essentially the same physical and chemical properties as the parent. Above all, they are colloids. As paraffin hydrocarbons, they are stable towards permanganate, nitric acid, and bromine. They resemble hydrocaoutchouc in giving, on heating, fission products of olefinic character. The previous observation that saturated hydrocarbons may be colloids is confirmed. Together with its chemical properties, the colloidal nature of hydrocaoutchouc is direct evidence in favour of the new conception of the structure of caoutchouc (A., 1922, i, 1043). Harries (A., 1923, i, 693) has asserted that the action of high-pressure hydrogen on caoutchouc at 270° gives pyrogenic decomposition products. This cannot be true, however, because pyrogenic decomposition of caoutchouc gives molecular disperse decomposition products, which would yield, on reduction, molecular disperse reduction products. Harries' objection is further vitiated by the low-temperature transformation of caoutchouc into the colloidal homologues of hydrocaoutchouc. W. E. E.

**Synthesis of Amygdalin.** R. KUHN and H. SOBOTKA (*Ber.*, 1924, 57, [B], 1767—1769).—Bromoacetogentiobiose is converted by ethyl *dl*-mandelate and silver oxide into a mixture of ethyl *d*-hepta-acetylamygdalate, m. p. 212.5—213.5° (corr.),  $[\alpha]_D^{20}$  —72.8° in chloroform, and ethyl *l*-hepta-acetylamygdalate, m. p. 189.5—191° (corr.), which are separated from one another by fractional crystallisation from methyl and ethyl alcohols. The same products are obtained by hydrolysing amygdalin with barium hydroxide solution, converting the *dl*-amygdalic acid thus produced into its ethyl ester, and acetylation of the latter substance.

The compound described by Campbell and Haworth (T., 1924, 125, 1337) as ethyl *dl*-hepta-acetylamygdalate is a derivative of *d*-mandelic acid.

In contrast to the previous practice, natural amygdalin, prunasin, and their derivatives which yield lævorotatory mandelic acid when hydrolysed are described as *d*-derivatives, since Freudenberg, Brauns, and Siegel (A., 1923, i, 215) have established the position of lævorotatory mandelic acid among the *d*- $\alpha$ -hydroxy-acids.

H. W.

**Strophanthin. V. Isomerisation and Oxidation of iso-Strophanthidin.** W. A. JACOBS and A. M. COLLINS (*J. Biol. Chem.*, 1924, **61**, 387—403; cf. A., 1923, i, 123; this vol., i, 65, 867).

—When strophanthidin is treated with cold methyl-alcoholic potassium hydroxide, it is converted quantitatively into  $\alpha$ -isostrophanthidin, m. p. 255—257°,  $[\alpha]_D^{25} - 34^\circ$  in methyl alcohol, which is precipitated on pouring the solution into water; more of the substance can be obtained by warming the mother-liquor after acidification to Congo-red. Unlike strophanthidin, it cannot be reduced with hydrogen and palladium, which suggests that isomerisation may involve a shift in the ethylenic linking. It gives an *oxime*, m. p. 236°, which can also be obtained by the action of methyl-alcoholic potassium hydroxide on strophanthidinoxime. On oxidation with sodium hypobromite,  $\alpha$ -isostrophanthidin gives a mixture of two monobasic, lactonic acids. The greater part of the product is  $\alpha$ -isostrophanthidic acid,  $C_{23}H_{32}O_7$ , leaflets with  $1H_2O$ , m. p. 231—233°,  $[\alpha]_D^{25} - 16.3^\circ$  in 95% alcohol; the *methyl ester* has a variable melting point,  $[\alpha]_D^{25} - 15^\circ$  in chloroform; the *benzoate* of the methyl ester has m. p. 230°; the *oxime* of the methyl ester, m. p. 263°. The other acid,  $C_{23}H_{30}O_7$ , was separated by means of its sparingly soluble ammonium salt; it forms needles with  $0.5H_2O$ , m. p. 230°, or anhydrous leaflets, m. p. 254—257°, from hot alcohol;  $[\alpha]_D^{25} - 69^\circ$  in 95% alcohol. On boiling with sodium hydroxide, the lactone group is hydrolysed with the formation of a dibasic acid,  $C_{23}H_{32}O_8$ , flat needles with  $1.5H_2O$ , m. p. 183°. The *methyl ester* of the lactonic acid has m. p. 253—256°,  $[\alpha]_D^{25} - 59.5^\circ$  in chloroform, and does not form a benzoate or an oxime. On oxidation in ammoniacal solution with potassium permanganate (1 mol. of oxygen),  $\alpha$ -isostrophanthidic acid gives a dibasic acid,  $C_{23}H_{32}O_8$ ,  $\alpha$ -isostrophanthic acid, which forms platelets with  $1H_2O$ , m. p. 232—234°,  $[\alpha]_D^{25} - 8^\circ$  in methyl alcohol. On heating, this acid loses 1 mol. of carbon dioxide. It can also be obtained directly from isostrophanthidin by oxidation in alkaline solution with permanganate (2 mols. of oxygen). The *dimethyl ester* has m. p. 224—225°,  $[\alpha]_D^{25} - 12^\circ$  in chloroform; the *benzoate* of the dimethyl ester has m. p. 201—203°.

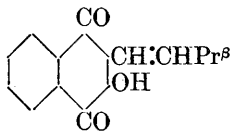
When  $\alpha$ -isostrophanthidic acid is boiled with dilute sodium hydroxide and then oxidised with permanganate (1 mol. of oxygen) the product consists of a mixture of  $\alpha$ -isostrophanthic acid and a second isomeric acid which forms needles, m. p. 277—279°,  $[\alpha]_D^{25} - 26^\circ$  in methyl alcohol, and is identical with the strophanthic acid previously obtained by the oxidation of strophanthidin (this vol., i, 65) and erroneously given the formula  $C_{23}H_{30}O_8$ . It is now called  $\beta$ -isostrophanthic acid and appears to be a stereoisomeride of the  $\alpha$ -compound. The strophanthic acid of Feist (A., 1900, i, 555) was probably a mixture of  $\alpha$ - and  $\beta$ -isostrophanthic acids.

C. R. H.

**Constitution of Santonin.** A. ANGELI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 10—16).—A reprint of work already published (A., 1907, i, 321; 1908, i, 543).

T. H. P.

**Mangostin, the Yellow Colouring Matter of the Rind of the Fruit of *Garcinia mangostana*.** J. DEKKER (*Rec. trav. chim.*, 1924, **43**, 727—730).—By crystallising from benzene the mixture of colouring matter and resin obtained by extracting the rind with alcohol, mangostin,  $C_{16}H_{16}O_4$ , is obtained in bright yellow needles, m. p. 176.5—177°. Fusion with alkali gives a product which has the odour of amyl alcohol but, after acidification, of valeric acid. Hence mangostin is possibly methoxyhydroxy-lapachol (lapachol has the annexed formula; cf. A., 1906, i, 873).



The presence of one methoxyl group is indicated, and the coloration which mangostin gives with ferric chloride points to the presence of a hydroxyl group. Methylation gives *methylmangostin*, yellow crystals, m. p. 122.5—123°, which contains two methoxyl groups and gives a colourless *acetyl* derivative, m. p. 196°. The mangostin obtained in this investigation does not reduce gold and platinum salts; hence the products of Schmid (*Annalen*, 1855, **93**, 83) and of Liechti (*Diss.*, Bern, 1891), which did so, were probably impure.

W. E. E.

**Preliminary Experiments on Feather Pigments.** W. D. BANCROFT (*J. Physical Chem.*, 1924, **28**, 1147—1150).—The red and yellow feather pigments which are or are not easily extracted by alcohol are respectively not fast or fairly fast to light. The solutions in all cases are yellow. The extracted pigment behaves like an acid dye, i.e., it does not dye cotton direct and dyes wool more strongly from an acid than from an alkaline bath. It is adsorbed by alumina.

M. B. D.

**Pyrylium Compounds. XIII. [Reactivity of Methyl Groups in the  $\alpha$ - and  $\gamma$ -Positions in Pyrylium Salts.** W. DILTNEY and J. FISCHER (*Ber.*, 1924, **57**, [B], 1653—1656; cf. Diltney, A., 1923, i, 699; Buck and Heilbron, T., 1923, **123**, 1395, 2521).—The reactivity of methyl groups in the  $\alpha$ - and  $\gamma$ -positions in pyrylium salts is established by their ability to react with aromatic aldehydes. The following salts are thus derived from 4 : 6-diphenyl-2-methylpyrylium compounds : 4 : 6-diphenyl-2-styrylpyrylium perchlorate, m. p. 235°; 4 : 6-diphenyl-2-p-methoxystyrylpyrylium perchlorate, m. p. 228—229°, and the additive compound of the chloride with ferric chloride, m. p. 198°; 4 : 6-diphenyl-2 : 4'-hydroxystyrylpyrylium perchlorate, m. p. 254°, and the ferric compound, m. p. 172°; 4 : 6-diphenyl-2 : 2'-hydroxystyrylpyrylium perchlorate, m. p. 248°, and the ferric salt, m. p. 174°; 4 : 6-diphenyl-2- $\beta$ -styrylvinylpyrylium perchlorate, m. p. 255°, and the ferric compound, m. p. 236°. 2 : 6-Diphenyl-4-methylpyrylium salts yield the following compounds : 2 : 6-diphenyl-4-styrylpyrylium perchlorate, m. p. 254—255°; 2 : 6-diphenyl-4-p-methoxystyrylpyrylium perchlorate, m. p. 272°; 2 : 6-diphenyl-4-p-hydroxystyrylpyrylium perchlorate, m. p. 265°; 2 : 6-diphenyl-4-o-hydroxystyrylpyrylium perchlorate, m. p. 243—244°; 2 : 6-diphenyl-4- $\beta$ -styrylvinylpyrylium perchlorate, m. p. 240°.

In reply to Schneider and Ross (A., 1923, i, 1111), it is admitted that the formation of 4:6-diphenyl-2-methylpyrylium salts from acetophenone and acetic anhydride may occur through the intermediate formation of dypnone, but experimental evidence is adduced in favour of the view that benzoylacetone is more probably an intermediate product. H. W.

**Sulphur as the Bridge Atom in the Middle Ring of some Anthracene Derivatives.** A. BISTRZYCKI and A. TRAUB (*Helv. Chim. Acta*, 1924, 7, 935—944; cf. A., 1922, i, 268).—In warm glacial acetic acid solution, hydrogen chloride causes *p*-tolualdehyde and thiobenzilic acid to condense almost quantitatively to give 4:4-diphenyl-2-*p*-tolyl-1:3-oxthiophan-5-one, prisms, m. p. 100—100·5°. Sulphuric acid converts this substance into 9-phenyl-2-methyl-9:10-dihydromesothioanthracene, greenish-yellow needles, m. p. 99·5—100·5°. Neither alcoholic phenylhydrazine nor boiling 10% alcoholic sodium hydroxide solution affects the substance, so that the sulphur cannot be bound as in a thioketone. Distilled with zinc dust under the conditions in which phenyldihydromesothioanthracene gives phenylanthracene, the present substance gives no solid product. At a higher temperature 2-methylanthracene is obtained.

Reduction in glacial acetic acid solution by zinc dust and hydrochloric acid gives 1-phenyl-3-*p*-tolylthiophthalan, needles, m. p. 103—104°. Oxidation in boiling glacial acetic acid solution by 4% potassium permanganate solution yields 2-*p*-toluoylbenzophenone. The condensation of thiobenzilic acid and cuminaldehyde gives 4:4-diphenyl-2-cumenyl-1:3-oxthiophan-5-one, m. p. 100—100·5°. From *o*-chlorobenzaldehyde 4:4-diphenyl-2-*o*-chlorophenyl-1:3-oxthiophan-5-one, m. p. 105·5°, is obtained, and is converted by sulphuric acid into 4-chloro-9-phenyl-9:10-dihydromesothioanthracene, green prisms, showing marked triboluminescence, m. p. 89°. Alcoholic ammonium hydroxide at 220—230° has no action on this compound. *m*-Chlorobenzaldehyde gives (quantitatively) 4:4-diphenyl-2-*m*-chlorophenyl-1:3-oxthiophan-5-one (m. p. 83—84°), and thence (probably) 3-chloro-9-phenyl-9:10-dihydromesothioanthracene (m. p. 102—103·5°). Whilst 2-*o*-nitrophenyl-4:4-diphenyl-1:3-oxthiophan-5-one could not be converted into an anthracene derivative, 2-*m*-nitrophenyl-4:4-diphenyl-1:3-oxthiophan-5-one gives 3-nitro-9-phenyl-9:10-dihydromesothioanthracene (m. p. 151° indef., depending on rate of heating). The following condensation products of thiobenzilic acid are all obtained in good yield by the usual method, but they do not give the corresponding mesothioanthracene derivatives: 4:4-diphenyl-2-*p*-nitrophenyl-1:3-oxthiophan-5-one (m. p. 148°), 4:4-diphenyl-2-*p*-dimethylaminophenyl-1:3-oxthiophan-5-one (m. p. 124° decomp.), 4:4-diphenyl-2-(*mp*-methylenedioxyphenyl)-1:3-oxthiophan-5-one (m. p. 119·5°), 1:4-di-2(5-keto-4:4-diphenyltrihydro-1:3-oxthienyl)benzene (m. p. 195—196°). W. E. E.

**Naphthathioindoxyls.** R. TOBLER, R. STOCKER, J. MÜLLER, and A. BUCHER (U.S. Pat. 1492054).—Treatment of thionaphtho-



isatin compounds in alkaline solution with a monohalogen acid, elimination of carbon monoxide, and ring closure by condensation yields naphthothioindoxyls. The following compounds are mentioned: *Naphthalene-1-thioglyoxylic acid*, m. p. 171—172°; *naphthalene-1-thioglycol-2-carboxylic acid*, m. p. 144—145°; 1:2-naphthothioindoxyl; 2:1-naphthothioindoxyl; 4-chloro-1:2-naphthothioindoxyl, m. p. 165° (5-chloro-, m. p. 176°); 5-chloro-2:1-naphthothioindoxyl, m. p. 146° (5-bromo-, m. p. 170°; 8-chloro-, m. p. 179°; 7-chloro-, m. p. 155°); 1-chloro-2:3-naphthothioindoxyl (acetyl derivative, m. p. 106°); 1-bromo-2:3-naphthothioindoxyl, m. p. 155°.

## CHEMICAL ABSTRACTS.

**Indigotin Group. V. Derivatives of "Thioindigo."** T. POSNER and E. WALLIS (*Ber.*, 1924, **57**, [B], 1673—1681; cf. Posner and Heumann, A., 1923, i, 953; Posner and Kemper, this vol., i, 1237).—The assumption made previously that the action of nitrous fumes on indigotin results in the replacement of the imino-hydrogen atoms by the nitroso group is confirmed indirectly by the observation that bisoxythionaphthen is only slowly attacked by this reagent, whereby it is converted into thionaphthenquinone,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{CO}$ , m. p. 121°.

Bisoxxythionaphthen is slowly oxidised by nitric acid (*d* 1.4) at the atmospheric temperature to the corresponding monosulphoxide,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{SO} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} C_6H_4$ , m. p. above 300°, which appears to be identical with the substance described by Bezdrík, Friedländer, and Koeniger (A., 1908, i, 200), and by Danaila (A., 1910, i, 411). The compound is readily reduced by sodium hyposulphite and sodium hydroxide to the dihydro substance, which, however, is oxidised by air to bisoxxythionaphthen. Addition of benzoyl chloride to the vat yields the *dibenzoyl* derivative,  $C_6H_4 \begin{smallmatrix} \text{C(Obz)} \\ \diagup \quad \diagdown \\ \text{SO} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{C(Obz)} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} C_6H_4$ , m. p. 214—215°, whereas the action of benzoyl chloride on the sulphoxide in the presence of boiling pyridine leads to the production of 3:3'-bisbenzoxxythionaphthen, m. p. 226°, which is also prepared by the action of benzoyl chloride on the hyposulphite vat from bisoxxythionaphthen or on the latter dissolved in boiling pyridine. The sulphoxide is transformed by reductive acetylation with acetic anhydride into 3:3'-bisacetoxxythionaphthen, m. p. 240°, which is obtained similarly from bisoxxythionaphthen. Warm sodium hydroxide solution converts the sulphoxide into thionaphthenquinone.

Bisoxxythionaphthen is transformed by nitric acid (94%) in the presence of glacial acetic acid into the corresponding *sulphone*,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{SO}_2 \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} C_6H_4$ , m. p. above 300°. The *dibenzoyl* derivative, m. p. 228—229° (decomp.), and the *diacetyl* compound, m. p. 206°, of the corresponding dihydro product are described. The monosulphone is transformed by sodium hydroxide solution (15%) into thionaphthenquinone and *thionaphthen-*

*quinone-S-dioxide*,  $\text{C}_6\text{H}_4\langle\text{CO}\rangle_{\text{SO}_2}\text{CO}$ , m. p.  $265^\circ$ , which is reduced by zinc dust and glacial acetic acid to 3-hydroxy-1-dioxythionaphthen, m. p.  $142^\circ$  (cf. Lanfry, A., 1913, i, 193).

6:6'-Diethoxybisoxythionaphthen is converted in the usual manner into the *dibenzoyl* derivative, m. p.  $260^\circ$ , and the *diacetyl* derivative, m. p.  $232^\circ$  (decomp.), of the corresponding dihydro compound.  
H. W.

**Angostura Alkaloids. II. Synthesis of Galipine.** E. SPÄTH and H. EBERSTALLER (*Ber.*, 1924, 57, [B], 1687—1690; cf. Späth and Brunner, this vol., i, 1226).—4-Methoxy-2-methylquinoline condenses with 3:4-dimethoxybenzaldehyde in the presence of zinc chloride at  $105^\circ$  to yield 4-methoxy-2- $\beta$ -3':4'-dimethoxyphenylethinylquinoline [hydrochloride, m. p.  $174$ — $176^\circ$  (decomp.)], which is reduced by hydrogen in the presence of palladised charcoal to 4-methoxy-2- $\beta$ -3':4'-dimethoxyphenylethylquinoline,  $\text{OMe}\cdot\text{C}_9\text{H}_5\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OMe})_2$ , m. p.  $113\cdot5^\circ$  (*picrate*, m. p.  $194^\circ$ ); the base is identical with natural galipine.

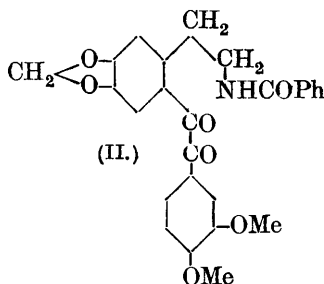
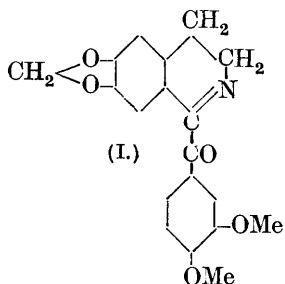
The isolation of the angostura alkaloids is conveniently effected by extraction of the bark with ethyl alcohol and concentration of the extract in a vacuum to a viscous syrup. The dark residue is treated with sodium hydroxide solution (25%), which dissolves the bulk of the coloured impurities and enables the alkaloids to be extracted with ether. The ethereal extract is repeatedly treated with dilute hydrochloric acid (1%), whereby cusparine and galipine are dissolved, whilst the more feebly basic alkaloids are removed from the remaining ethereal solution by hydrochloric acid (10%). Cusparine is separated from its mixture with galipine as the sparingly soluble oxalate.  
H. W.

**Synthesis of  $\psi$ -Pelletierine.** R. C. MENZIES and R. ROBINSON (*J. Chem. Soc.*, 1924, 125, 2163—2168).—Aqueous solutions of calcium acetonedicarboxylate, glutardialdehyde, and methylamine were mixed and kept for 24 hours. The mixture was then acidified (to Congo-red) with hydrochloric acid, boiled to eliminate carbon dioxide, cooled, rendered alkaline, and the calcium removed as oxalate. Extraction with ether then gave an oil which was distilled in a high vacuum. The distillate afforded a sparingly-soluble *picrate*, which, after recrystallisation from water, decomposition with sodium hydroxide, and extraction with ether etc. afforded a crystalline base. Recrystallisation from light petroleum yielded crystals, m. p.  $48\cdot5^\circ$ , identical with  $\psi$ -pelletierine. *Dipiperonylidene- $\psi$ -pelletierine*, m. p.  $226$ — $227^\circ$ , forms yellow, microscopic plates or prisms.

Adipdialdehyde similarly gave rise to an oily base possessing properties to be expected of a homo- $\psi$ -pelletierine. It yielded a *dipiperonylidene* derivative and a *methiodide*.  
F. G. W.

**Oxidation of Substituted 1-Benzyl-3:4-dihydroisoquinolines and a Synthesis of Papaveraldine.** J. S. BUCK, R. D. HAWORTH, and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1924, 125, 2176—2185).—When 6:7-methylenedioxy-3':4'-dimethoxy-1-

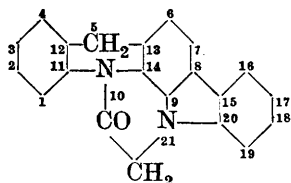
benzyl-3 : 4-dihydroisoquinoline (cf. Haworth, Perkin, and Rankin, this vol., i, 1098) is exposed to the air in alcoholic solution, 3' : 4'-dimethoxy-1-benzoyl-6 : 7-methylenedioxy-3 : 4-dihydroisoquinoline (I), m. p. 151° [hydride, m. p. 209—211°; oxime, m. p. 232° (decomp.)], is obtained. This, and its homologues, develop a brilliant green coloration when boiled with acetic anhydride. Reduction with tin and hydrochloric acid affords the corresponding 1 : 2 : 3 : 4-tetrahydroisoquinoline derivative (*loc. cit.*, 1099). Treatment with benzoyl chloride yields the benzoyl derivative (probably II; cf. Reissert, A., 1905, i, 925), pale yellow needles, m. p. 158°, from which (I) is re-formed on boiling with 40% sulphuric acid. When (I) is heated with methyl-alcoholic potassium hydroxide, it is oxidised to 3' : 4'-dimethoxy-1-benzoyl-6 : 7-methylenedioxyisoquinoline, m. p. 208° [picrate, m. p. 206—207° (decomp.); oxime,



m. p. 260° (decomp.)]. 3' : 4'-Methylenedioxy-1-benzoyl-6 : 7-dimethoxy-3 : 4-dihydroisoquinoline, prisms, m. p. 151—152°, is obtained similarly to (I). The hydride, m. p. 192°; picrate, m. p. 227° (decomp.) after softening at 215°; and oxime, m. p. 223—224°, are described. It yields the tetrahydroisoquinoline derivative on reduction, and forms a pale yellow benzoyl derivative (see II), m. p. 151°, which yields an amorphous monoxime, and an o-nitrobenzoyl derivative, m. p. 175—176°. The action of aqueous permanganate, or of methyl-alcoholic potassium hydroxide, affords 3' : 4'-methylenedioxy-1-benzoyl-6 : 7-dimethoxyisoquinoline, m. p. 199—200° [picrate, m. p. 243°; oxime, m. p. 263—264° (decomp.)], together with, in the latter case, a substance,  $C_{19}H_{17}O_6N$ , m. p. 294—296°. 6 : 7 : 3' : 4'-Tetramethoxy-1-benzyl-3 : 4-dihydroisoquinoline was obtained as an oil (picrate, m. p. 168°) by the action of phosphoryl chloride in toluene on homoveratroylhomoveratrolylamine. It was oxidised as above to 6 : 7 : 3' : 4'-tetramethoxy-1-benzoyl-3 : 4-dihydroisoquinoline, a cream-coloured powder, m. p. 180—191°. The hydrochloride,  $C_{20}H_{21}O_5N \cdot HCl \cdot H_2O$ , yellow, m. p. 183°; hydride, orange, m. p. 186° (decomp.); oxime, m. p. 247—248° (decomp.); and benzoyl derivative, pale yellow, m. p. 160°, are described. When warmed with methyl-alcoholic potassium hydroxide, the base yielded 6 : 7 : 3' : 4'-tetramethoxy-1-benzoylisoquinoline, m. p. 208°, identical with papaveraldine.

F. G. W.

**Strychnine and Brucine. II.** G. R. CLEMO, W. H. PERKIN, jun., and R. ROBINSON (*J. Chem. Soc.*, 1924, **125**, 1751—1804).—Perkin and Robinson (T., 1910, **97**, 305) have suggested that the strychnine molecule possessed the carbon-nitrogen skeleton of an anhydro-(5 : 10-dihydro)-acridindoline-21-acetic acid (annexed



formula, the novel numbering of which should be noted). Substances having this skeleton have now been synthesised. The immediate aim of the work was to reproduce if possible either deoxystrychnine or dihydrostrychnoline (Tafel, A., 1892, 1012) but this has not been achieved.

When 9-amino-5 : 10-dihydroacridine (see below) is treated with ethyl chloroacetate and the product hydrolysed, *anhydro-5 : 10-dihydroacridine-9-aminoacetic acid*, m. p. 168° (a crystallographic description is given), is obtained [acetyl derivative, m. p. 174—175°; nitroso derivative, m. p. 167° (decomp.)]. When the nitroso derivative is reduced by zinc dust and acetic acid in presence of cyclohexanone, condensation takes place and *anhydro-5 : 10 : 16 : 17 : 18 : 19-hexahydroacridindoline-21-acetic acid*, yellow plates, m. p. 206°, is formed. This affords the corresponding *acid*, an amorphous substance, when treated with methyl-alcoholic potassium hydroxide, but the product is not wholly reconverted into the anhydride by the action of ethyl-alcoholic hydrochloric acid, some being also oxidised to *ethyl 16 : 17 : 18 : 19-tetrahydroacridindoline-21-acetate*, m. p. 172° (see below). Strychnic acid does not behave in a similar way. When the above anhydride is reduced electrolytically in alcoholic sulphuric acid suspension—and only by this means—it affords 21-β-hydroxyethyl-5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-octahydroacridindoline, an amorphous, gummy substance which yields a crystalline *diacetyl* derivative, m. p. 235°. When the latter is hydrolysed by methyl-alcoholic potassium hydroxide it is presumably simultaneously oxidised as the product has the properties of an acridine derivative (fluorescent solution in sulphuric acid). In its formation and acetylation the parent substance resembles tetrahydrostrychnine (Tafel, *loc. cit.*), but not in this other behaviour.

Anhydrohexahydroacridindoline-21-acetic acid suffers partial reduction when it is distilled over zinc dust at 20 mm. and by repeated treatment is thus converted into 10 : 21-etheno-5 : 10 : 16 : 17 : 18 : 19-hexahydroacridindoline, a yellow substance, m. p. 181—182°, which gives red salts (the *hydrochloride* and *sulphate* are described). This compound is formulated as an etheno compound, and not as an *N*-vinyl derivative, for reasons that are discussed in detail and are based on evidence published elsewhere (cf. this vol., i, 1345). As a by-product, formed by oxidation in the later operations, 16 : 17 : 18 : 19-tetrahydroacridindoline-21-acetic acid, an amorphous substance, is obtained; its *ethyl* ester forms orange prisms, m. p. 172°. From the etheno derivative, by reduction with sodium amalgam in presence of an excess of carbon dioxide, 10 : 21-ethano-

5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline*, yellow prisms, m. p. 209°, is produced; in this, as it yields no acetyl derivative, the 10 : 21 bridge is still intact. Further reduction, by electrolysis of an alcoholic sulphuric acid suspension at 35—45°, converts the ethano compound into what is most probably 21-ethyl-5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline*, m. p. 127° (yielding an *acetyl* derivative, m. p. 173°, and a *sulphate* which is decomposed by ammonia), together with 21-ethyl-5 : 6 : 7 : 8 : 9 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*dodecahydroacrindoline*, a strongly basic resinous substance—the *sulphate*, m. p. 230° (decomp.), is not decomposed by ammonia—yielding an *acetyl* derivative,  $C_{21}H_{27}N_2Ac$ , which also is resinous. The ethenotetrahydro, ethano- and ethyl-octahydro, and the ethyldodecahydro compounds do not exhibit the physiological properties characteristic of strychnine.

Compounds having the complete "strychnine skeleton" were synthesised only in the above way; earlier abortive attempts resulted in the production of the following compounds, some of which, indeed, were made use of in the experiments described above.

2'-Nitrodiphenylamine-6-carboxylic acid, obtained from anthranilic acid and *o*-chloronitrobenzene, is converted by sulphuric acid at 100° into 9-nitroacridone (cf. Ullmann, A., 1907, i, 842), the 3(?) *sulphonic acid* of which yields a *chloride*, m. p. 270—274°. When 9-nitroacridone is reduced with ammonium sulphide 9-aminoacridone is obtained, and this with ethyl bromoacetate affords (eventually) *acridone-9-aminoacetic acid*, a gelatinous substance; the *methyl* ester forms yellow prisms, m. p. 237—238°, and affords a *nitroso* derivative, decomp. 180°; the *ethyl* ester forms yellow needles, m. p. 195°, and affords a *nitroso* derivative, m. p. 185—186° (decomp.). The latter, the nitroso ethyl ester, undergoes a condensation when it is reduced with zinc and acetic acid in presence of *cyclohexanone*, but in the reaction the carbethoxymethyl group is wholly removed, and the product is not the expected anhydroketo-hexahydroacrindolineacetic acid, but 5-*keto*-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline*, dull yellow prisms, m. p. above 380° (the *hydrochloride*, *hydrobromide*, *nitrate*, and *sulphate*, all bright red substances, are described). This substance is also obtained (and so its constitution verified) as follows : 9-aminoacridone is converted by the action of nitrous acid into *acridonediazole*, m. p. 266°, and this readily yields the desired product when it is reduced by zinc dust and acetic acid in presence of *cyclohexanone*.

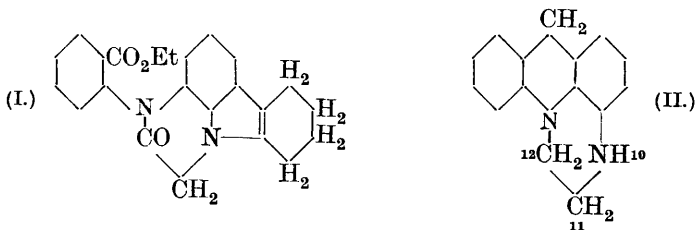
The above keto compound, when reduced by sodium amalgam and an excess of carbon dioxide, affords 5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline*, m. p. 187—205° (the *hydrochloride* and *sulphate* are red), which is oxidised by boiling its alcoholic solution in contact with air to 16 : 17 : 18 : 19-*tetrahydroacrindoline*, m. p. 230—231° (this also forms red salts : *hydrochloride*, *sulphate*, and *picrate*).

2'-Aminodiphenylamine-6-carboxylic acid, m. p. 210° (*hydrochloride*, m. p. 260°), is obtained by reducing the nitro compound mentioned above with ferrous sulphate and ammonia. This acid

is converted at its m. p. into the *anhydro* derivative (2'-amino-phenylantranil?), m. p. 250° [*acetyl* derivative, m. p. 248°; *nitroso* derivative, m. p. 202° (decomp.)]. The aminodiphenylamine-carboxylic acid interacts with phenanthraquinone to afford *flav-induline-o-carboxylic acid*, m. p. 310° (decomp.). It also yields, when treated with nitrous acid, 1-o-carboxyphenyl-1 : 2 : 3-benzotriazole, m. p. 217° (decomp.); this product resisted all attempts to convert it into acridonediazole or into an indole derivative.

From *o*-phenylenediamine and *o*-chlorobenzoic acid, 6-carboxy-diphenylamine-2'-*o*-aminobenzoic acid (*s*-di-*o*-carboxyphenyl-*o*-phenylenediamine), m. p. 258°, is obtained; this is decomposed, when heated under diminished pressure, and converted into *s*-di-phenyl-*o*-phenylenediamine, m. p. 109°, b. p. 280—290°/40 mm., the *diacetyl* derivative of which has m. p. 281° [Wieland's base (A., 1913, i, 1386) is most probably *o*-aminotriphenylamine].

When 2'-aminodiphenylamine-6-carboxylic acid is treated with sodium formaldehyde-bisulphite followed by potassium cyanide and, finally, by sodium hydroxide, 6-carboxydiphenylamine-2'-aminoacetic acid, m. p. 212°, is produced; this, by the action of alcoholic hydrochloric acid, is converted into the ester of the *anhydro* derivative, namely, *anhydro*-6-carbethoxydiphenylamine-2'-aminoacetic acid, m. p. 153°, of which the *nitroso* derivative (m. p. 117°) undergoes the usual condensation when reduced in presence of cyclohexanone, yielding *anhydro*-8-*o*-carbethoxyphenyl-amino-1 : 2 : 3 : 4-tetrahydrocarbazole-9-acetic acid (I), yellow prisms,



m. p. 172°; the dibasic acid of which this is the *anhydro* ester, namely, 8-*o*-carboxyphenylamino-1 : 2 : 3 : 4-tetrahydrocarbazole-9-acetic acid, has m. p. 243° (*acetyl* derivative, m. p. 250°) and when it is heated with sulphuric acid gives no acridoline derivative but only *anhydro*-8-*o*-carboxyphenylamino-1 : 2 : 3 : 4-tetrahydrocarbazole-9-acetic acid, m. p. about 255°.

9-Amino-5 : 10-dihydroacridine, m. p. 114°, is obtained either through 9-nitrothioacridone, m. p. 236° (from the nitroacridone and phosphorus pentasulphide), or, better, by reducing the nitroacridone itself with sodium amalgam in presence of an excess of carbon dioxide. Its *acetyl* derivative has m. p. 177°; when this is oxidised with potassium dichromate 9-acetamidoacridine, m. p. 117°, is obtained, and hydrolysis with boiling 60% sulphuric acid then affords 9-aminoacridine, orange prisms, m. p. 105—106° (*hydrochloride*, m. p. 234°, decomp.). The latter interacts with ethyl chloroacetate to afford *ethyl acridine*-9-aminoacetate, m. p. 109°

(the *acid* has m. p. about 185°, decomp.), the *nitroso* derivative (m. p. 115—117°) of which is remarkable in giving no condensation product when it is reduced with zinc and acetic acid in presence of cyclohexanone.

The *toluene-p-sulphonyl* derivative, m. p. 169—170° (*hydrochloride*, m. p. 242°), of 9-aminoacridine interacts with ethyl *toluene-p-sulphonate* to yield the *toluene-p-sulphonyl* derivative (m. p. 175—176°) of 9-ethylaminoacridine, orange-red plates, m. p. 65° (*acetyl* derivative, m. p. 95°).

Anhydro-5 : 10-dihydroacridine-9-aminoacetic acid (see above) is converted by the action of phosphorus pentachloride into a compound,  $C_{30}H_{23}O_3N_4ClP$ , m. p. 175—178°.

When anhydrodihydroacridineaminoacetic acid is electrolytically reduced it yields what is probably 11 : 12-dihydroacridoxaline (II), a gummy substance with a pronounced irritant action on the skin. The *acetyl* derivative of this compound has m. p. 152°, but even when this is hydrolysed the parent reappears as a gum. It was thought at first that this product was the ethylaminoacridine described above (there being the two possibilities), but the independent preparation showed that this was not so.

The *toluene-p-sulphonyl* derivative (m. p. 190—191°) of 9-amino-5 : 10-dihydroacridine affords a  $\beta$ -chloroethyl derivative (m. p. 147—148°) when it is treated with  $\beta$ -chloroethyl *toluene-p-sulphonate*, but this resists condensation to form a dihydrocarboxaline ring. The analogous  $\beta$ -hydroxyethyl derivative (m. p. 154—155°) is obtained when ethylene chlorohydrin is used, and this also will not undergo intramolecular condensation. When it is oxidised in hot acetic acid solution with potassium dichromate, the *toluene-p-sulphonyl* derivative (m. p. 156°) of the corresponding acridine is obtained, and this affords the parent compound, namely, 9- $\beta$ -hydroxyethylaminoacridine, m. p. 109—110°, when hydrolysed with boiling 60% sulphuric acid. This is reduced by treatment with sodium amalgam in presence of much carbon dioxide to 9- $\beta$ -hydroxyethylamino-5 : 10-dihydroacridine, m. p. 122—123° (*diacetyl* derivative, m. p. 148°; partial hydrolysis affords the *monoacetyl* derivative, m. p. 147—148°); fruitless experiments were made to close the dihydrocarboxaline ring in this compound, using a variety of condensing agents.

When the potassium compound of the *toluene-p-sulphonyl* derivative of 9-amino-5 : 10-dihydroacridine and bromodimethylacetal are heated together at 100° in methyl-alcoholic solution the *dimethylacetalysulphonyl* derivative, m. p. 121°, is obtained; subsequent treatment with ethyl-alcoholic hydrochloric acid produced an amorphous substance.

9-Amino-5 : 10-dihydroacridine and bromodimethylacetal (with sodium acetate, and a little copper, in alcoholic solution) afford eventually 9-aminoacridine *dimethylacetal*, m. p. 87°, which is converted by reduction with sodium amalgam into the corresponding derivative of the 5 : 10-dihydroacridine, m. p. 63—64°.

When the aminodihydroacridine interacts with ethyl bromoacetate *ethyl anhydro-5 : 10-dihydroacridine-9-aminodiacetate*, m. p.

154—156°, is obtained, the parent *acid* of which has m. p. 192° (after losing 1 mol. MeOH—of crystallisation?). This acid decomposes when heated at 20 mm., yielding a distillate consisting of *anhydro-5 : 10-dihydroacridine 9-methylaminoacetic acid*, m. p. 131—132°.

**6-Nitro-9-methylacridone** (m. p. above 300°, prepared from 4-nitrotolylanthranilic acid) yields, when reduced with sodium amalgam in the manner indicated above, **6-amino-9-methyl-5 : 10-dihydroacridine**, orange prisms, m. p. 118°, and **9-chloroacridone** (Ullmann, *loc. cit.*) similarly affords **9-chloro-5 : 10-dihydroacridine**, needles, m. p. 79° (unstable), or prisms, m. p. 90—91° (stable form).  
W. A. S.

### Determination of Constitution by Spectroscopic Methods.

**Constitution of Amino-acids. I.** H. LEY and F. H. ZSCHACKE (*Ber.*, 1924, 57, [B], 1700—1707).—Comparison of the absorption curves of piperidinoacetic acid with those of its sodium salt, hydrochloride, ethyl ester, and sodium acetate shows that it is impossible that the acid exists in the normal form,  $C_5H_{10}N \cdot CH_2 \cdot CO_2H$ , since the absorption of the acid is not intermediate between that of the sodium salt and the ester. The close identity of the absorption curves of the acid and sodium acetate suggests further that the normal form cannot be present to an appreciable extent. The choice between the constitutions indicated by the schemes  $R < \begin{smallmatrix} NH_2 \cdots H \\ CO \cdots O \end{smallmatrix}$  and  $\cdot NH_3 \cdot R \cdot CO_2'$  cannot be effected on the bases

of optical measurements. In the case of aromatic amino-acids, such as *o*-aminobenzoic acid and the acids of the pyridine series, the neutral form greatly predominates.  
H. W.

### Stereochemistry of Saturated Tervalent Nitrogen. VI. Attempts to Prepare Optically Active Compounds of Tervalent Nitrogen.—(See i, 1299.)

**6-Methoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline.** L. HELFER (*Helv. Chim. Acta*, 1924, 7, 945—950).—The initial stages in the synthesis of this compound are described as follows: *m*-nitrobenzaldehyde  $\rightarrow$  *m*-aminobenzaldehyde  $\rightarrow$  *m*-hydroxybenzaldehyde  $\rightarrow$  *m*-methoxybenzaldehyde  $\rightarrow$  *m*-anisylacrylic acid  $\rightarrow$  *m*-anisylpropionic acid  $\rightarrow$  *methyl m-anisylpropionate* (m. p. 29—30°, b. p. 150—152°/14 mm.)  $\rightarrow$  *m-anisylpropionamide* (m. p. 56°, b. p. 218—219°/9 mm.)  $\rightleftharpoons$   $\beta$ -*m-anisylethylamine* (b. p. 247—248° or 122—123°/7 mm.). The last substance is a strong base forming a *carbonate*; *hydrochloride*, m. p. 145—146°; *picrate*, m. p. 134°; and *chloroplatinate*, m. p. 204—205° (decomp.). The action of formaldehyde on  $\beta$ -*m-anisylethylamine* gives  $\beta$ -*m-anisylethylmethylethylamine*, a viscous oil. Evaporated to dryness with hydrochloric acid, this gives the *hydrochloride* of 6-methoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline. The latter is a strong base (b. p. 143—144°/6 mm.), forming a crystalline *carbonate*; *hydrochloride*, m. p. 233—234°; *picrate*, m. p. 173—174° (decomp.); *chloroplatinate*, orange-red, m. p. 198°;

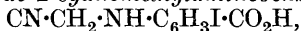


and *nitrosoamine*, a yellow oil. When the base is oxidised by alkaline permanganate, 4-methoxyphthalimide (m. p. 231°) is obtained together with some 4-methoxyphthalic acid (T., 1907, 91, 103).  
W. E. E.

**Isatin and Related Compounds. VI. 5-Iodoisatin and 5:5'-Di-iodoindigotin.** W. BORSCHÉ, H. WEUSSMANN, and A. FRITZSCHE (*Ber.*, 1924, 57, [B], 1770—1775).—5-Iodoisatin, m. p. 264—265°, is prepared by the action of iodine monochloride on a solution of isatin in glacial acetic acid or by the action of concentrated sulphuric acid on *p*-iodo-oximinoacetanilide,  $C_6H_4I \cdot NH \cdot CO \cdot CH : N \cdot OH$ , m. p. 180—182° (prepared from *p*-iodoaniline, hydroxylamine, and chloral hydrate). 5-Iodoisatin-3-hydrazone, decomp. 240° after becoming discoloured at 170°, is described. 5-Iodo-1-methylisatin, m. p. 175°, is obtained by methylation of 5-iodoisatin with methyl sulphate and sodium hydroxide, or from 1-methylisatin and iodine chloride. 5-Iodoisatin is transformed by acetone in the presence of aqueous-alcoholic potassium hydroxide solution into 6-iodo-2-methylquinoline-4-carboxylic acid, m. p. 290°, which passes at 300° into 6-iodo-2-methylquinoline, m. p. 107—108° (*picrate*, m. p. 194—195°). Similarly, acetophenone and 5-iodoisatin give 6-iodo-2-phenylquinoline-4-carboxylic acid, m. p. 249—250°, from which 6-iodo-2-phenylquinoline, m. p. 143—144°, is derived. 6-Iodo-2-hydroxyquinoline-4-carboxylic acid, m. p. above 320°, is converted by a solution of phosphorus pentachloride in phosphoryl chloride into a mixture of 2-chloro-6-iodoquinoline-4-carboxylic acid, m. p. 215—216°, and 6-iodo-2-hydroxyquinoline-4-carboxyl chloride, m. p. 265—266°.

5-Iodoisatin chloride, m. p. 226—228°, prepared from iodoisatin and phosphorus pentachloride in the presence of benzene, is transformed by heating with aniline into 5-iodo-2-aniloisatin, m. p. 223—224°, and thence by the action of ammonium sulphide and hydrogen sulphide into 5:5'-di-iodoindigotin.

5-Iodoanthranilic acid, m. p. 212—214° (decomp.), is conveniently prepared by the action of iodine monochloride on anthranilic acid dissolved in glacial acetic acid. It is converted by acetic anhydride into 5-iodo-2-acetamidobenzoic acid, m. p. 241—242°. Attempts to prepare the latter compound by the direct iodination of acetamidobenzoic acid yielded a mixture of unchanged material and 3:5-di-iodoanthranilic acid, m. p. 232—233°; if a larger proportion of iodine chloride is used, 2:4:6-tri-iodoaniline, m. p. 186°, is also produced. 5-Iodo-2-cyanomethylaminobenzoic acid,



m. p. 217°, is obtained together with an unidentified substance, m. p. 184—186°, by the action of potassium cyanide and formaldehyde on 5-iodoanthranilic acid in aqueous solution. It is hydrolysed by 3*N*-sodium hydroxide solution to 5-iodo-2-carboxymethylaminobenzoic acid, m. p. 207—208°, which is more conveniently obtained from phenylglycine-*o*-carboxylic acid and iodine chloride. It appears to lose a part of the iodine when fused with potassium hydroxide.  
H. W.

**Transformation of Isatogen Derivatives into Isatins.**

P. RUGGLI and W. LEONHARDT (*Helv. Chim. Acta*, 1924, 7, 898—907).—The by-product previously obtained (this vol., i, 1106) from the action of acetic anhydride and sulphuric acid on 6-nitro-2-phenylisatogen varies according to the proportion of sulphuric acid. It is yellow (for additive products of nitrophenylisatogen and acetic anhydride, see below) for acid percentages below 3, and red when the percentage is 3 to 6, and then consists chiefly of 6-nitro-1-phenylisatin, m. p. 232° (*ammonium, potassium, barium*, and *silver* salts described; *methyl ether*, reddish-gold leaflets, m. p. 82°). The barium salt, when heated in acetic acid solution, affords 4-nitro-1-phenylisatin, yellow crystals, m. p. 288—290° (decomp.). With *o*-phenylenediamine, the nitrophenylisatin affords 6-nitro-1-phenylindophenazine, yellow needles, m. p. above 310° (decomp.). The *oxime* of the nitroisatin forms yellow needles, m. p. 227—230° (decomp.), and is converted by diazomethane into the *methyl ether*, golden-yellow tablets, decomp. 170—175°. The corresponding *hydrazone* forms yellow leaflets, m. p. 220—225° (decomp.), and the  $\beta$ -phenylhydrazone, brick-red needles, m. p. 238° (decomp.). The latter, when heated with excess of phenylhydrazine, gives 6-amino-1-phenylisatin- $\beta$ -phenylhydrazone, red needles, m. p. 213° (*diacetyl* derivative, orange-yellow needles, m. p. 255—256°). From the above nitrophenylisatin mother-liquors, 4-nitrobenzoylanthranil (m. p. 179°) and 4-nitrobenzoylanthranilic acid (m. p. 252°) were also obtained. By treatment with acetic anhydride the latter is converted into the former.

Nitrophenylisatogen forms a labile *additive* compound (yellow needles, decomp. 65—70°) with acetic anhydride (1 mol.) when treated with a mixture of the latter with sulphuric acid. W. E. E.

**Fission of the Pyridine Nucleus during Reduction.**

B. D. SHAW (*J. Chem. Soc.*, 1924, 125, 1930—1934).—When pyridine is reduced with sodium and aqueous alcohol (95%) instead of absolute alcohol, little or no piperidine is formed, but ammonia is evolved and a resinous nitrogen-free product is obtained, with traces of a volatile oil, possibly pentamethylene oxide. Simple derivatives of pyridine also suffer this disruption (cf. Mumm and Brodersen, this vol., i, 82). Ammonia is readily given off when 2-stilbazole is similarly reduced and the product, after repeated treatment to ensure complete conversion, consists chiefly of 2- $\beta$ -phenylethyltetrahydropyran, m. p. 77°. Quantitative experiments with pyridine indicate that the scission takes place at the dihydro stage of the reduction. W. A. S.

**Vinyl Derivatives, especially of Carbazole and Tetrahydrocarbazole, and their Behaviour with Acids.** G. R. CLEMO and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1924, 125, 1804—1814).—By interaction of toluene-*p*-sulphonanilide and  $\beta$ -chloroethyl toluene-*p*-sulphonate toluene-*p*-sulphon- $\beta$ -chloroethylanilide, m. p. 76°, is obtained. When treated with potassium iodide in hot amyl alcohol, it affords the  $\beta$ -iodo analogue, m. p. 81—82°; with diethylamine in alcohol at 160° it yields a product from which,

by hydrolysis,  $\beta$ -diethylaminoethylaniline, b. p.  $163^{\circ}/17$  mm., is obtained; similarly, with *o*-chloroaniline, potassium carbonate and a little copper powder, the *toluene-p-sulphonyl* derivative, m. p.  $110^{\circ}$ , of  $\beta$ -*o*-chlorophenylaminoethylaniline, b. p.  $238-242^{\circ}/20$  mm. (*hydrochloride*, m. p.  $185^{\circ}$ ), is produced. Further, treatment with methyl-alcoholic potassium hydroxide effects the conversion into *toluene-p-sulphonvinylanilide*, m. p.  $96-97^{\circ}$ ; this unites with bromine to form an unstable *dibromo* compound, which is converted by warm methyl-alcoholic potassium hydroxide into *toluene-p-sulphon- $\beta$ -bromo- $\alpha$ -methoxyethylanilide*, m. p.  $78-79^{\circ}$ . The vinyl derivative is readily decomposed when it is treated with dilute sulphuric acid, the parent anilide and acetaldehyde being formed. This agrees, and so do the observations described below, with the results obtained by other investigators (cf. *e.g.*, von Braun and Kirschbaum, A., 1920, i, 154) of the behaviour of *N*-vinyl derivatives.  $\beta$ -Chloroethylaniline (cf. Nemirowsky, A., 1885, 741) is unstable; it "polymerises" to a chlorine-free solid substance of unknown constitution; its *hydrochloride*, m. p.  $156-158^{\circ}$ , is obtained by hydrolysing the above *toluene-p-sulphonyl* derivative with a mixture of acetic and hydrochloric acids. When part of the product is directly benzoylated (using a benzene solution of benzoyl chloride and an excess of sodium hydroxide), the chlorine atom is simultaneously removed and *benzo- $\beta$ -hydroxyethylanilide*, m. p.  $78^{\circ}$ , is obtained. When  $\beta$ -chloroethylaniline hydrochloride is treated with sodium nitrite, it affords an oil which, by the action of alcoholic hydrogen chloride is converted into *p-nitroso- $\beta$ -chloroethylaniline*, m. p.  $90^{\circ}$  (decomp.  $120^{\circ}$ ), the *hydrochloride* of which has m. p.  $182^{\circ}$  (decomp.); when the intermediate oily nitrosoamine is reduced by zinc dust and acetic acid in presence of cyclohexanone,  $\beta$ -chloroethyltetrahydrocarbazole, m. p.  $56-57^{\circ}$ , is obtained, together with a *by-product*, m. p.  $141^{\circ}$ . 9-Vinyltetrahydrocarbazole, b. p.  $210^{\circ}/24$  mm., is produced by the customary treatment with methyl-alcoholic potassium hydroxide. When this is treated with 50% sulphuric or alcoholic hydrochloric acid it is decomposed and a solid product is formed; this is due apparently to interaction of the acetaldehyde and tetrahydrocarbazole produced, because if a little hydrazine be added to the reaction mixture, tetrahydrocarbazole is obtained. 9-Vinyltetrahydrocarbazole cannot be prepared from 9- $\beta$ -hydroxyethyltetrahydrocarbazole, m. p.  $69-70^{\circ}$ , b. p.  $230-235^{\circ}/14$  mm., which is obtained when  $\beta$ -hydroxyethylphenylnitrosoamine is reduced, as above, in presence of cyclohexanone. Carbazole and  $\beta$ -chloroethyl *toluene-p-sulphonate* afford 9- $\beta$ -chloroethylcarbazole, m. p.  $130-131^{\circ}$ , from which 9-vinylcarbazole, m. p.  $66^{\circ}$ , is readily obtained. This also is decomposed by acids, when hydrazine is present, and carbazole is regenerated; if the hydrazine be absent, a complex solid substance is produced.

W. A. S.

**Reduction Products of 1-Nitro- and 3-Nitro-carbazole.**  
T. C. WHITNER, jun. (*J. Amer. Chem. Soc.*, 1924, 46, 2326-2329).  
—3-Nitro- and 1-nitro-carbazole, obtained by nitration of carb-

azole in acetic acid at 60° (cf. Ziersch, A., 1909, i, 961), on heating with alcoholic sodium or potassium hydroxide are reduced to 3-azoxycarbazole, yellow, m. p. 208—209°, and 1-azoxycarbazole, yellow, m. p. 183—185°, respectively, in yields of 70—80%. Reduction of the azoxycarbazoles in alcoholic solution with zinc dust gives an 80% yield of 3-azocarbazole, red, m. p. 215°, and 1-azocarbazole, reddish-brown, m. p. 196—197°, respectively. Reduction of 1-nitro-, 1-azoxy-, or 1-azo-carbazole with zinc dust in alcoholic potassium hydroxide yields 1-aminocarbazole, m. p. 226—228° (acetyl derivative, m. p. 170—171°). 3-Aminocarbazole, m. p. 254° (cf. Ruff and Stein, A., 1901, i, 619; Ullmann, A., 1898, i, 591) is similarly obtained from the corresponding 3-carbazole derivatives.

R. B.

**3-Hydroxyquinoline-4-carboxylic Acids.** S. BERLINGOZZI and G. B. CAPUANO (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 91—94).—3-Hydroxy-2-methylquinoline-4-carboxylic acid (cf. this vol., i, 314) may be obtained by the condensation of isatoic acid with chloroacetone in presence of sodium hydroxide, and 3-hydroxy-2-phenylquinoline-4-carboxylic acid (*loc. cit.*) by the similar condensation of isatoic acid with  $\omega$ -bromoacetophenone (cf. also A., 1923, i, 482).

3-Hydroxy-2-*p*-anisylquinoline-4-carboxylic acid, prepared similarly from isatoic acid and *p*-chloroacetylanisole, crystallises in lustrous, golden-yellow rosettes, m. p. about 190° (decomp.), and forms an intensely fluorescent alcoholic solution. When heated above its melting point, it loses carbon dioxide with formation of 3-hydroxy-2-*p*-anisylquinoline (cf. A., 1923, i, 483). The colours of various (precipitated) salts of the above acids are recorded.

T. H. P.

**Structure of the Protein Molecule.** E. ABDERHALDEN and E. SCHWAB (*Z. physiol. Chem.*, 1924, **139**, 68—75).—By condensation of isobutylpiperazine (this vol., i, 876) with  $\alpha$ -bromoiso-hexoyl bromide, *di- $\alpha$ -bromoisohexoylisobutylpiperazine*, m. p. 283° (decomp.) after previously sintering, has been obtained. This reacts with ammonia to form *dileucylisobutylpiperazine*, which, on reduction by the method previously employed (*loc. cit.*) yields a mixture of isobutylpiperazine and reduced dileucylisobutylpiperazine (isolated as the *tetrahydrochloride*,  $C_{20}H_{48}N_4Cl_4$ ). By similar methods of reduction,  $\beta$ -amino- $\delta$ -methylpentan- $\alpha$ -ol (leucinol),  $CHMe_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot OH$ , isolated as the *hydrochloride*, has been obtained from leucylglycine, and 2-methylpiperazine, m. p. 245°, from glycyl-*D*-alanine anhydride. *Dichloroacetylmethylpiperazine* on treatment with ammonia gives *diglycylmethylpiperazine*. E. S.

**Preparation of Compounds of Diketopiperazines with Amino-acids and Polypeptides.** E. ABDERHALDEN and E. KLARMANN (*Z. physiol. Chem.*, 1924, **139**, 64—67).—When refluxed with chloroacetyl chloride for 2 hours at 60—70°, 2 : 5-dihydroxy-dihydropyrazine dibenzyl ether (Karrer, Gränacher, and Schlosser, this vol., i, 212) yields 1 : 4-di[chloroacetyl]-2 : 5-diketopiperazine

(A., 1923, i, 1025; this vol., i, 877), and not the expected *O*-dichloroacetyl derivative.

By heating glycine anhydride for 4 hours at 160° with thionyl chloride, a substance,  $C_4H_2ON_2Cl_3$ , m. p. 168—169° (uncorr.), is obtained. E. S.

**Formation of Diketopiperazines from Polypeptides.** E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1924, **139**, 147—168).—On heating in a sealed tube at 150—160° for 6 hours with water, dilute hydrochloric acid, or dilute sulphuric acid, dipeptides give the corresponding anhydrides (diketopiperazines) in a yield which may vary from 20—90% of the theoretical. The only exception to this statement so far encountered is *dl*-valyl-*dl*-leucine, which gave no anhydride under these conditions. Prolonged boiling of the dipeptides in aqueous solution gave only traces of anhydrides. Small amounts of anhydrides have been obtained similarly from some tripeptides, but in no case where the tripeptide was composed of more than two different amino-acids.

C. R. H.

**Parabanic Acid.** R. ANDREASCH (*Monatsh.*, 1924, **45**, 9—12).—Thiocarbamide and cyanogen do not form thioparabanic acid. Interaction of acetylthiocarbamide and chloroacetic acid gave thiohydantoin. Attempts to add cyanogen to acetylthiocarbamide, and to carbamide and its methyl and phenyl derivatives were unsuccessful. Ethylparabanic acid has m. p. 127—128°.

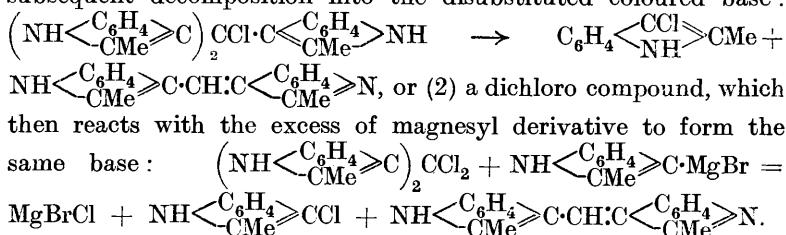
The product of reduction of dimethylparabanic acid or cholestrophan (A., 1882, 1054) is definitely proved to be 5-hydroxy-1:3-dimethylhydantoin (cf. Biltz and Heidrich, A., 1921, i, 817), since it is shown that for its reoxidation to cholestrophan, dichromate equivalent to two hydrogen atoms per mol. is required.

F. M. H.

**"Indigosol."** A. BEIL (*Z. angew. Chem.*, 1924, **37**, 745—746).—Leuco-indigotin is converted into an acid ester by treatment, in the presence of a tertiary base, with sulphur trioxide or substances which liberate it. The sodium salt of the ester, *Indigosol O*, is a nearly colourless powder, stable in the air and easily soluble in water, is unaffected by alkalis, and is decomposed by mineral acids only on prolonged boiling. Indigotin is regenerated by gentle oxidation (*e.g.*, with ferric chloride, or sodium nitrite, dichromate, or chlorates) in the presence of an acid. Indigosol has no affinity for vegetable fibres, but is substantive for wool, and possesses many practical advantages for the dyeing and printing of cotton and wool. [Cf. B., 1924, 934.] W. T. K. B.

**Indole Group. XI. Di-indylmethane.** B. ODDO and G. SANNA (*Gazzetta*, 1924, **54**, 682—687).—An attempt to prepare an indole derivative corresponding with hexaphenylethane by treating magnesium indolyl (or 2-methylindolyl) bromide with carbon tetrachloride did not give the expected result, since, under the most varied conditions, this reaction yielded always the di-

substituted methane derivative which is obtained from magnesium indolyl bromide and chloroform (A., 1922, i, 313; 1923, i, 715). Apparently attachment of more than two indole nuclei to one and the same carbon atom is not possible, probably owing to the proclivity of such nuclei to pass into the coloured indolidenic form. The reaction of magnesium 2-methylindolyl bromide with carbon tetrachloride may result in the initial formation of either (1) the normal trisubstituted leuco-derivative, which undergoes subsequent decomposition into the disubstituted coloured base:



T. H. P.

**Isomeric Acylindazoles of K. von Auwers.** J. MEISENHEIMER and A. DIEDRICH (*Ber.*, 1924, 57, [B], 1715—1723).—The general existence of 2-acylindazoles in isomeric labile and stable forms has been attributed by von Auwers and his co-workers (A., 1919, i, 455; 1920, i, 638, 640; 1922, i, 682, 684) to stereoisomerism conditioned by the presence of an asymmetric tervalent nitrogen atom. This conception is compatible with the tricyclic constitution of indazoles, but cannot be extended to the more recently adopted dicyclic constitution (cf. von Auwers, this vol., i, 878). The non-formation of stereoisomerides from 3-substituted indazoles suggests the possibility that one form of the “isomerides” is actually a 3-derivative, but this view is not supported by the experimental evidence now adduced. The only remaining alternative to the acceptance of the stereoisomeric formulation lies in the possibility that one form is a 1-compound. This conception has been rejected by von Auwers, since 1-acetylindazole, obtained from *o*-aminobenzaldoxime, is not identical with either of the “stereoisomeric 2-acetylindazoles.” Re-examination of the former product renders very probable that it is not a derivative of indazole but is derived from the seven-membered ring,  $\text{C} \begin{array}{c} \text{C-C:N} \\ \text{N:C:O} \end{array}$ . The products described by von Auwers are therefore regarded as 1- and 2-acylindazoles.

3-Benzoylindazole, m. p. 188—189°, is prepared by the action of a considerable excess of magnesium phenyl bromide on 3-cyanoindazole in ethereal solution; the *acetyl* derivative, m. p. 121°, 2:4-dinitrophenylhydrazone, m. p. 277°, and the *oxime*, m. p. 175°, are described. 3-Acetylindazole, m. p. 182°, yields an *acetyl* derivative, m. p. 123°, an *oxime*, m. p. 222°, and a 2:4-dinitrophenylhydrazone, m. p. above 320°. The acyl compounds differ completely from von Auwers’ “stereoisomeric” acetyl- and benzoyl-indazoles.

*o*-Aminobenzaldoxime is readily converted by glacial acetic acid and acetic anhydride into *o*-acetamidobenzaldoxime, which is transformed by concentrated sulphuric acid into "4:5-benzo-7-methylhept-1:2:6-oxdiazine"  $C_6H_4 \begin{smallmatrix} C(OH):N \\ N=CM_e \end{smallmatrix} O$  (von Auwers' 1-acetylindazole). The substance is oxidised by perbenzoic acid in alcoholic solution to 3-hydroxy-4:5-benzo-7-methylhept-1:2:6-oxdiazine,  $C_6H_4 \begin{smallmatrix} C(OH):N \\ N=CM_e \end{smallmatrix} O$ , m. p. 209°; attempts to establish the constitution of the compound by its production from the oxime of methyl acetylanthranilate were unsuccessful. 3-Acetoxy-4:5-benzo-7-methylhept-1:2:6-oxdiazine has m.p. 117°. If von Auwers' conception is adopted the compound just mentioned must be identical with the diacetyl derivative of *o*-hydrazinobenzoic anhydride, m. p. 113—114°, and the oxidation product with *mono*-acetyl-*o*-hydrazinobenzoic anhydride, m. p. 211°; this, however, is not the case. The oxidised product may be regarded as a cyclic ether of benzhydroxamic acid; it could not be synthesised from *o*-aminobenzhydroxamic acid since the latter is immediately converted by acetic anhydride into the *diacetyl* derivative, m. p. 128°, with which, after hydrolysis, the desired ring closure could not be effected.

H. W.

**Constitution of Acylindazoles.** K. VON AUWERS (*Ber.*, 1924, 57, [B], 1723—1730).—As a result of the observations of Meisenheimer and Diedrich (preceding abstract) the constitution assigned previously to the "1-acylindazoles" is considered to have lost greatly in probability. The conception of these compounds as heptoxdiazines is not regarded as established, since the constitution of 3-hydroxy-7-methyl-4:5-benzohept-1:2:6-oxdiazine has not been placed beyond doubt and proof has not been adduced that the oxidation takes place without rupture of the ring of the parent compound.

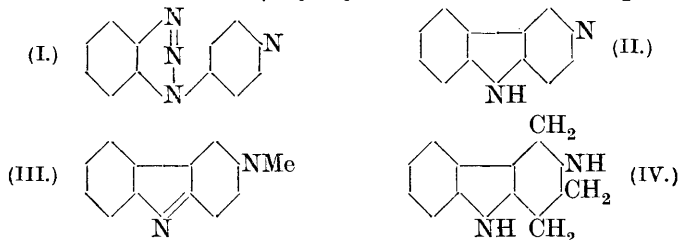
The "1-acylindazoles" are conveniently prepared by dissolving *o*-aminobenzaldoxime in the requisite acid and saturating the solution with dry hydrogen chloride at the atmospheric temperature or by treating a solution of the acylated oxime in glacial acetic acid in the same manner. "1-Acetylindazole" is converted by methyl iodide into an amorphous *methiodide*,  $C_{10}H_{11}ON_2I$ , decomp. above 90°, by bromine in glacial acetic acid into a very unstable *dibromide* and by the halogen in dilute hydrochloric acid solution into a *monobromo* derivative, m. p. 168—169°. 1-iso-*Butyrylindazole* (or 7-isopropyl-4:5-benzohept-1:2:6-oxdiazine) has m. p. 108—108.5°; the *nitrate* and the additive compound with mercuric chloride dissolve sparingly in water. 1-iso-*Valerylindazole* (7-isobutyl-4:5-benzohept-1:2:6-oxdiazine) has m. p. 85—86°,  $d_4^{20} 1.0620$ ,  $n_D^{20} 1.58638$ ; the *nitrate* and the additive compound with mercuric chloride have been prepared. 1-*Benzoylindazole* (7-phenyl-4:5-benzohept-1:2:6-oxdiazine), m. p. 141° (the *nitrate* and the additive compound with mercuric chloride are described), is obtained from *o*-benzamidobenzaldoxime, m. p. 163—164°. *o*-Aminoacetophenoneoxime, propionic acid, propionic anhydride,

and hydrogen chloride yield 1-*propionyl*-3-methylindazole (3-methyl-7-ethyl-4 : 5-benzohept-1 : 2 : 6-oxdiazine), m. p. 138°, which gives a *nitrate* and an additive compound with mercuric chloride. 1-Formyl-3-phenylindazole (3-phenyl-4 : 5-benzohept-1 : 2 : 6-oxdiazine), m. p. 167—168°, gives an additive compound with mercuric chloride. 1-Benzoyl-3-phenylindazole (3 : 7-diphenyl-4 : 5-benzohept-1 : 2 : 6-oxdiazine), m. p. 168—169°, and its additive compound with mercuric chloride are described.

Benzaldehyde and *o*-aminobenzaldoxime yield the compound  $C_{14}H_{14}O_2N_2$ , m. p. 135—136°, which gives a *monobenzoyl* derivative, m. p. 138—139°. The *benzoyl* derivative of *o*-nitrobenzaldoxime has m. p. 120—121°.

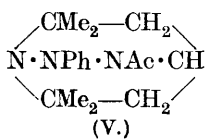
H. W.

**5-Carboline and some Derivatives.** R. ROBINSON and S. THORNLEY (*J. Chem. Soc.*, 1924, **125**, 2169—2176).—N- $\gamma$ -Pyridyl-*o*-phenylenediamine, m. p. 173·5°, obtained by heating 4-chloropyridine (b. p. 41°/13 mm.; 49°/18 mm.) with *o*-phenylenediamine at 98—140°/40 mm., forms a *hydrochloride*, and yields a *base*, probably  $\gamma$ -pyridylbenziminazole, m. p. 123°, when boiled in absolute formic acid. 1- $\gamma$ -Pyridylbenzotriazole (I), m. p. 113·5°



[*trihydrate*, m. p. 82°; *hydrochloride*, m. p. 262° (decomp.)], obtained from the above pyridyl-*o*-phenylenediamine by the action of nitrous acid, yields 5-carboline (II), m. p. 225°, when heated with excess of phosphoric acid (*d* 1·75). 5-Carboline distils unchanged at atmospheric pressure. The *hydrogen oxalate*, m. p. 226° (decomp.), and the *picrate* are described. The *methosulphate* when treated with hot concentrated potassium hydroxide yields 5-methyl-5-isocarboline (III), m. p. 203—204°, subliming at 138° in a vacuum. This base is hygroscopic and its aqueous solution is strongly alkaline. The *methosulphate*, m. p. 210—211°, with potassium hydroxide gives a colourless precipitate. 5-Carboline is reduced by sodium and *n*-butyl alcohol to 3 : 4 : 5 : 6-tetrahydro-5-carboline (IV), m. p. 215·5°, a strong base; 5-acetyl derivative, m. p. after softening, 254·5°. Acetyltriacetoneaminophenylhydrazone, m. p. 107°, could not be transformed into an indole derivative, and therefore possibly

has the structure (V). When triacetoneamine-methylphenylhydrazone is warmed with dilute sulphuric acid, 1 : 4 : 4 : 6 : 6-pentamethyl-3 : 4 : 5 : 6-tetrahydro-5-carboline is obtained. This (+1 MeOH) has m. p. 80—86° after softening at 78°. After being heated at 111°, the substance resolidifies, and has m. p. 92—93°. Crystallised from





light petroleum, it has m. p.  $180^{\circ}$  after sintering at  $160^{\circ}$ , and partly melting and resolidifying at  $170^{\circ}$ . F. G. W.

### Effect of Sulphur on the Colour of Triphenylmethane Dyes.

H. S. HOLT and E. E. REID (*J. Amer. Chem. Soc.*, 1924, **46**, 2329—2333).—The auxochromic effect of the alkylthiol group in triphenylcarbinol derivatives observed by Brand and Stallmann (A., 1921, i, 664) has now been observed in a series of malachite-green derivatives containing the alkylthiol group in the ortho or para position in the third ring. The auxochromic effect is greatest when the sulphur occupies the para position, but diminishes with increasing mass of the alkyl group. The methylthiol group is a stronger auxochrome than methoxyl, and the shift is towards the blue.

*p*-Aminophenyl methyl sulphide, obtained by the methods previously described (Waldron and Reid, this vol., i, 95; Foster and Reid, this vol., i, 1243), when diazotised and treated with cuprous bromide and potassium bromide, yields *p*-bromophenyl methyl sulphide, m. p.  $27^{\circ}$ . *p*-Bromophenyl isopropyl sulphide, b. p.  $120^{\circ}/11$  mm.,  $d_{25}^{25}$  1.2338; *p*-bromophenyl isoamyl sulphide, b. p.  $140$ — $143^{\circ}/15$  mm.,  $d_{25}^{25}$  1.1467; *p*-bromophenyl benzyl sulphide, m. p.  $48^{\circ}$ ; *p*-bromophenyl methyl sulphone, yellow, m. p.  $97.5^{\circ}$ ; *o*-bromophenyl isopropyl sulphide, b. p.  $130$ — $135^{\circ}/11$  mm.,  $d_{25}^{25}$  1.2804, and *o*-bromophenyl phenyl sulphide, b. p.  $175$ — $177^{\circ}/12$  mm.,  $d_{25}^{25}$  1.3733, were similarly prepared. With the exception of *p*-bromophenyl benzyl sulphide and methyl sulphone and *o*-bromophenyl phenyl sulphide, which do not react, these bromophenyl alkyl sulphides were convertible in presence of iodine into Grignard reagents; the latter when treated with Michler's ketone in benzene solution yielded the dyes  $(\text{NMe}_2 \cdot \text{C}_6\text{H}_4)_2\text{C}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{SR}$  as orange solids turning green on exposure to air. R. B.

**Constitution of Guinea-green B.** H. WALES (*J. Amer. Chem. Soc.*, 1924, **46**, 2124—2128).—Guinea-green B is sodium hydrogen *s*-*pp'*-dibenzyl-diethyldiaminotriphenylcarbinoldisulphonate. The free acid is brown and the disodium salt colourless, and the "organic material not dye" present in Guinea-green B is mainly the disodium salt. The free acid titrates very slowly with titanous chloride, and the higher results frequently obtained by very slow titration are due to the slow conversion of the disodium salt into the more readily reducible sodium hydrogen salt. The latter can be titrated in the presence of the disodium salt by titrating at  $60$ — $70^{\circ}$  in the presence of sodium hydrogen tartrate. The titration can be checked by a spectrophotometric method, using a disodium phosphate-acetic acid buffer solution,  $p_{\text{H}}$  6.0. R. B.

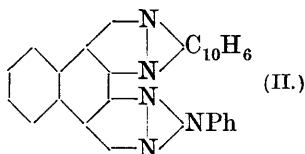
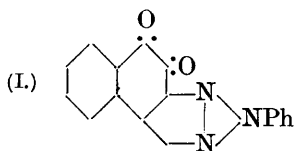
**Reduction of certain Vat Dyes by means of Alkaline Sodium Hyposulphite.** J. H. YOE (*J. Physical Chem.*, 1924, **28**, 1211—1217).—The rate of reduction of ponsol-blue G (chloro-anthraquinone-1 : 2 : 1' : 2'-dihydroazine) by alkaline sodium hyposulphite at  $40^{\circ}$  is very great, the consequent peptisation, however, being less rapid, similar to ponsol-yellow G (A., 1923, i, 236).

The reduced dye is in colloidal solution and is coagulated by salts. The amount of dye peptised was determined by the change in colour of the solution with time, and shows that the hyposulphite concentration has no effect above a certain value and that the optimum conditions are obtained with 0.25*N*-sodium hydroxide.

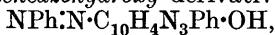
M. B. D.

**o-Quinones derived from 2-Aryl- $\alpha\beta$ -naphthatriazoles.** G. CHARRIER (*Gazzetta*, 1924, 54, 610—616).—Treatment of certain 2-aryl- $\alpha\beta$ -naphthatriazoles with potassium dichromate and sulphuric acid under conditions which convert phenanthrene into phenanthraquinone results in the quantitative formation of the corresponding quinones. That the latter are ortho-quinones of the phenanthraquinone type is shown by their marked physical and chemical resemblance to phenanthraquinone and by their reaction with *o*-diamines to give the corresponding azines and with phenylhydrazine hydrochloride to form the hydroxyazo derivatives. It seems probable that anthracene bears the same relation to the  $\beta\beta$ -naphthatriazoles that phenanthrene does to the  $\alpha\beta$ -naphthatriazoles.

2-Phenyl- $\alpha\beta$ -naphthatriazolequinone (I), obtained by oxidation of



2-phenyl- $\alpha\beta$ -naphthatriazole, forms orange-yellow needles, m. p. 207°, sublimes unchanged, and with hot alcoholic potassium hydroxide yields the brownish-green coloration characteristic for *o*-quinones. Its *benzeneazohydroxy* derivative,



bright red needles, m. p. 232°, is obtained by the action of phenylhydrazine. The corresponding *naphthazine* (II), forms a microcrystalline, yellow powder, m. p. 262°, and yields deep red salts.

2-*p*-Chlorophenyl- $\alpha\beta$ -naphthatriazolequinone,  $\text{C}_{16}\text{H}_8\text{O}_2\text{N}_3\text{Cl}$ , forms golden-yellow needles, m. p. 204°, its *benzeneazohydroxy* derivative, orange needles, m. p. 227°; the corresponding *naphthazine* is a yellow powder, m. p. 280°.

T. H. P.

**Hydrolysis of Auramine.** W. C. HOLMES and J. F. DARLING (*J. Amer. Chem. Soc.*, 1924, 46, 2343—2348).—The hydrolysis of auramine in aqueous solution has been studied using a volumetric method based on the titration of the dye with a standard indigotin solution. The velocity of hydrolysis increases with the temperature and with the acidity of the solution, and, as in the hydrolysis of sucrose and of esters, the catalytic activity of the hydrogen ions is stimulated by the presence of other ions. The rate of hydrolysis is not influenced to a measurable extent by the relative purity of the dye samples used, and hydrolysis with dilute hydrochloric acid affords a convenient volumetric method for the determination

of auramine or auramine-G. At the end of the hydrolysis, the solution is made alkaline and the ammonia distilled over and titrated, the small amount of dye unhydrolysed by the acid being decomposed by the alkali into Michler's ketone and ammonia. Auramine-G is less readily hydrolysed than auramine. R. B.

**Action of Azoimide on Azodicarboxylic Esters.** R. STOLLÉ and G. ADAM (*Ber.*, 1924, **57**, [B], 1656—1659).—Azoimide and methyl azodicarboxylate in the presence of ethyl or amyl ether give 5-methoxytetrazole,  $\begin{smallmatrix} \text{N} \cdot \text{NH} \\ | \quad | \\ \text{N} - \text{N} \end{smallmatrix} \text{C} \cdot \text{OMe}$ , m. p. 159° (decomp.), and methyl iminodicarboxylate,  $\text{NH}(\text{CO}_2\text{Me})_2$ , m. p. 134°. Under similar conditions, ethyl azodicarboxylate gives 5-hydroxytetrazole, 5-ethoxytetrazole, m. p. 98° (the silver salt is described), and ethyl iminodicarboxylate, m. p. 48°. The alkoxytetrazoles are readily hydrolysed by 20% hydrochloric acid to 5-hydroxytetrazole, m. p. 254° (decomp.). H. W.

**Synthesis of Terephthal-green and Terephthal-brilliant-green from Cymene.** M. T. BOGERT and P. S. NISSON (*Proc. Nat. Acad. Sci.*, 1924, **10**, 421—426).—Terephthalyl chloride, prepared from cymene through methyl terephthalate (cf. Bogert and Harris, A., 1920, i, 65), interacts with dimethylaniline at 100° in presence of zinc chloride or other condensing agent, yielding the dye  $\text{C}_6\text{H}_4 \left[ \text{C} \begin{smallmatrix} \swarrow \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \\ \searrow \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \text{Cl} \end{smallmatrix} \right]_2$ , eventually isolated as zinc double salt. This compound is analogous to malachite-green and is termed by the authors "terephthal-green." The analogue of brilliant-green, termed "terephthal-brilliant-green" is obtained when diethylaniline is used. The two dyes both give yellower shades of green (on silk or wool) than their prototypes; they are more fugitive to light but faster than the latter to washing, milling, perspiration, and stoving, and are equally resistant to acid, alkali, or a bleaching solution. When terephthalyl chloride and dimethylaniline are brought together without a condensing agent, interaction takes place, not at 100°, but when the mixture is boiled; methyl chloride is evolved, and the *methylanilide*,  $\text{C}_6\text{H}_4(\text{CO} \cdot \text{NMePh})_2$ , m. p. 212—213°, is formed (cf. the action of benzoyl chloride on dimethylaniline, Hess, A., 1885, 783). W. A. S.

**Behaviour of Acetylene towards Nitrogen.** L. FRANCESCONI and A. CIURLO (*Gazzetta*, 1924, **54**, 687—697).—Under the influence of the silent electric discharge, a mixture of acetylene and nitrogen yields a compound which contains nitrogen and has a fulvene structure, and may be termed *pernitrogenated azofulvene*. This compound forms reddish-yellow laminæ, has a strong aromatic odour, and decomposes violently, without melting, at above 210°. When heated in a closed tube with solid potassium hydroxide, a basic odour recalling that of nicotine is emitted. Like the similar substances described by Losanitsch (A., 1908, i, 866; ii, 32), the compound increases rapidly in weight in the air, giving a darker, opaque *peroxidised azofulvene* which decomposes violently at 230—

235° and effects active discharge of an electrometer. It absorbs chlorine, bromine, and iodine in considerable quantities and reacts with other substances.

T. H. P.

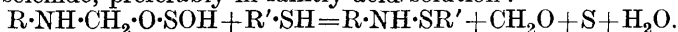
### Electrometric Studies on Azo and Hydrazo Compounds.

E. BIILMANN and J. H. BLOM (*J. Chem. Soc.*, 1924, 125, 1719—1731).—An investigation of the reduction potential of the system azo compound—hydrazo compound on the same lines as those with quinhydrone and alloxantin for subjects (cf. A., 1923, ii, 605; 1921, ii, 372).

Two pairs of compounds were studied, *viz.*, 3:3'-diaminoazo-benzene (termed azoaniline) and the corresponding hydrazo compound, and 3:3'-diamino-4:4'-dimethylazobenzene (termed azo-toluidine) and the corresponding hydrazo compound. These were chosen because, being basic in character, they could be readily dissolved in acid to solutions of suitable concentration. At a temperature of 291° Abs. and a hydrogen pressure of 760 mm. the reduction potential for the azo—hydrazoaniline system (in 0.1*N*-hydrochloric acid) is 0.4137 volt, and for the azo—hydrazo-toluidine system 0.3754 volt. The potential of the azo—hydrazo electrode, depending as it does on the proportion of azo to hydrazo compound, changes with time; this is evidently due to the conversion of the hydrazo compound into a benzidine or semidine derivative. From the observations made, the velocity constant of this conversion has been calculated for the two examples studied.

W. A. S.

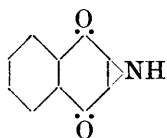
**Preparation of Thio or Seleno Derivatives of Primary Aromatic Amines.** FARBERWERKE VORM. MEISTER, LUCIUS, UND BRÜNING (D.R.-P. 386615; from *Chem. Zentr.*, 1924, i, 2631).—Derivatives of the hypothetical thiohydroxylamine,  $\text{NH}_2\text{SH}$ , or dialkyldithiohydroxylamines,  $\text{RN}(\text{SR}')_2$ , are obtained by treating the condensation products of aromatic amines and aldehydesulphoxylates with hydrogen sulphide, mercaptans, etc., or hydrogen selenide, preferably in faintly acid solution:



The products separate as yellow precipitates; the following are described: *product* from hydrogen sulphide and *o*-toluidine *N*-methylenesulphoxylate, m. p. about 97°; the crystalline *product* from *p*-aminobenzoic acid and sodium formaldehydesulphoxylate,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OSONa}\cdot 2\text{H}_2\text{O}$ , reacts with thioacetic acid to give *S*-acetyl-*p*-thiohydroxylaminobenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SAC}$ , m. p. 153°. Anthranilidomethylenesulphoxylate and ethyl mercaptan afford *p*-ethylthiohydroxylaminobenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SEt}$ , m. p. 97—99°. Aniline *N*-methylenesulphoxylate and thioacetic acid yield *SS*-diacetyldithiodihydroxyaniline,  $\text{NPh}(\text{SAC})_2$ , m. p. 72°. Anthranilidomethylenesulphoxylate reacts with hydrogen selenide at 40—50° to give a substance,  $\text{C}_{16}\text{H}_{14}\text{O}_6\text{N}_2\text{SSe}$ , m. p. 40°, decomp. 80°. The condensation *product* of *o*-phenylenediamine and formaldehydesulphoxylate reacts with hydrogen selenide to give a substance,  $\text{C}_{14}\text{H}_{19}\text{O}_7\text{N}_4\text{S}_3\text{Se}$ , reddish crystals, m. p. 183—184°.

F. A. M.

**Derivatives of Azoimide.** A. KORCZYŃSKI [with ST. NAMYSLOVKI] (*Bull. Soc. chim.*, 1924, [iv], **35**, 1186—1194).—The replacement of halogen atoms by azide groups when substituted quinones are treated with azoimide (Fries and Ochwat, A., 1923, i, 842) is a general reaction and mobile halogen atoms in compounds such as picryl chloride are replaced in the same way. With the unsubstituted naphthaquinones, azoimide reacts with the CH group ortho to the carbonyl yielding products,  $C_{10}H_5O_2N$ , which are analogous to the anthranils obtained by Schaarschmidt (A., 1916, i, 856) and by Gattermann (A., 1916, i, 857; 1921, i, 818). The diazido- $\alpha$ -naphthaquinone obtained by Fries and Ochwat (*loc. cit.*) could not be transformed into a dianthranil, and to account for the resistance of the benzene ring in the naphthalene molecule to



the formation of a dianthranil, the annexed formula is suggested for the mono-anil. This finds some support in the behaviour of sulphuryl azide towards *p*-xylene (Curtius and Schmidt, A., 1922, i, 776). The azides are slightly stable, and although the azide group exercises an important influence on the colour

of these compounds, this influence is irregular, and the azide group sometimes functions as a bathochrome and sometimes as hypsochrome, possibly in consequence of a change of structure in the group  $N_3 \cdot N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} N \rightleftharpoons \cdot N : N : N$ . The statement that azides on alkaline

reduction yield hydrazo compounds could not be confirmed.

On treatment with one equivalent of sodium azide in glacial acetic acid at  $100^\circ$ , chloroanil is converted into 3 : 5 : 6-trichloro-2-azido-*p*-benzoquinone, dark orange needles, m. p.  $147\text{--}149^\circ$ , exploding slightly on rapid heating, whilst with two equivalents of azide in boiling alcoholic solution 3 : 6-dichloro-2 : 5-diazido-*p*-benzoquinone is obtained, a slight excess of sodium azide giving a small quantity of reddish-violet explosive substance, probably the triazidochloroquinone. Excess of sodium azide in alcoholic solution at  $20^\circ$  converts the trichloroazidoquinone into tetrazido-*p*-benzoquinone. Similarly, tetrabromo-*o*-benzoquinone in glacial acetic acid yields an explosive, black substance which is probably tetra-azido-*o*-benzoquinone. Tetrabromodiphenoquinone in alcoholic suspension yields tetra-azidodiphenoquinone, a black powder which explodes at  $30^\circ$  or by friction or shock. 1 : 4-Naphthaquinone in acetic acid with one equivalent of sodium azide yields 2 : 3-imino-1 : 4-naphthaquinone, reddish-brown laminæ, m. p.  $203\text{--}204^\circ$ , also crystallising with 1 mol. of acetic acid (lost at  $110^\circ$ ). Similarly, 1 : 2-naphthaquinone yields 3 : 4-imino-1 : 2-naphthaquinone, brown laminæ, losing acetic acid of crystallisation at  $110^\circ$ , then decomp.  $300^\circ$ . 2-Aminofluorenone, obtained by reduction of 2-nitrofluorenone with sodium sulphide, on diazotisation and treatment of the diazonium chloride with sodium azide, gives 2-azidofluorenone, yellow laminæ, darkening at  $115^\circ$ , m. p.  $117^\circ$ , slightly explosive. On heating in an atmosphere of carbon dioxide, boiling in glacial acetic acid, or exposing to light, the azide is converted into a brown, amorphous substance,  $C_{13}H_7ON$ , not melting below  $300^\circ$ .

Similarly, aminoazobenzene is converted into *p*-azidoazobenzene, pale yellow needles, m. p. 91—93°, and toluylene-red, obtained by boiling *p*-nitrosodimethylaniline with *m*-tolylenediamine and treatment with ammonia to precipitate the colour but leave the hydro-base in solution, gives 3-azido-6-dimethylamino-2-methylphenazine, red needles, m. p. 171—172° (decomp.).

Picryl chloride in alcoholic solution reacts with aqueous sodium azide giving 2 : 4 : 6-trinitro-1-azidobenzene, m. p. 89—90° (decomp.), which darkens in colour on exposure to light and on boiling with acetic acid is converted into 4 : 6-dinitro-1 : 2-dinitrosobenzene, pale yellow needles, m. p. 172°, decomposed by light, which is also obtained directly from picryl chloride by the action of sodium azide in acetic acid solution at 100°. On warming with aniline in ethereal solution, picryl azide is converted into 2 : 4 : 6-trinitrodiphenylamine (Bamberger and Müller, A., 1900, i, 217).

R. B.

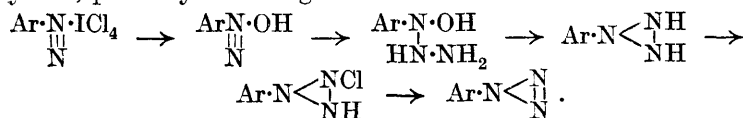
### Diazonium Tetrachloroiodides and Chloroplumbates.

F. D. CHATTAWAY, F. L. GARTON, and G. D. PARKES (*J. Chem. Soc.*, 1924, 125, 1980—1991).—Diazonium tetrachloroiodides,  $\text{Ar}\cdot\text{N}_2(\text{Cl}_4\text{I})$  (cf. Chattaway and Garton, this vol., i, 270), are obtained, in quantitative yield, when cooled solutions of diazonium chlorides are poured into cooled solutions of iodine trichloride in strong hydrochloric acid. They can be preserved indefinitely in sealed tubes or in an atmosphere of dry chlorine, and react generally in the same way as simple diazonium salts. With hydriodic acid, iodine is liberated quantitatively:  $\text{Ar}\cdot\text{N}_2\cdot\text{ICl}_4 + 4\text{HI} = \text{ArI} + \text{N}_2 + 2\text{I}_2 + 4\text{HCl}$ , this rendering iodometric analysis possible. When warmed with cuprous chloride or bromide in concentrated acid solution, or with potassium cyanocuprite, the diazonium tetrachloroiodides yield chloro, bromo, or cyano compounds, always accompanied by small quantities of the iodo derivative. The action of water yields phenols, with chlorophenols as by-products, whilst the action of alcohol causes the replacement of the diazo group chiefly by chlorine, and only to a lesser extent by hydrogen. The following *diazonium tetrachloroiodides*, yellow, crystalline powders, melting with decomposition at the temperatures quoted, are described: *o*-toluene-, 81.5°; *p*-toluene-, 95°; *o*-chlorobenzene-, 148°; *p*-chlorobenzene-, 111°; 2 : 4-dichlorobenzene-, 150°; 2 : 5-dichlorobenzene-, 141°; 2 : 4-dibromobenzene-, 120°; 2 : 4 : 6-tribromobenzene-, 135°; *o*-nitrobenzene-, 125.5°; *m*-nitrobenzene-, 92°; and *p*-nitrobenzene-, 103°.

Diazonium chloroplumbates,  $(\text{Ar}\cdot\text{N}_2)_2(\text{PbCl}_6)$ , are obtained by the addition of solutions of diazonium salts to solutions of lead tetrachloride in strong hydrochloric acid. They form insoluble, yellow, crystalline solids, stable in the dry state, exploding at definite temperatures which vary only slightly according to the rate of heating. Their reactions are similar to those of the diazonium tetrachloroiodides, except for the absence of iodine. The following *diazonium chloroplumbates*, exploding at the temperatures stated, are described: *o*-toluene-, 78—80°; 2 : 4-dichlorobenzene-, 183—184°; *p*-bromobenzene-, 139—141°; 2 : 4-dibromobenzene-, 117—118°;

2:4:6-tribromobenzene-, 114—116°; *o*-nitrobenzene-, 120—122°. The following diazonium chloroplumbates previously described (Sakellarios, this vol., i, 220) explode at the following temperatures: benzene-, 80—81°; *p*-chlorobenzene-, 145—150°; *p*-toluene-, 72—75°; *m*-nitrobenzene-, 161—163°; and *p*-nitrobenzene-, 132—133°.

When diazonium tetrachloroiodides or chloroplumbates are added to concentrated aqueous ammonia, azoimides are obtained in good yields, probably according to the scheme:



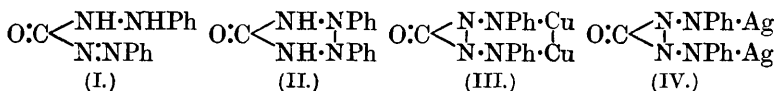
2:5-Dichlorophenylazoimide, pale yellow crystals, m. p. 30°, and *o*-tolyl azoimide, pale yellow oil, b. p. 70°/20 mm., are described.

1-(2:4-Dichlorophenyl)-1:2:3-triazole, obtained by the action of 2:4-dichlorophenylazoimide on acetylene in acetone solution at 100° under pressure (cf. Dimroth, A., 1910, i, 645), has m. p. 80°. 1-(2:5-Dichlorophenyl)-1:2:3-triazole, m. p. 78°; 1-(2:4-dibromophenyl)-1:2:3-triazole; 1-*o*-tolyl-1:2:3-triazole, yellow oil; and 1:1'-(4:4'-diphenyllyl)bis-1:2:3-triazole, pale yellow needles, m. p. 326° (decomp.), were prepared. *o*-Tolyl azoimide reacts with ethyl acetoacetate in presence of sodium ethoxide to form 1-*o*-tolyl-5-methyl-1:2:3-triazole-4-carboxylic acid, m. p. 138° (decomp.), whilst the halogen substituted phenyl azoimides and diphenyl-4:4'-bisazoimide yield similarly the corresponding ethyl esters as primary products. Ethyl 1-(2:4-dichlorophenyl)-5-methyl-1:2:3-triazole-4-carboxylate, m. p. 270° (decomp.), yields on hydrolysis the free acid, m. p. 169.5° (decomp.); 1-(2:5-dichlorophenyl)-5-methyl-1:2:3-triazole-4-carboxylic acid has m. p. 158°; ethyl 1-(2:4-dibromophenyl)-5-methyl-1:2:3-triazole-4-carboxylate, m. p. 302° (decomp.), yields the free acid, m. p. 173°; 1:1'-(4:4'-diphenyllyl)bis-5-methyl-1:2:3-triazole-4-carboxylic acid has m. p. 245° (decomp.). The following 1:2:3-triazoles were prepared by heating the corresponding 4-carboxylic acids above their melting points: 1-(2:4-dichlorophenyl)-5-methyl-, m. p. 69°; 1-(2:5-dichlorophenyl)-5-methyl-, m. p. 51°; 1-(2:4-dibromophenyl)-5-methyl-, m. p. 87°; and 1:1'-(4:4'-diphenyllyl)bis-5-methyl-1:2:3-triazole, m. p. 227°. Phenyl-1:2:3-triazoles unsubstituted in the triazole ring have strong, mushroom-like odours, whilst the corresponding 5-methyl derivatives are odourless.

F. G. W.

**Relationship between Atomic Grouping and Specific Affinity. II. Diphenylcarbazone, its Salts, and those of the supposed Diphenylcarbodiazone.** F. FEIGL and A. F. LEDERER (*Monatsh.*, 1924, 45, 63—68).—"Diphenylcarbodiazone" is regarded as a second form of diphenylcarbazone, and the structure of the isomerides and their salts is discussed. Certain discrepancies and anomalies are pointed out and theories of the constitution of the metallic salts of diphenylcarbazone and diphenylcarbodiazone are criticised (Cazeneuve, A., 1900, i, 465; 1901, i, 297). From

diphenylcarbazone (I) salts are derived by replacing the hydrogen atom of the anilino group by univalent metal. Cazeneuve's



directions for preparing diphenylcarbodiazone, m. p. below 100°, led to a product, m. p. 164° with explosion, which is considered to be a cyclic diphenylcarbazone (II). III represents a salt with a bivalent metal, and IV the likewise unstable silver salt.

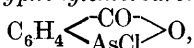
F. M. H.

**Organic Compounds of Arsenic. I. Carboxylated Aromatic Arsinic Acids and Arseno Compounds.** E. MASCHMANN (*Ber.*, 1924, **57**, [B], 1759—1766).—5-Amino-o-tolylarsinic acid, m. p. 235—236° (decomp.) after darkening at 200°, is prepared by reducing 5-nitro-o-tolylarsinic acid with ferrous sulphate and sodium hydroxide at 80°. 5-Nitro-o-carboxyphenylarsinic acid, m. p. 264—265° (decomp.) after darkening at 210°, obtained by the oxidation of 5-nitro-o-tolylarsinic acid by potassium permanganate, is reduced by sodium amalgam and methyl alcohol to 5-amino-o-carboxyphenylarsinic acid, m. p. 219—220° (decomp.), which is converted by nitrous acid into 5-hydroxy-o-carboxyphenylarsinic acid, decomp. indefinite. 5-Amino-o-tolylarsinic acid is diazotised and the diazonium solution is treated with cuprous cyanide; the nitrile thus obtained is hydrolysed by potassium hydroxide to 5-carboxy-o-tolylarsinic acid which remains unchanged below 300°. The compound is oxidised by potassium permanganate in alkaline solution to 2:5-dicarboxyphenylarsinic acid, decomp. indefinite. 5-Carboxy-o-tolylarsinic acid is converted by sulphuric acid and nitric acid (*d* 1.4) at 0—10° into 3-nitro-5-carboxy-o-tolylarsinic acid which is unchanged below 300°; it is reduced by ferrous sulphate and sodium hydroxide to 3-amino-5-carboxy-o-tolylarsinic acid. 2-Nitro-p-toluidine is transformed by diazotisation and treatment of the diazonium solution with sodium arsenite into 2-nitro-p-tolylarsinic acid, m. p. 241—242° (decomp.), which is oxidised by potassium permanganate to 2-nitro-4-carboxyphenylarsinic acid, m. p. 226—227° (decomp.), from which 2-amino-4-carboxyphenylarsinic acid, decomp. 225—226° (the acetyl derivative is described), and 2-hydroxy-4-carboxyphenylarsinic acid, decomp. indefinite, are obtained in the usual manner. 2-Nitro-p-tolylarsinic acid is reduced by sodium amalgam and methyl alcohol to 2-amino-p-tolylarsinic acid, decomp. 185°. 5-Nitro-2-carboxyphenylarsinic acid is reduced by hypophosphorous acid and potassium iodide to 5:5'-diamino-2:2'-dicarboxyarsenobenzene; 5:5'-dihydroxy-2:2'-dicarboxyarsenobenzene and 3:3'-diamino-5:5'-dicarboxy-2':2'-dimethylarsenobenzene are prepared in a similar manner. 4:4'-Dicarboxy-2:2'-diaminoarsenobenzene (the hydrochloride is described) is obtained by the action of stannous chloride and potassium iodide on 2-nitro-4-carboxyphenylarsinic acid.

H. W.

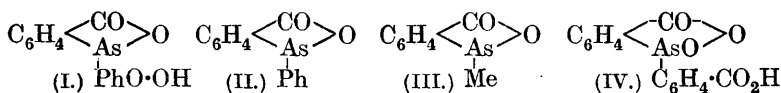


**Organic Compounds of Arsenic. I. Derivatives of o-Benzarsinic Acid.** J. A. AESCHLMANN and N. P. McCLELAND (*J. Chem. Soc.*, 1924, 125, 2025—2035).—When benzarsinic acid is reduced in aqueous solution by sulphur dioxide and a little hydriodic acid, the *hydrated o-benzarsenious oxide*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{As}(\text{OH})_2$ , is obtained, which melts at  $89^\circ$  and resolidifies at  $140^\circ$  with formation of the anhydride,  $\left[\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO} \\ \text{As} \\ \text{O}\end{smallmatrix}\right\rangle\right]_2\text{O}$ , m. p.  $231^\circ$  after sintering at  $225^\circ$ . Anhydrous *o-benzarsenious oxide* is obtained by crystallising the hydrated compound from ether or benzene. It yields *o-benzarsenious chloride* when treated with hydrogen chloride in benzene or chloroform, and this, on distillation in a vacuum, affords *o-carboxyphenylchloroarsinous anhydride*,



m. p.  $145^\circ$ , b. p. about  $220^\circ/15\text{ mm.}$ , which is also obtained by distilling the product of the action of phosphorus trichloride on *o-benzarsinic acid* in chloroform. *Benzophenone-o-dichloroarsine*,  $\text{Bz}\cdot\text{C}_6\text{H}_4\cdot\text{AsCl}_2$ , m. p.  $107\text{--}108^\circ$ , was obtained from dichloro-*o*-arsinobenzoyl chloride (cf. Lewis and Cheetham, A., 1923, i, 407) and benzene using aluminium chloride in carbon disulphide. *Benzophenone-o-arsinic acid*, m. p.  $215\text{--}219^\circ$ , and *benzophenone-o-arsenious oxide*, m. p.  $105\text{--}200^\circ$  (incomplete), were obtained from the dichloroarsine by treatment with alkali and hydrogen peroxide, and alkali alone, respectively. By treating benzophenone-*o*-dichloroarsine with sodium hydroxide and methyl iodide, converting the resulting iodoarsine (m. p.  $110\text{--}114^\circ$ ) into the oxide by means of alcoholic potassium hydroxide, and treating this with hydrogen chloride in benzene, *benzophenone-o-methylchloroarsine*, m. p.  $88^\circ$ , was obtained. Attempts to eliminate hydrogen chloride from this compound, by the action of aluminium chloride, failed. *Benzophenone-o-methylarsinic acid*, m. p.  $186^\circ$ , could not be dehydrated to form a ring compound.

*o-Carboxydiphenylarsinic anhydride* (I), m. p. not below  $300^\circ$ , was prepared by condensing benzenediazonium chloride with sodium benzarsinite. It is not affected by sulphuric acid at  $100^\circ$ . *o-Carboxydiphenylarsinous anhydride* (II), m. p.  $133^\circ$ , was obtained by reducing the above arsenic acid, and is also produced by the



distillation, in a vacuum, of *o-carboxydiphenylchloroarsine*, m. p.  $163^\circ$ , prepared by condensing an alkaline solution of phenyldichloroarsine with diazotised anthranilic acid, reducing the product with sulphur dioxide, and treating the resulting acid with hydrogen chloride in benzene. On crystallising this compound (m. p.  $163^\circ$ ) from benzene, a *product*, m. p.  $125^\circ$ , was obtained. The *acid chloride* of *o-carboxydiphenylchloroarsine* distils unchanged in a vacuum and partly crystallises. Treated with aluminium chloride.

it yields benzophenone-*o*-dichloroarsine. *o*-Carboxyphenylmethylarsinous anhydride (III), m. p. 106°, b. p. 220°/15 mm., obtained by the action of methyl iodide and sodium hydroxide on benzarsenious oxide, yields *o*-carboxyphenylmethylarsinic acid, m. p. 310°, on oxidation, and this, on reduction and treatment of the reduction product with hydrogen chloride in benzene, affords *o*-carboxyphenylmethylchloroarsine, m. p. 141°, which loses hydrogen chloride on distillation in a vacuum. *oo'*-Dicarboxydiphenylarsinic anhydride (IV), m. p. 255°, obtained by condensing benzarsenious oxide with diazotised anthranilic acid, yields *oo'*-dicarboxydiphenylarsinous anhydride, m. p. 251—255°, on reduction, and this, on treatment with hydrogen chloride in methyl alcohol, affords *oo'*-dicarbomethoxydiphenylchloroarsine, m. p. 184°.

F. G. W.

**Residual Affinity and Co-ordination. XX. Chromic and Cobaltic Lakes of Mordant Azo-dyes.** G. T. MORGAN and J. D. M. SMITH (*J. Chem. Soc.*, 1924, **125**, 1731—1739).—Eriochrome-red B (4-sulpho- $\beta$ -naphthol-1 : 4'-azo-1'-phenyl-3'-methyl-5'-pyrazolone) contains one "chelate" group: it yields, with chromic fluoride, a *chromic* lake, and, with roseocobaltic chloride, first a *cobaltic* lake, then the *mono*- and *di*-roseocobaltic salts of the latter. Similarly, Palatine-chrome-black 6B ( $\beta$ -naphthol-1 : 1'-azo- $\beta$ -naphthol-4-sulphonic acid) yields *chromic* and *cobaltic* lakes and the *di*-roseocobaltic salt of the latter. Diamond-black PV (1 : 5-dihydroxynaphthalene-2 : 2'-azophenol-4'-sulphonic acid) yields a *chromic* lake, but with roseocobaltic chloride affords only the lake of the oxidised dye (8-hydroxy- $\alpha$ -naphthaquinone-7 : 2'-azophenol-4'-sulphonic acid) and its *mono*- and *di*-roseocobaltic salts. Metachrome-brown B (4 : 6-dinitrophenol-2-azo-*m*-toluylenediamine) gives a *cobaltic* lake. *o*-Carboxybenzeneazo- $\beta$ -naphthol affords a *di*-roseocobaltic salt of the cobaltic lake, and from *m*-acetylbenzeneazo- $\beta$ -naphthol-6-sulphonic acid only the *triammonium monoroseocobaltic* salt is obtained. Constitutional formulæ for these compounds are discussed (cf. T., 1922, **121**, 2857, etc.).

W. A. S.

**Residual Affinity and Co-ordination. XXI. Boron  $\beta$ -Diketone Difluorides.** G. T. MORGAN and R. B. TUNSTALL (*J. Chem. Soc.*, 1924, **125**, 1963—1967).—Boron trifluoride reacts with  $\beta$ -diketones, but unlike the trichloride yields no boronium salt, but a difluoride, in which there is no ionisable fluorine atom. Thus, with acetylacetone, reaction takes place and heat is evolved, *boron acetylacetone difluoride*,  $\text{CH} \begin{smallmatrix} \text{CMe}\cdot\text{O} \\ \text{CMe}\cdot\text{O} \end{smallmatrix} \text{BF}_2$ , m. p. 43°, is obtained.

*Boron benzoylacetone difluoride*, m. p. 155°, and *boron dibenzoylmethane difluoride*, m. p. 191°, were prepared in a similar way. Analytical methods are described.

W. A. S.

**Residual Affinity and Co-ordination. XXII. Optically Active Salicylatocobalt Diethylenediammines.** G. T. MORGAN and J. D. M. SMITH (*J. Chem. Soc.*, 1924, **125**, 1996—2004).—*Salicylatodiethylenediamminecobaltic chloride dihydrate*,  $\text{YCl}(\text{H}_2\text{O})_2$ ,

where Y is the complex  $\text{en}_2\text{Co} \left\langle \begin{smallmatrix} \text{O} \\ \text{O} \cdots \text{CO} \end{smallmatrix} \right\rangle \text{C}_6\text{H}_4$ , was obtained as purplish-red plates by treating *trans*-dichlorodiethylenediammine-cobaltic chloride with silver oxide and adding salicylic acid (1 mol.) to the filtrate. As a by-product, *disalicylatodiethylenediammine-cobaltic salicylate*,  $[\text{en}_2\text{Co}(\text{C}_7\text{H}_5\text{O}_3)_2]\text{C}_7\text{H}_5\text{O}_3$ , was obtained as pale violet-pink needles. The *carbonato dihydrate*,  $\text{Y}_2\text{CO}_3(\text{H}_2\text{O})_2$ , violet-red plates, was obtained from the above chloride by the action of silver carbonate, and was converted by treatment with *d*- and *l*-camphorsulphonic acids, respectively, into *l*-complex-*d*-camphorsulphonate,  $\text{YC}_{10}\text{H}_{15}\text{O}_4\text{S}(\text{H}_2\text{O})_2$ , bright red plates,  $[\alpha]_{\text{Li}, 6708} -41.3^\circ$ ,  $[M]_{\text{Li}}$  for the complex ion  $-290.4^\circ$ , and *d*-complex-*l*-camphorsulphonate,  $[\alpha]_{\text{Li}} +33^\circ$ ,  $[M]_{\text{Li}}$  for the complex ion  $+242.1^\circ$ . From these optically active salts the following were obtained by double decomposition: *d*- and *l*-chloromercurate hydrates,  $[\text{YH}_2\text{O}]\text{HgCl}_3$ ,  $[M]_{\text{Li}} +288^\circ$  and  $-294.4^\circ$ , respectively; and *d*- and *l*-bromomercurate hydrates,  $[\text{YH}_2\text{O}]\text{HgBr}_3$ ,  $[M]_{\text{Li}} \pm 294^\circ$ . The racemic halomercurates form purplish-red plates of paler tint than the active isomerides, and are much less soluble in water. The active salts remain active if crystallised from boiling water, or left in solution for six weeks. The following racemoid salts are also described: *iodomercurate hydrate*,  $\text{YH}_2\text{O}.\text{HgI}_3$ , dark purple-red, flattened needles; *nitrate trihydrate*,  $\text{YNO}_3(\text{H}_2\text{O})_3$ , dark red, deliquescent needles; *hydrogen dichloride trihydrate*,  $\text{YHCl}_2(\text{H}_2\text{O})_3$ , scarlet, plates; *hydrogen dinitrate*,  $\text{YH}(\text{NO}_3)_2$ , dark red plates; and *hydrogen carbonate*,  $\text{YHCO}_3$ , bright red, diamond-shaped and six-sided plates. The retention of only one mol. of water or one hydrion in the complex ion is ascribed to the unique affinity of the one carbonyl oxygen of the complex. An analogous explanation is suggested for the formation of oxonium salts.

F. G. W.

**Relation of Chemical Structure to Rate of Hydrolysis of Peptides. I. Synthesis, Physical Constants, and Rates of Hydrolysis of Methylated Peptides.** P. A. LEVENE, H. S. SIMMS, and M. H. PFALTZ (*J. Biol. Chem.*, 1924, **61**, 445—464).—Glycylsarcosine, sarcosylglycine, and sarcosylsarcosine have been synthesised, their dissociation constants, isoelectric points, and relative rates of hydrolysis determined and compared with corresponding values for glycylglycine. (In the following,  $k_a$  represents the acidic dissociation constant,  $k_b$  that of the amino group.) *Glycylsarcosine*, from chloroacetylsarcosine and ammonium hydroxide, has m. p. 200—201°,  $k_a$   $1.48 \times 10^{-3}$ ,  $k_b$   $0.576 \times 10^{-5}$ , isoelectric point  $p_H$  5.68. *Sarcosylglycine*, from chloroacetylglycine and methylamine, has m. p. 195—197°,  $k_a$   $0.794 \times 10^{-3}$ ,  $k_b$   $0.537 \times 10^{-5}$ , isoelectric point  $p_H$  5.80. *Sarcosylsarcosine* has m. p. 180—185°,  $k_a$   $1.38 \times 10^{-3}$ ,  $k_b$   $2.09 \times 10^{-5}$ , isoelectric point  $p_H$  5.98. Glycylglycine has  $k_a$   $0.759 \times 10^{-3}$ ,  $k_b$   $0.195 \times 10^{-5}$ , isoelectric point  $p_H$  5.59. The hydrolyses were conducted at 100° with 1 mol. equivalent of acid; under these conditions all except sarcosylsarcosine followed the normal course of a bimolecular reaction; hydrolysis experiments with smaller quantities of acid indicate that anhydride formation

is probably the explanation of the anomalous behaviour of sarcosyl-sarcosine.

C. R. H.

**Anhydride Structure of Silk Fibroin.** E. ABDERHALDEN and E. SCHWAB (*Z. physiol. Chem.*, 1924, **139**, 169—180).—Among the products of the reduction, by sodium and alcohol, of silk peptone (obtained by hydrolysing silk fibroin with 70% sulphuric acid at incubator temperature) there have been isolated methylpiperazine, 3-methyl-6-hydroxymethylpiperazine (as *dihydrochloride*) and a compound which appears to be the *tetrahydrochloride* of the piperazine corresponding to an anhydride of the glycylalanyl-glycyltyrosine previously obtained by Fischer and Abderhalden (*A.*, 1907, i, 737) from silk fibroin. For comparison with this compound the authors prepared 2:6-di-*p*-hydroxyphenylmethylpiperazine by the reduction of tyrosine anhydride; this piperazine gives a *hydrochloride*, m. p. 265°, and does not give Millon's reaction. By the hydrolysis of silk fibroin with cold 70% sulphuric acid, alanylserine anhydride and an *anhydride* (alanine, tyrosine, glycine, 1:1:2 mols., less water, 4 mols.) were obtained. The latter gave a negative ninhydrin reaction and a positive picrate test, whereas a similar compound obtained previously (*loc. cit.*) had these properties reversed. It is from the alanylserine anhydride, presumably, that the methylhydroxymethylpiperazine is formed. C. R. H.

**Anhydride Structure of Proteins.** E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1924, **139**, 181—204).—The fact that Jaffé's reaction for creatinine (*A.*, 1886, 1056) is given by diketopiperazines in general has been confirmed by tests carried out on the anhydrides of numerous amino-acids and dipeptides; in all cases the reaction was positive in the case of the anhydride and negative with the original amino-acid or peptide. Similar results were obtained with the reaction of von Bittó using *m*-dinitrobenzene and *m*-phenylenediamine. These two reactions have been utilised to investigate the question of the occurrence in proteins of preformed diketopiperazines; in many proteins and in the peptones derived therefrom, it was possible to demonstrate the presence of such compounds. The significance of this result in relation to the theory of the constitution of proteins is fully discussed. Included in the paper is a severe criticism of the work of Ssadikov and Zelinsky (this vol., i, 1122).

C. R. H.

**Origin of the Humin formed during the Acid Hydrolysis of Proteins.** R. A. GORTNER (*Z. physiol. Chem.*, 1924, **139**, 95—96).—Polemical (cf. Edlbacher, this vol., i, 891). E. S.

**Dakin's Method Applied to Edestin.** T. B. OSBORNE, C. S. LEAVENWORTH, and L. S. NOLAN (*J. Biol. Chem.*, 1924, **61**, 309—313).—Dakin's butyl alcohol method of extraction (*A.*, 1919, i, 150) has been modified by dropping the concentrated solution of amino-acids into 7 volumes of butyl alcohol, which is rapidly stirred at the ordinary temperature. The products of hydrolysis of edestin were investigated by this method; no evidence could be obtained of the presence of  $\beta$ -hydroxyglutamic acid, which, in

view of the fact that edestin may serve as the sole source of protein in a satisfactory diet for young rats, indicates that this amino-acid is not essential for growth. Part of the dry residue of the butyl alcohol extract was soluble in ethyl alcohol and appeared to consist of diketopiperazines. C. R. H.

**Basic Amino-acids Yielded by Casein.** C. S. LEAVENWORTH (*J. Biol. Chem.*, 1924, **61**, 315—316).—The nitrogen, other than that of lysine, contained in the substances which can be precipitated by phosphotungstic acid from the products of hydrolysis of casein, amounts to 1.1% of the total nitrogen of the casein; it is therefore improbable that casein contains any hitherto unidentified basic amino-acid. C. R. H.

**Correlation between the Spectra of various Hæmoglobins and their Relative Affinities for Oxygen and Carbon Monoxide.** M. L. ANSON, J. BARCROFT, A. E. MIRKSY, and S. OINUMA (*Proc. Roy. Soc.*, 1924, **B**, **97**, 61—83).—The relation  $\log K = 0.05 \times \text{span}$ , in which  $K$  is the equilibrium constant of the equation  $\text{CO} + \text{HbO}_2 \rightleftharpoons \text{CO-Hb} + \text{O}_2$  and the "span" is the difference, in Ångström units, between the positions of maximum intensity of the  $\alpha$ -oxyhæmoglobin and carbon monoxide-hæmoglobin spectral bands, has been found to hold for the hæmoglobins from a number of mammals. The span varies from 43 to 56 units in different species and also in individuals of the same species; these variations appear to be due to the specificity of the globin portion of the molecule. The similar relation  $\log 1/C_{T_1} - \log 1/C_{T_2} = 0.049 (A_{T_1} - A_{T_2})$  exists between the shift in the absorption bands and change in affinity of hæmoglobin for oxygen during change in temperature;  $C_{T_1}$  and  $C_{T_2}$  represent, at temperatures  $T_1$  and  $T_2$ , respectively, the concentration of oxygen in solution when the hæmoglobin is half-saturated, and  $A_{T_1}$  and  $A_{T_2}$  the corresponding positions of maximum intensity of the  $\alpha$ -bands. E. S.

**Hexagonal Crystals of Horse Hæmoglobin.** E. MÖLLENHOFF (*Z. Biol.*, 1924, **82**, 153—154).—Hexagonal crystals can be obtained without putrefaction taking place. The action which takes place during putrefaction is considered to be one of reduction. O. O.

**The Carbohydrate Group of Thymus-nucleic Acid.** H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1924, **139**, 205—211; cf. this vol., i, 439).—The "glucal" reactions of Feulgen (A., 1914, i, 1098; 1918, i, 85; this vol., i, 1132) for thymus-nucleic acid are due to the elimination from the carbohydrate part of the molecule of 2-hydroxymethylfurfuraldehyde; these reactions are not given by dextrose itself, but are obtained (especially the green pine-shaving reaction) with more or less intensity in the cases of some di- and poly-saccharides and glucosides. The variations in the reactions are apparently due to differences in the linking of the carbohydrate portion to the rest of the molecule. C. R. H.

## Biochemistry.

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**Muscular Exercise, Lactic Acid, and the Supply and Utilisation of Oxygen.** IV—VI. A. V. HILL, C. H. N. LONG, and H. LUPTON (*Proc. Roy. Soc.*, 1924, **B**, 97, 84—138).—IV. *Methods of studying the respiratory exchanges in man, during rapid alterations produced by muscular exercise, and while breathing various gas mixtures.*—The Douglas bag is considered more satisfactory than the closed gas chamber. The technique of the method is discussed with special reference to gaseous mixtures containing a high proportion of oxygen. Where the mixtures contain more than 50% of oxygen serious errors are liable to occur.

V. *The recovery process after exercise in man.*—After moderate short-lived exercise recovery is rapid and practically complete in a few minutes. This is due to the oxidative removal of lactic acid in the muscles where it was formed. After severe or prolonged exercise, the same initial rapid phase occurs, but this is followed by a protracted process, which represents the oxidative removal of lactic acid which has had time (owing to an inadequate oxygen supply) to diffuse from the muscles. These facts enable a distinction to be made between “moderate” exertion, which is followed by the initial phase only, and “severe” exertion, which is followed by both phases. During the early stages of recovery after severe exercise there is an elimination of carbon dioxide and a high respiratory quotient; during the later stages, a retention of carbon dioxide and a low respiratory quotient. The carbon dioxide so retained was used as a measure of lactic acid removed, and the oxygen used in recovery as a measure of the energy used in the removal of the acid. From these two quantities the “efficiency” of recovery in man has been calculated and found to agree with the value obtained for isolated frogs’ muscle and also with that found by the amount of the lactic acid removed during any recovery interval compared with the recovery oxygen used in that interval. The time course of the recovery process while breathing oxygen-enriched air is not appreciably different from that while breathing atmospheric air, and the main process of recovery is practically unaffected by the higher oxygen pressures.

VI. *The oxygen debt at the end of exercise.*—Only about 5% of the oxygen debt is due to the extra circulatory and respiratory effort associated with recovery. It is considered that the remainder is utilised in restoring lactic acid to its precursor. The breathing of oxygen mixtures allows a considerable increase in the maximum oxygen debt. (Cf. this vol., i, 1128.) O. O.

**Content of Sodium Chloride in the Blood of certain Marine Invertebrates.** M. DUVAL (*Compt. rend.*, 1924, 179, 706—708).—The blood of various marine invertebrates, especially of the crustaceans, contains appreciably less sodium chloride than the

sea-water in which they are found. Equality between the osmotic pressures of the blood and of the water is effected by the other components of the blood. The blood of *Sipunculus nudus*, however, contains exactly the same proportion of sodium chloride as sea-water.

T. H. P.

**Changes in Blood Electrolytes in Ether Acidosis.** J. H. AUSTIN, G. E. CULLEN, H. C. GRAM, and H. W. ROBINSON (*J. Biol. Chem.*, 1924, **61**, 829—840).—In the acidosis following ether anaesthesia there is, in the blood, a rise in the concentration of chloride ion, a fall in that of hydrogen carbonate, and a slight fall in that of the total base. These observations are, in themselves, insufficient to account for the increase in hydrogen-ion concentration which is simultaneously observed, and necessitate the hypothesis that the increased acidity is brought about by the presence of other unidentified anions. The authors suggest the liberation of lactic acid in the tissues as a possible cause of the phenomenon. (In this connexion, cf. Ronzoni, Koechig, and Eaton, this vol., i, 1258.)

C. R. H.

**Experimental Alterations in the Calcium Content of Human Serum and Urine.** C. P. STEWART and J. B. S. HALDANE (*Biochem. J.*, 1924, **18**, 855—857).—The calcium content of human serum can be raised by 10 to 20% by ingestion of calcium and ammonium chlorides, by breathing 6 to 7% carbon dioxide, or by forced breathing. It can be lowered by 10 to 20% by ingestion of sodium hydrogen carbonate. The urinary calcium output is increased by ingestion of ammonium chloride and is little affected by sodium hydrogen carbonate.

S. S. Z.

**Changes in the Phosphorus Partition in Human Blood during Ammonium Chloride Acidosis.** H. D. KAY (*Biochem. J.*, 1924, **18**, 1133—1138).—There is a rise in inorganic phosphorus during ammonium chloride acidosis. The "lecithin" or lipin phosphorus changes in a similar way in this condition. The organic acid-soluble phosphorus (*i.e.*, the organic fraction after precipitating the blood with trichloroacetic acid) shows an immediate fall at the outset followed by a slow return to normal after several days. This change takes place in the portion of the fraction which is resistant to hydrolysis by the bone enzyme. The significance of these changes is discussed.

S. S. Z.

**Chemical Changes in the Blood during Fasting and subsequent Re-feeding.** S. MORGULIS and A. C. EDWARDS (*Amer. J. Physiol.*, 1924, **68**, 477—498).—During prolonged fasting, the non-protein and urea nitrogen of the blood of dogs usually increases, then remains constant, and finally increases again; the amino-acid nitrogen remains constant or suffers at first a slight temporary diminution; the uric acid of the blood increases progressively; the creatinine remains constant, but the creatine first diminishes and then rapidly rises. The sugar and chlorides, which diminish at first, increase again during the later stages. When the animals are

once again fed, very extensive changes occur in the composition of the blood, which eventually reaches a normal condition.

A. A. E.

**Chemical Changes in Blood of Dogs after Thyro-parathyroidectomy.** I. GREENWALD (*J. Biol. Chem.*, 1924, **61**, 649—657).—After removal of the thyroids and parathyroids of dogs there was found, during the resulting tetany, no change in the titratable alkali, sugar, or nucleotide nitrogen of the blood, a decrease in the calcium, and a slight increase in the acid-soluble phosphorus; in view of the marked decrease in the excretion of phosphates which follows parathyroidectomy, it appears that, in this condition, phosphorus must be deposited in the tissues.

C. R. H.

**Amino-acid Content of the Blood and its Significance as a Test of Liver Function.** M. VON FALKENHAUSEN (*Arch. exp. Path. Pharm.*, 1924, **103**, 322—328).—The results of determinations of the amino-acid content of human blood, both normal and pathological (including diseases of the liver), give no support to the view that the liver plays an important part in intermediary protein metabolism. Determinations of the amino nitrogen content of the blood following ingestion of amino-acids are of no value as tests of liver function.

E. S.

**Possible Significance of Hexosephosphoric Esters in Ossification. IV. Phosphoric Esters of the Blood.** H. W. GOODWIN and R. ROBISON (*Biochem. J.*, 1924, **18**, 1161—1162).—Two phosphoric esters were isolated from the blood. One of these reduces Fehling's solution and is laevorotatory. It is hydrolysed by the bone enzyme. The other does not reduce Fehling's solution and is not acted on by the enzyme.

S. S. Z.

**Rate of Elimination of Inorganic Salts from the Blood Stream.** O. BARKUS (*Amer. J. Physiol.*, 1924, **69**, 35—40).—After intravenous injection, chlorides disappeared from sheep's blood almost immediately, phosphates first rapidly and then slowly; results with sulphates were untrustworthy.

CHEMICAL ABSTRACTS.

**Carbohydrate Metabolism. I. Variations in the Nature of the Blood-sugar.** L. B. WINTER and W. SMITH (*Proc. Roy. Soc.*, 1924, **B**, **97**, 20—40).—Normal blood filtrates have a lower rotation than would be expected from their copper-reducing power on the assumption that the reducing substance present consists solely of an equilibrium mixture of  $\alpha$ - and  $\beta$ -glucose; the rotation, however, slowly increases and in 3 to 4 days corresponds with the reducing power. Filtrates from the blood of diabetics, on the other hand, have a high rotation which remains constant or diminishes only slightly. After mild hydrolysis (dilute hydrochloric acid), the rotation and reducing power of the normal filtrates correspond, whilst this treatment increases the rotation without affecting the reducing power of diabetic filtrates.



After injection of either thyroid extract or adrenaline, the blood of rabbits resembles diabetic blood in the above respect, but behaves normally when these substances are injected successively, although there is an increase in total blood-sugar. The blood of rabbits in convulsions due to insulin has a low rotation and no reducing power; the convulsions are relieved by adrenaline alone or by a mixture of thyroid and adrenaline. The mechanism of the action of insulin is discussed. E. S.

**Hyperglycæmia after Parenteral Administration of Protein.** W. LAUFBERGER (*Z. ges. exp. Med.*, 1924, **39**, 487—494; from *Chem. Zentr.*, 1924, i, 2794).—Intravenous injection of minimal amounts of protein causes hyperglycæmia in rabbits. The course of the hyperglycæmia varies with the protein used. Caffeine does not cause an appreciable hyperglycæmia in spayed females.

G. W. R.

**Effect of Ultra-violet Light on the Content of Fat and Sugar in the Blood of Animals deprived of Vitamins.** D. ALPERN (*Strahlentherapie*, 1923, **15**, 661—666; from *Chem. Zentr.*, 1924, i, 2887).—The water and sugar in the blood of normal animals increase as the result of ultra-violet radiation. Less marked results are obtained in the case of the fat content. There is generally an increase in the light petroleum and ethyl alcohol fractions without corresponding increase in the cholesterol content. The blood of animals deprived of vitamins exhibits the same changes.

G. W. R.

**Alcohol. I. Determination of Ethyl Alcohol in Blood.** H. KIONKA and P. HIRSCH (*Arch. exp. Path. Pharm.*, 1924, **103**, 282—294).—The alcohol is removed from the blood by distillation at 40° under diminished pressure, using an efficient condensing arrangement, and its content in the distillate determined by means of an interferometer. E. S.

**Alcohol. II. Alcohol Content of Human Blood in the Fasting Condition, and after Ingestion of Carbohydrates or of Small Amounts of Alcohol.** G. KÜHN (*Arch. exp. Path. Pharm.*, 1924, **103**, 295—312).—Values varying between 0.0006 and 0.0051% were found for the alcohol content of the blood of fasting individuals. No regular variations in these values were observed following a carbohydrate meal. Ingestion of small amounts of alcohol (two glasses of beer) together with a meal poor in carbohydrates, however, produced uniform increases which reached a maximum in about an hour. E. S.

**Effect of Cations on Red Blood-corpuscles.** W. ASHBY (*Amer. J. Physiol.*, 1924, **68**, 250—261, 585—610, 611—621).—Chlorides of sodium, magnesium, calcium, strontium, and barium increase, and of potassium and lithium decrease the resistance of human red blood-corpuscles to hypotonic sodium chloride solution. It is suggested that potassium can combine with the substance of the corpuscle in a manner different from that of

sodium. Changes produced by calcium and magnesium are not accounted for by loss of potassium. The red corpuscles of rabbit's, horse's, and pig's blood, having a high potassium content, behave similarly; those of cat's, dog's, and steer's blood, in which sodium predominates, are affected by univalent cations in the reverse manner, but as before with magnesium and calcium. It is argued that the distribution of sodium and potassium between cells and serum must be due to specific mutual relationships between the ion and cell-substance.

CHEMICAL ABSTRACTS.

**Changes in  $p_H$  of Blood with Coagulation.** E. F. HIRSCH (*J. Biol. Chem.*, 1924, **61**, 795—805).—In the process of clotting blood becomes more acid, the average decrease in  $p_H$  observed being 0.09. It is suggested that the normal process of clotting may be brought about by changes in reaction following changes in the tension of carbon dioxide.

C. R. H.

**Blood Coagulation, Anti-coagulants, and Hæmolysis.** J. W. PICKERING and F. E. TAYLOR (*Proc. Roy. Soc.*, 1924, **B**, **97**, 1—19).—A parallelism exists between hæmolysis and the inception (*i.e.*, the pre-clot phase) of the clotting of blood. Thus, potassium oxalate and sodium citrate inhibit the hæmolytic actions of heterologous sera, a specific hæmolysin, and cobra venom; this inhibition is removed by calcium chloride, which also restores coagulability. Too large a concentration of calcium chloride, however, inhibits hæmolysis, but it is also known to prevent coagulation. Other anti-coagulants (Witte's peptone, leech extract, neutralised thymus- and yeast-nucleic acids, novarsenol) which inhibit the pre-clot phase also restrain the hæmolytic actions of the above substances. Further examples are discussed in the original. These results are interpreted in favour of the theory of the coagulation of blood advanced by Pickering and de Souza (*Biochem. J.*, 1923, **17**, 747).

E. S.

**Hæmolytic Action of the Soaps.** E. PONDER (*Biochem. J.*, 1924, **18**, 845—851).—The stearates, palmitates, and oleates are hæmolytic. The stearates are the least and the oleates the most active in this respect. The changes of shape of the erythrocytes are very similar to those produced by saponin and by bile salts. This lytic action of soaps is inhibited by the presence of serum, plasma, and a solution of hæmoglobin, especially in the case of oleates. If, however, these substances are added to the soap after this has been allowed to act on the cells a slight acceleration in the lytic action may be effected. Sodium and potassium soaps behave similarly. The time-dilution curves are logarithmic, whilst the time-temperature curves are hyperbolic. The percentage hæmolysis curve of sodium oleate (the only soap with which these observations can be made) is of the sigmoid type and shows, when suitable concentrations are used, a slight positive skewness. Solutions of the soaps tend to lose their hæmolytic power on keeping.

S. S. Z.

**Colorimetric Determination of Blood  $p_H$  at Body Temperature.** A. B. HASTINGS and J. SENDROY, jun.—(See ii, 869.)

**Determination of Gases in Blood and other Solutions by Vacuum Extraction and Manometric Measurement.** I. D. D. VAN SLYKE and J. M. NEILL. II. C. R. HARRINGTON and D. D. VAN SLYKE.—(See ii, 872.)

**Determination of Carbon Dioxide in Serum in presence of Ether.** J. H. AUSTIN.—(See ii, 873.)

**Micro-determination of Proteins in Blood-serum.** W. BERGER and L. PETSCHOCHE.—(See ii, 636.)

**Determination of the Protein Fractions in Serum and Plasma.** H. W. KNIPPING and H. L. KOWITZ.—(See ii, 636.)

**Rôle of Phosphates in Carbohydrate Metabolism.** I. Action of the Muscle Enzyme on the Organic Phosphorus Compounds of Blood. II. Effect of Insulin Administration on the Distribution of Phosphorus Compounds in Blood and Muscle. H. D. KAY and R. ROBISON (*Biochem. J.*, 1924, **18**, 1139—1151).—From experiments with muscle enzyme, which hydrolyses hexosediphosphoric but not hexosemonophosphoric ester, on the phosphoric esters of blood it is concluded that a hexosediphosphoric ester may be present in the blood; the evidence, however, is not entirely conclusive. The greater part of the organic phosphate of the blood, which is hydrolysable by the bone enzyme, is not hydrolysed by muscle (this vol., i, 904). Evidence is produced that after the administration of insulin organic phosphoric esters are synthesised in the corpuscles at the expense of the inorganic phosphate originally present in the blood plus additional phosphate drawn from other tissues. These esters are chiefly of the type not hydrolysed by the bone enzyme, but it is probable that sugar or a sugar derivative enters into their molecule, and on the basis of 1 mol. of dextrose per atom of phosphorus, the phosphoric acid thus esterified would account for nearly 40% of the sugar simultaneously disappearing from the blood. No changes are found in the amount of inorganic phosphate or total acid-soluble phosphorus in muscle, following insulin administration, but there is a marked increase (50%) in the amount of phosphoric esters ("lactacidogen-P") hydrolysed during 3 hours' autolysis of the macerated muscle at 38°. The phosphate for this increased "lactacidogen" is apparently drawn from the muscle. There is no evidence as to the origin of the carbohydrate portion of the molecule, but it accounts for more than seven times the amount of dextrose which disappears from the blood. S. S. Z.

**Relationship of Phosphates to Carbohydrate Metabolism.** I. Time Relationship of the Changes in Phosphate Excretion caused by Insulin and Sugar. S. S. SOKHEY and F. N. ALLAN (*Biochem. J.*, 1924, **18**, 1170—1184).—The administration of insulin to normal animals results in an immediate reduction in the excretion of inorganic phosphate and ammonia and in the titratable acidity of the urine. The nitrogen excretion in these circumstances increases in the first 6 hours after the administration of the insulin,

whilst the excretion of creatinine is unaffected. The volume of the urine is usually diminished in the first 3- or 6-hour periods after insulin and is followed by a compensatory increase usually appearing in the post-hypoglycemic period. The administration of sugar induced an increased excretion of phosphate, but a decrease in the excretion of nitrogen. The joint effect of insulin and sugar brings about a decrease in the phosphate and nitrogen excretion. The administration of acid does not alter the excretion of phosphate. The phosphorus excretion of diabetic dogs without insulin is very high. Administration of insulin causes a decrease in the excretion, then an increase, with return to the level for a normal dog. These changes are discussed and their significance is suggested.

S. S. Z.

#### **Acid-Base Exchanges in Mammalian Voluntary Muscle.**

S. ANDREWS, F. BEATTIE, and T. H. MILROY (*Biochem. J.*, 1924, **18**, 994—1008).—In the expressed juice from frozen muscle there are present at least three systems which carry base in a readily disposable form, namely, the inorganic phosphates, the organic phosphate precursors, and the colloidal or protein salts. When lactic acid is produced as a result of heating the juice, the acid secures its base from all these systems, the buffering capacity depending especially on the base derivable from the hydrolysed organic phosphate precursor, and also from the constituents of the juice which do not pass into the ultrafiltrate. If there is no inorganic phosphate increment accompanying the acid production, the buffering capacity is diminished, as the sole base-carrying systems which are then in evidence are the pre-formed inorganic phosphates and the proteins.

S. S. Z.

**Antiketogenesis. V. Ketolytic Reaction. Action of Glycollaldehyde and of Glyoxal.** P. A. SHAFFER and T. E. FRIEDEMANN (*J. Biol. Chem.*, 1924, **61**, 585—623; cf. A., 1921, i, 754; 1923, i, 166).—Glycollaldehyde, like dextrose, has the power of accelerating the oxidation of acetoacetic acid by hydrogen peroxide in alkaline solution. The previous view that the ketolytic reaction consisted in the condensation of an intermediate oxidation product of dextrose with acetoacetic acid with the formation of a readily oxidisable product, led to similar experiments with glyoxal, which is known to be an intermediate product in the course of the oxidation of glycollaldehyde to formic acid. Owing, however, to the extreme rapidity with which glyoxal is oxidised in alkaline solution, it does not, under these conditions, condense with acetoacetic acid, and therefore cannot act ketolytically. It is therefore necessary to assume that the ketolytic power of glycollaldehyde is due to the condensation of the aldehyde itself with acetoacetic acid, probably by Knoevenagel's reaction (A., 1898, i, 446), the condensation being accelerated by the rapid oxidative removal of the product. The hypothesis is supported by a quantitative analysis of the products of the ketolytic reaction; this analysis further indicates that 2 mols. of acetoacetic acid condense with 1 mol. of glycollaldehyde. It is suggested that the ketolytic action

of dextrose may similarly be due to the direct condensation of the hexose itself, by virtue of its aldehydic properties, with 2 mols. of acetoacetic acid. C. R. H.

**Synthesis of Menthol-glycuronic Acid in the Rabbit.** A. J. QUICK (*J. Biol. Chem.*, 1924, **61**, 679—683).—After administration of small doses of menthol to rabbits almost 50% is excreted in the form of menthol-glycuronic acid; the amount conjugated decreases as the dose approaches the lethal amount. During prolonged administration of sub-lethal doses, the daily excretion of menthol-glycuronic acid remains practically constant. C. R. H.

**Decomposition of Sugar in the Lungs.** E. SLUITER (*Arch. Néerland. Physiol.*, 1924, **9**, 461—479).—Perfusion experiments with blood containing added dextrose show that the sugar content of the blood falls for a time and then remains nearly constant; the failure to fall to a lower level may be due to the change of  $p_H$  of the blood caused by the production of lactic acid, inhibiting further glycolysis. The amount of sugar disappearing is not proportional to its concentration in the blood, nor does it give rise to the theoretical quantity of lactic acid. H. J. C.

**Influence of "Collargol Blockade" of the Liver on Intermediary Metabolism.** SUGANUMA (*Biochem. Z.*, 1924, **144**, 141—146).—Observations have been made of the effect of intravenous injections of collargol on the hepatic functions of starving dogs. The secretion of bile is diminished but later returns to supra-normal levels. The sugar and amino-acid content of the blood are increased; the former, however, becomes sub-normal before returning to normal values. Collargol injection lowers the urea content of the blood. The rise in blood-sugar is ascribed to stimulation of the liver cells, whilst the decreased blood-urea follows on the inhibition of the "star" cells of Kupfer. J. P.

**Relation of Arginine and Histidine to Growth.** W. C. ROSE and G. J. COX (*J. Biol. Chem.*, 1924, **61**, 747—773).—Rats fed on a diet of which the sole source of nitrogen is completely hydrolysed casein grow at a slower rate than those fed on the unhydrolysed protein; if the hydrolysis products are treated with silver sulphate and barium hydroxide to remove arginine and histidine, the residual mixture of amino-acids does not suffice for growth or maintenance of weight. The addition of 0.1 g. of histidine monohydrochloride per 100 g. of food to the diet, which had been made deficient by the above treatment, restores its growth-promoting properties, whereas the addition of even large amounts of arginine does not do so. The latter observation is in contradiction to the conclusions of Ackroyd and Hopkins (*A.*, 1917, **i**, 237) regarding the interchangeability of arginine and histidine in metabolism. C. R. H.

**Comparative Ability of Deficient Proteins and Ammoniacal Organic Salts partially to Satisfy the Minimum Nitrogen Requirements.** E. F. TERROINE, P. FLEURET, and T. STRICKER (*Arch. Intern. Physiol.*, 1923, **22**, 43—86).—During the adminis-

tration of a nitrogen-free diet, preceded by injection of ammonium salts, the nitrogen excreted was of the same order as that obtained when gelatin had been given. The economy value resultant from ammonium salts when the minimum nitrogen reserve is used up is smaller than that from gelatin, probably on account of the presence of some amino-acids. The amount of nitrogen necessary for endogenous metabolism can be regarded as the sum of (a) the amount of "differentiated" nitrogen in the form of amino-acids, and (b) that of "undifferentiated" nitrogen (of ammonia), often masked by nitrogen of amino-acids or ammonium salts.

## CHEMICAL ABSTRACTS.

**Changes in the Lime Content of the Hen's Egg during Development.** R. H. A. PLIMMER and J. LOWNDES (*Biochem. J.*, 1924, **18**, 1163—1169).—Shell-less eggs contain more than sufficient lime for the needs of the developing chick. The lime content of eggs increases during the development of the chick; it enters the egg from the shell. A similar increase occurs in pigeons' eggs during development. S. S. Z.

**"Lecitiburin," a Lecithin from the Eggs of the Shark.** H. P. PONCE (*Anal. Asoc. Quím. Argentina*, 1924, **12**, 5—12).—A note describing the preparation from the eggs of the shark of a lecithin, m. p. 70°, to which the name "lecitiburin" is given.

G. W. R.

**Chemical Composition of Edible Viscera from Meat-producing Animals.** W. C. POWICK and R. HOAGLAND (*J. Agric. Res.*, 1924, **28**, 339—346).—Analyses are recorded of edible viscera of steers, pigs, calves, and lambs. In general, the food values depend mainly on the protein content. Livers corresponded closely with lean beef in nitrogen content, but other organs were inferior in this respect. With the exception of hearts, tongues, lungs, and stomachs, the organs examined usually contained more phosphorus than lean beef. [Cf. *B.*, 1924, 961.] A. G. P.

**Determination of Glycogen in the Placenta.** R. CLOGNE, (MLLE.) WELTI, and M. PICHON (*Bull. Soc. Chim. biol.*, 1924, **6**, 788—790).—Determinations of placental glycogen by the method of Bierry and Gruziewska, and by an improved modification of this method, give values varying between 0.60 and 1.66%. J. P.

**Cholesterol Content of the Bile, Blood, and Flesh of the Hippopotamus.** J. A. GARDNER (*Biochem. J.*, 1924, **18**, 777—784).—The bile of the hippopotamus contains both free and ester cholesterol to the extent of 0.47% of the solid matter. Small quantities of free and ester cholesterol were also found in the blood and in the flesh of this animal. S. S. Z.

**Inositol. II. Synthesis of Inositol in the Animal Body.** J. NEEDHAM (*Biochem. J.*, 1924, **18**, 891—904).—The animal body seems to possess the power of synthesising inositol. Rats fed on an inositol-free diet for 8 months contained the normal amount of

free inositol. No diminution in the body-content of inositol was observed when a lasting and vigorous excretion of the compound was induced in rats subsisting on an inositol-free diet. S. S. Z.

**Uric Acid in the *Pieridae*: Quantitative Study.** V. B. WIGGLESWORTH (*Proc. Roy. Soc.*, 1924, **B**, 97, 149—155).—In *Pieris brassicae*, the wings of the male contain more uric acid than do those of the female. This difference is attributed to the greater size of the wing scales which cover the androconia of the male. The total amount of uric acid is unchanged during pupal life. The *Pieridae* appear to differ from other families in the use to which uric acid is put rather than in the amount produced. O. O.

**Bioluminescence. V. Luciferin of *Cypridina Hilgendorffi*.** S. KANDA (*Amer. J. Physiol.*, 1924, 68, 435—443).—The methyl-alcoholic extract of *Cypridina* is evaporated to a small volume, ethyl alcohol is added, the liquid filtered, and the filtrate evaporated to dryness. The residue is dissolved in distilled water saturated with hydrogen, and the luciferin is completely precipitated on saturation with ammonium sulphate. The precipitate after rapid drying is again extracted with water saturated with hydrogen, or with absolute methyl or ethyl alcohol. The luciferin, the presence of which is indicated by the production of light with *Cypridina* luciferase, gives Molisch's reaction, but neither Millon's nor the ninhydrin reaction. It is not precipitated by acids, alkalis, or salts other than ammonium sulphate; results obtained with alkaloidal reagents were not conclusive. A. A. E.

**Circulation of Lead in the Organism Investigated by a Radio-chemical Method.** I. A. CHRISTIANSEN, G. HEVESY, and S. LOMHOLT (*Compt. rend.*, 1924, 179, 291—293).—Lead hydroxide mixed with olive oil containing a little lamp-black and some radium-*D* was injected into rabbits and guinea-pigs. A diagram is given showing lead distribution in faeces, urine, and viscera together with that found at the point of injection. The proportion of lead found in the liver and faeces is greater whilst that in the kidneys and urine is less than in the case of bismuth. H. J. E.

**Micro-determination of Silicon and its Concentration in certain Organs.** G. BERTRAND.—(See ii, 872.)

**Determination of Cystein.** Y. OKUDA.—(See ii, 792.)

**Determination of Cystine.** Y. OKUDA.—(See ii, 793.)

**Mammary Secretion. V. I. Further Research on the Threshold and Effects of Protein "Excess." II. Quantitative Relation of Vitamin-*B* to Protein.** G. A. HARTWELL (*Biochem. J.*, 1924, 18, 785—794).—A high proportion of protein in the diet of the lactating rat produces an abnormal condition in the young. There is, however, a quantitative relationship between protein and vitamin-*B* in the diet; if the latter is increased when the protein is increased no evil results ensue, but the rate of growth of the suckling is impaired. The function of vitamin-*B* is primarily

concerned with the metabolism of protein or with the nitrogen part of the protein molecule. S. S. Z.

**Mineral Content of Human Milk in Normal and Rachitic Families.** S. V. TELFER (*Biochem. J.*, 1924, **18**, 809—813).—No appreciable differences were found in the composition of the milks of women whether the infants developed rickets or not. S. S. Z.

**Organic Constituents of Saliva.** H. UPDEGRAFF and H. B. LEWIS (*J. Biol. Chem.*, 1924, **61**, 633—648).—A modification of the technique of Folin and Wu (A., 1919, ii, 308) is described, which is suitable for the removal of proteins from saliva, and the average concentrations of the non-protein nitrogenous constituents of normal saliva have been determined and compared with corresponding figures for blood. The total non-protein nitrogen of saliva is 37% of that of blood, but the relationship between the individual constituents is different in the two fluids, e.g., in saliva there is relatively much ammonia and urea and practically no amino-acid nitrogen. C. R. H.

**Analysis of Urine.** MAX WEINTRAUT (*Arch. Pharm.*, 1924, **262**, 360—368).—A discussion of the determinations necessary for diagnostic purposes, and of the results produced by various pathological conditions. B. F.

**Exchanges of the Blood and the Excretion of Urobilin.** G. KÜHL (*Arch. exp. Path. Pharm.*, 1924, **103**, 247—259).—Contrary to Whipple's view (*Arch. intern. Med.*, 1922, **29**, No. 6), the urobilin excreted in the urine and faeces is derived solely from the destruction of hæmoglobin. When injected into normal dogs, hæmoglobin is converted quantitatively into urobilin and excreted as such; in anæmic animals, however, part of the hæmoglobin is retained. Following loss of hæmoglobin (withdrawal of blood), the excretion of urobilin falls below the normal. E. S.

**Photochemical Reaction of Urine.** A. VON SOÓS (*Z. klin. Med.*, 1924, **98**, 347—352; from *Chem Zentr.*, 1924, i, 2789).—In dark urines, substances are found which inhibit the action of photographic developers on silver chloride which has been exposed to light. This effect is attributed to protective colloids. G. W. R.

**Effect of Alcoholic Extract of Commercial Dextrose on Urinary Reducing Substance.** C. C. WANG and A. R. FELSHER (*J. Biol. Chem.*, 1924, **61**, 659—665).—Ingestion of commercial dextrose causes a greater excretion of reducing substances than does the same weight of pure dextrose; the effect is due to an unidentified constituent of the commercial preparation which can be extracted therefrom with alcohol. The extract alone produces no excretion of reducing substance. C. R. H.

**Rapid Determination of Lead in Urine.** L. J. FAIRHALL.—(See ii, 873.)

**Determination of Menthoglycuronic Acid in Urine.** A. J. QUICK.—(See ii, 876.)



**Direct Nesslerisation Micro-Kjeldahl Method and a Modification of the Nessler-Folin Reagent for Ammonia.** F. C. KOCH and T. L. McMEEKIN.—(See ii, 871.)

**Glycolytic Properties of the Cancer Cell.** N. WATERMAN (*Arch. Néerland. Physiol.*, 1924, 9, 573—587).—Warburg's observation that the glycolytic power of carcinoma tissue from a rat was abnormally high has been confirmed for several types of tumour (man and rats) by measuring the carbon dioxide displaced from a Ringer solution containing added dextrose and excess of sodium hydrogen carbonate. The effect of calcium salts on this glycolysis has been studied and the lactic acid produced has been determined. It is found that normal pancreatic tissue from several types of animal possesses a definite though much smaller power to convert sugar into lactic acid. Attempts to raise the glycolytic power of normal tissue to the high level of that of tumour tissue (kidney tissue with its very low glycolytic power was used) were made; addition of phosphates to the Ringer solution was without effect: hexosephosphate gave inconclusive results; extraction of triturated carcinoma tissue with physiological saline and addition of the extract to the medium caused a rise in glycolytic action in some cases.

H. J. C.

**Calcium Content of the Blood-serum in Cases of Gout.** V. COATES and P. C. RAIMENT (*Biochem. J.*, 1924, 18, 921—924).—There is a considerable rise in the calcium of the blood-serum in cases of gout.

S. S. Z.

**Chemical and Physico-chemical Changes in Blood in Experimental Nephritis.** J. MOSONYI (*Z. klin. Med.*, 1924, 99, 500—505; from *Chem. Zentr.*, 1924, i, 2788).—After poisoning with cantharidin, the elimination of nitrogen in dogs remains normal. The freezing point of the blood rises to  $-0.512^{\circ}$  and then sinks gradually to normal. After uranium poisoning, marked nitrogen retention occurs and the freezing-point of the blood rises to  $-0.53^{\circ}$ , then falls to  $-0.638^{\circ}$ , and subsequently becomes normal after repeated small rises. Mercuric chloride poisoning causes at first an increase in the nitrogen content of the blood. After 7 days, the residual nitrogen falls considerably below normal, and remains at this level until the end of the illness.

G. W. R.

**Nephropathic Action of the Dicarboxylic Acids and their Derivatives. I. Tartaric, Malic, and Succinic Acids. II. Glutaric and Malonic Acids.** W. C. ROSE (*J. Pharm. Exp. Ther.*, 1924, 24, 123—146, 147—158).—The acids were administered subcutaneously to rabbits and their effect on renal activity determined by analyses of the blood constituents and by the phenolsulphonephthalein test; in a few cases, histological examinations of the kidneys were made. Tartaric and glutaric acids exerted a pronounced, and *dl*-malic acid a slight nephropathic action, while *l*-malic, succinic, and malonic acids were inactive. The renal-toxic action of certain acids appears to be associated with their slow oxidation in the organism. From the fact that calcium

glutarate has a greater solubility than calcium succinate it is concluded that the toxicity of the glutarates is not due to the deposition of the insoluble calcium salt in the kidney. E. S.

**Relation of the Fat-soluble Factor to Rickets and Growth in Pigs.** III. S. S. ZILVA, J. GOLDING, J. C. DRUMMOND, and V. KORENCHESKY (*Biochem. J.*, 1924, **18**, 872—880).—Rickets characterised by the presence of significant amounts of osteoid tissue can be induced in pigs on a diet in which dried separated milk is the main source of the fat-soluble vitamins. S. S. Z.

**Chemical Basis for the Treatment of Tuberculosis. Action of Steapsin and Insulin on Tubercle Bacilli.** L. G. ROBINOVITCH and G. W. STILES (*Amer. Rev. of Tuberculosis*, 1924, **9**, 587—612).—Lipase in alkaline solution to which is added a "co-hydrolyser" of bees-wax (chloroform), acts as a decorticator of tubercle bacilli, presumably by hydrolysing the lipoid outer membrane. Insulin produces the same effect as lipase. J. P.

**Action of Alkaloids on the Field-locust (*Acridides*).** R. BECKER (*Arch. exp. Path. Pharm.*, 1924, **100**, 335—348).—The pharmacological actions of alcohol, ethereal oils, chloroform, xylene, benzene, acids, alkalis, and salts on the female of the field-locust are briefly recorded. At greater length are described investigations on the action of alkaloids, including physostigmine, veratrine, cocaine hydrochloride, nicotine, caffeine-sodium salicylate, morphine hydrochloride, arecoline hydrobromide, pilocarpine hydrochloride, and also of mixtures of these alkaloids. Similar effects to those obtained by the alkaloids, *i.e.*, paralysis, vibration of the jumping legs, etc., are obtained by the application of heat.

W. O. K.

**Action of Chemical Irritants on the Vitality of Protozoa, as Measured by the Rate of Division.** H. HANDOVSKY, E. DU BOIS-REYMOND, and C. M. VON STRANTZ (*Arch. exp. Path. Pharm.*, 1924, **100**, 273—287).—Cantharidin, undecylenylvanillylamide, amyl nitrite, and arsenious oxide usually inhibit the rate of division of *Balantiophorus minutus*. Histamine hydrochloride inhibits it at first and then later accelerates it. Cantharidin and arsenious oxide appear occasionally to have a stimulating action on some of the cells of a culture.

W. O. K.

**Action of Some Compounds on the Excitability of the Nervus Ischiadicus of the Frog.** H. HANDOVSKY and R. ZACHARIAS (*Arch. exp. Path. Pharm.*, 1924, **100**, 288—293).—Morphine hydrochloride, chloral hydrate, alcohol, urethane, camphor, cocaine hydrochloride, veratrine, strychnine nitrate, and hydrogen peroxide increase in low concentration and decrease in high concentration the excitability of the nervus ischiadicus of the frog. Phenol, antipyrine, and novocaine were depressants, and caffeine an excitant, at all concentrations tested. Arsenious oxide was without effect. The inorganic ions present also influence the excitability, the potassium ion tending to increase it.

W. O. K.  
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**Leucocytogetic Properties of Copper Potassium Cyanide.** E. TROCELLO (*Rassegna Clin. Terap. Sci. aff.*, 1923, **22**, 148—167; from *Chem. Zentr.*, 1924, i, 70).—Intravenous injection of a 0.2% aqueous solution of "cuprocyan" results in an increase in the number of leucocytes in the blood of rabbits. The effect is partly shown by the lymphocytes. G. W. R.

**Pharmacological Investigations on Iron: Colloidal Ferrous Sulphide prepared in Presence of Gelatin. II. Experiments on Rabbits by Intravenous Injections.** L. SABBATANI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 473—479).—The effects on rabbits of intravenous injections of the colloidal ferrous sulphide prepared by the method previously elaborated (this vol., ii, 116) are described. Whether *in vitro* or *in vivo* or in tissues isolated from the dead body, the sulphide passes into hydrated ferric hydroxide, which remains tenaciously held at the point where the sulphide was first fixed and is difficult to observe, as its colour is easily confused with that of the tissues themselves. T. H. P.

**Pharmacological Investigations on Iron. V. Colloidal Ferrous Sulphide prepared in Presence of Gelatin.** L. SABBATANI (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 8—13; cf. this vol., ii, 116, and preceding abstract).—Details are given of the effects produced in dogs by intravenous injection of colloidal ferrous sulphide prepared in presence of gelatin. T. H. P.

**Induced Oxidation and the Explanation of the Internal Use of Iron Salts and of Fever.** N. R. DHAR (*J. Physical Chem.*, 1924, **28**, 943—947).—The induced oxidation of fats, proteins, sugars, etc. by air at the ordinary temperature in the presence of sodium sulphite or of freshly-precipitated ferrous hydroxide (T., 1917, **111**, 690; A., 1921, ii, 36, 37, 391; 1922, i, 1210) is regarded as a close analogue of the processes which occur in the body. Fever is described as an auto-catalytic reaction accelerated by foreign substances, *e.g.*, bacterial secretions. S. S.

**"Nitritoid Crisis" Produced by Arsenobenzene Derivatives. VI. Experiments on Isolated Organs with Plain Muscle.** A. BUSACCA (*Arch. Farm. speriment. Sci. aff.*, 1924, **23**, 58—71).—Neosalvarsan in 0.01% solution is without effect on vascular musculature of isolated lung, which is without sympathetic innervation. In 0.01% solution, it produces enlargement of the pupil of the isolated eye of a frog, whilst at higher concentrations it acts as a local caustic and produces constriction. In 0.02% solution neosalvarsan and oxidised neosalvarsan stimulate motility in the plain muscle of certain human organs. With higher doses this effect is maintained in the case of neosalvarsan, whilst in the case of oxidised neosalvarsan, a depressant effect is produced. Neosalvarsan in therapeutic doses stimulates the terminal fibres of the sympathetic system, and it is suggested that this system is involved in the "nitritoid crisis." G. W. R.

**Toxicity of Chaulmoogra Oil.** B. E. READ (*J. Pharm. Exp. Ther.*, 1924, 24, 221—258).—Ethyl hydnocarpate causes the same disturbances as the oil and hydnocarpic acid as the ethyl or glyceryl ester, or salt, appears to be the most active constituent of preparations of the oil. Toxic doses of hydnocarpates cause hæmolysis, renal irritation, and fatty infiltration of the liver. Increased lymph flow follows intravenous injection of ethyl hydnocarpate. Administered in this way, it kills rabbits in a dose of 0.5 c.c. per kg. body-weight, causing hypersensitivity with lowered blood calcium, inco-ordinated movements, and finally death from respiratory failure.  
H. J. C.

**Theory of Narcosis.** M. CLOETTA and H. THOMANN (*Arch. exp. Path. Pharm.*, 1924, 103, 260—281).—During narcosis with ether, alcohol, or “somnifen,” the calcium content of the plasma of dogs is depressed (8—15%), the depression running parallel with the narcosis; corresponding with this depression, the potassium content of the plasma is increased. On the other hand, excitation with *ac*-tetrahydro- $\beta$ -naphthylamine produces a rise in the calcium content. In conformity with these results, injection of substances which precipitate calcium (oxalates, phosphates) decreases the action of the above narcotics, the phosphates being the more effective in this respect. Administration of calcium increases the narcotic action in the case of frogs, but this effect has not been observed with dogs. No significant changes occur in the density, viscosity, or protein content of the plasma during narcosis, nor is the stability of the plasma colloids towards increases in temperature or changes in the concentration of ions altered; the surface tension, however, usually decreases slightly, but it is doubtful if this is of significance for narcosis. These results suggest that narcotics produce a disturbance in the ionic equilibrium in the brain and perhaps in other organs.  
E. S.

**Narcotic Leucocytosis. Experimental Researches on Guinea-pigs.** R. SEYDERHELM and E. HOMANN (*Arch. exp. Path. Pharm.*, 1924, 100, 322—334).—Ether, chloroform, ethyl chloride, ethyl bromide, chloral hydrate, urethane, alcohol, sulphonal, and morphine, which induce narcosis when administered to a guinea-pig, also cause a marked leucocytosis in that animal, whilst scopolamine, which does not cause narcosis in the guinea-pig, does not give rise to a leucocytosis. There would therefore appear to be a definite leucocytosis, associated with the effect of drugs causing narcosis.  
W. O. K.

**Comparative Toxicity of Novocaine, Neocaine, Procaine, and Apohesine. Effect of Intravascular Injections.** W. R. MEEKER and E. B. FRAZER (*J. Pharm. Exp. Ther.*, 1924, 22, 375—392).—Novocaine (German), and the corresponding products, neocaine (French) and procaine (American), have equal toxicity as determined by the minimum lethal dose on intravenous injection into rabbits under uniform conditions, and are equally effective as local or regional anæsthetics. The American product “apohesine” is more toxic.  
W. O. K.

**Study of Two Series of Procaine Derivatives with Reference to the Relationship between their Pharmacological Action and Chemical Constitution.** H. L. SCHMITZ and A. S. LOEVENHART (*J. Pharm. Exp. Ther.*, 1924, **24**, 159—166).—Determinations have been made of the relative anæsthetic activities and toxicities of various substituted aminoethanol and aminopropanol esters of *p*-aminobenzoic acid, using the rabbit's cornea for the former measurements, and mice for the latter. In both series, the anæsthetic activity increased with increase in the size of the substituent alkyl groups, the *isopropyl* compounds being more active than the *n*-propyl compounds. The toxicity, however, also increased. In the aminoethanol series this increase was proportional to the increase in anæsthetic activity, whilst in the case of the aminopropanol series it was greater than the anæsthetic activity. Hence, although the members of the latter series have greater anæsthetic activities than those of the former, their therapeutic indices are smaller.

E. S.

**Local Anæsthetic Properties of *p*-Aminobenzoyldiisopropylaminoethanol Hydrochloride ("Isocaine"), Cocaine, Procaine, and Butyn.** H. L. SCHMITZ and A. S. LOEVENHART (*J. Pharm. Exp. Ther.*, 1924, **24**, 167—177).—"Isocaine" has approximately the same efficiency as cocaine in anæsthetising the cornea and only three-tenths of its toxicity. It is twice as toxic as procaine, and hence is less suitable for paralysis of sensory nerve trunks, although it has about the same efficiency as the latter substance for this purpose. Butyn has ten times the toxicity of procaine; it is more efficient (but more toxic) than cocaine in anæsthetising the cornea, and only half as efficient as procaine for paralysis of sensory nerves. The minimum lethal doses of the drugs differ with different species.

E. S.

**Colloid Chemistry of Protoplasm. III. Viscosity of Protoplasm at Various Temperatures. IV. Heat of Coagulation of Protoplasm.** L. V. HEILBRUNN (*Amer. J. Physiol.*, 1924, **68**, 645—648; **69**, 190—199).—III. Maximal viscosities were observed in the protoplasm of the egg of the clam *Cumingia* at 2°, 15°, and 30°.

IV. The temperature of coagulation of the protoplasm of sea urchin and *Cumingia* eggs is below that of proteins, but the coefficient is similar. The coagulation of protoplasm is probably associated with a change in the physical state of the emulsified fats.

CHEMICAL ABSTRACTS.

**Biochemistry of Skin and the Chemical Basis of Skin Swelling.** M. KAYE and D. J. LLOYD (*Biochem. J.*, 1924, **18**, 1043—1057).—There is an absolute identity of the conditions producing hardness in the interfibrillary fluid in which the fibrils and fibres of skin are embedded with those causing irreversible coagulation of proteins, and it is concluded that the cementing of the fibrils in some dried skins must be due to coagulation. Sub-

found to remove the coagulated interfibrillary matter. The colloidal swelling of skins is due to the network of skin fibres which consist of collagen, and the swelling in acid and in alkaline solution is brought about by the formation of ionisable salts of collagen. The removal of free amino groups in the skin reduces the amount of acid absorbed and combined. The swelling in acid solution is due to the presence of free amino groups. S. S. Z.

**Nature of Foetal Re-adsorption.** N. H. LONG and A. S. PARKES (*Biochem. J.*, 1924, **18**, 800—805).—Intra-uterine absorption of the foetus is due to autolysis of the latter and not to the action of uterine enzymes. S. S. Z.

**Autolysis. XII. Experimental Atrophy of Muscle Tissue.** K. K. CHEN, W. MEEK, and H. C. BRADLEY (*J. Biol. Chem.*, 1924, **61**, 807—827).—During 9 weeks after section of the sciatic and femoral nerves in rabbits the muscles supplied by these nerves lost 50% in weight; they showed no increased water content. Such atrophic muscle contains the same amount of free amino-acids as healthy muscle and slightly more peptides; when subjected to sterile autolysis, it develops the same reaction as normal muscle but liberates more free amino-acids than the latter. It is suggested that this is due to a gradual alteration of the structural cell-proteins into a digestible form during the process of atrophy. C. R. H.

**Effect of Heat on the Activity of the Peroxydase in Milk.** G. SPITZER and M. C. TAYLOR (*J. Dairy Sci.*, 1924, **7**, 234—244).—By use of the Storch reaction in comparative experiments on various mixtures of sterilised with raw milk, it was shown that the greater part of the peroxydase is inactivated at 85°. The rate of inactivation is a function of the temperature and time of exposure and appears to follow a definite law. CHEMICAL ABSTRACTS.

**Laws of the Action of Laccase : Influence of the Reaction of the Medium.** P. FLEURY (*Compt. rend.*, 1924, **179**, 709—711; cf. A., 1924, i, 594, 697, 921, 1144).—The optimum value of  $p_H$  for the action of laccase varies from 6.7 to 7.6 as the percentage of guaiacol initially present in the solution varies from 1 to 0.25. The action of the laccase is regarded as the resultant of two phenomena, one being the fixation of the guaiacol by the enzyme and the other its oxidation; the former of these becomes less, and the latter more intense as the value of  $p_H$  increases. T. H. P.

**Oxydases.** J. CLARENS (*Bull. Soc. chim.*, 1924, [iv], **35**, 1198—1206).—Using the constant-volume ureometer previously described (Job and Clarens, A., 1909, ii, 826), the oxidation of quinol in alkaline solution has been studied by measuring the rate of absorption of oxygen. The oxidation is proportional to the alkalinity of the solution and, owing to the formation of acid oxidation products, the oxidation ceases when the acidity reaches a certain value. If the acidity is removed by the addition of calcium carbonate, the oxidation continues at a rate determined by the velocity of reaction of the calcium carbonate with the acid oxidation products. The velocity of oxidation is increased by the presence of manganous

salts. The acceleration is attributed to the power of manganese to form complexes with hydroxyl ions, thereby favouring the action of hydroxyl ions on the quinol in the presence of oxygen, a view supported by the fact that iron and copper salts similarly accelerate the oxidation. Oxidation in the presence of the oxydase of lucerne follows a different course. The oxidation products are not acid and the oxidation continues regularly; if the oxydase is destroyed by heat or by using very strongly alkaline solutions, the oxidation of the quinol continues until the alkalinity of the solution disappears owing to the formation of acid oxidation products, a certain number of hydroxyl ions being, however, immobilised in a complex with the oxydase. This second mode of oxidation of quinol in presence of an oxydase is also catalysed by manganous salts. R. B.

**Xanthine Oxydase. I. Preparation and Properties of the Active Material.** M. DIXON and S. THURLOW (*Biochem. J.*, 1924, **18**, 971—975).—Xanthine oxydase is associated with the caseinogen of milk, and a stable preparation can be obtained by treating the milk with an equal volume of saturated ammonium sulphate solution. The precipitated caseinogen and fat are then dried between filter-paper, thoroughly extracted with ether, and the residue is dried. The enzyme can be adsorbed from a neutral solution of this preparation almost completely by alumina and filter-paper. Charcoal adsorbs it only slightly. It is destroyed by alcohol and acetone and slowly by atmospheric oxygen. Ether, chloroform, toluene, and glycerol do not inactivate it. The presence of fat in a finely-divided state, as in milk, accelerates the action of the enzyme. Hypoxanthine and xanthine on keeping in neutral solution become incapable of oxidation by the enzyme. S. S. Z.

**Xanthine Oxydase. II. Dynamics of the Oxydase System.** M. DIXON and S. THURLOW (*Biochem. J.*, 1924, **18**, 976—988).—The following results on the dynamics of xanthine oxydase have been obtained by employing the method of reducing methylene-blue to its leuco base in a vacuum. The reaction velocity is not affected by hydrogen-ion concentration between  $p_H$  5.5 and 9. Above  $p_H$  9 and below  $p_H$  4, the enzyme is destroyed. Between  $p_H$  4 and 5, the reaction velocity is very small, but no destruction occurs. The reaction velocity is directly proportional to the enzyme concentration, but is independent of methylene-blue concentration providing it is not very small. The reaction velocity is independent of purine-base concentrations up to a certain critical concentration, beyond which it decreases. This critical concentration becomes higher with increased enzyme concentration. Below the critical concentration of the substrate hypoxanthine reduces methylene-blue twice as fast as xanthine does, but as the inhibition begins the rates approach one another and become equal when inhibition is complete; the reaction velocity is then dependent on methylene-blue concentration. On addition of purines other than the substrate, the reaction velocity is also eventually decreased. The authors incline to the view that Schardinger enzyme and xanthine oxydase are identical. S. S. Z.

**Xanthine Oxydase. III. Reduction of Nitrates.** M. DIXON and S. THURLOW (*Biochem. J.*, 1924, **18**, 989—992).—The “atite” of Haas and Hill (this vol., i, 349) is identical with the oxydase or oxydases of milk. Xanthine oxydase reduces nitrates to nitrites in the presence of hypoxanthine, xanthine, adenine, or aldehyde. The rate of reduction of nitrate is proportional to that of the reduction of methylene-blue under various conditions. The inhibitory effect of purines is also observed in this case (see preceding abstract).  
S. S. Z.

**Phosphoric Esterase of Blood.** M. MARTLAND, F. S. HANSMAN, and R. ROBISON (*Biochem. J.*, 1924, **18**, 1152—1160).—The inorganic phosphate in the laked whole blood and in laked corpuscles increases rapidly at first and then more slowly, until after 4 days it amounts to 93% of the organic acid-soluble phosphorus in both cases. The rate of hydrolysis is greater at a  $p_H$  slightly on the acid side of the normal blood reaction and close to the neutral point. The enzyme responsible for the hydrolysis is present in both plasma and corpuscles or is possibly adsorbed by the latter from the plasma. It resembles the muscle esterase in its ability to hydrolyse hexosediphosphoric esters and in its relative inactivity towards hexosemonophosphoric and glycerophosphoric esters. A portion of the esters hydrolysable by bone is also hydrolysed by the blood enzyme during the early stages of autolysis, but the remaining portion is very resistant. It is found that no significant change in the reducing power occurred during the early stages of the autolysis in laked blood or corpuscles, although 50% of the phosphoric esters might be hydrolysed. In the later stages of the hydrolysis, a rise of about 30% in the sugar value is usually observed. In unlaked whole blood at a  $p_H$  somewhat above normal, synthesis of phosphoric esters was observed; when the  $p_H$  rises above or falls below certain limits, the rate of hydrolysis of the phosphoric esters becomes greater than the rate of synthesis and the inorganic phosphate increases. At a  $p_H$  somewhat lower than 7.0, the rate of hydrolysis may approach that in laked blood.  
S. S. Z.

**A. Use of Invertase. B. Repeated Use of the Same Preparation of Invertase.** E. K. O. SCHMIDT (*Z. Ver. deut. Zuckerind.*, 1924, **817**, 727—786).—A.—A solution of invertase prepared by the autolysis of yeast can be concentrated at 30°/30 mm. without much loss of activity. A study of the effect of invertase on solutions containing different concentrations of sucrose shows that the time required to reduce the rotatory power of the solution to zero increases with the concentration of sucrose, somewhat more slowly than the latter up to 20% sucrose, and more quickly between 20% and 50% sucrose. The optimum temperature for the action of yeast invertase is about 55°. The less pure the sugar, the less active is the invertase.

B.—At 55°, at which temperature zymase is destroyed, whole yeast can be used for the inversion of sucrose; it is possible, after inversion is complete, to remove the yeast by filtering the solution through a collodion filter and use it for the inversion of a second



lot of sucrose, or to make the process of inversion continuous by sucking the sucrose solution slowly through such a filter covered with a layer of yeast. Preparations obtained by the adsorption of invertase on charcoal are not suited for repeated use because the enzyme is readily dissolved out from the adsorbate, but the dried residue of a mixture of a solution of invertase with one of gelatin can be used for the inversion of at least eleven successive quantities of sucrose without loss of activity.

C. R. H.

**Mode of Action of Invertase.** H. VON EULER and K. JOSEPHSON (*Arkiv Kemi, Min., Geol.*, 1924, 9, No. 4, 1—6).—It is calculated that for invertase  $k_a=10^{-7}$ ,  $k_b=10^{-11}$ , with the isoelectric point about  $p_H=5$ ; viscosity measurements show a minimum at  $p_H=4-5$ . Reaction-producing molecules of catalyst+substrate are postulated, their formation and decomposition discussed, and their concentration is estimated at  $10^{-8}$  for 0.1*N*-sucrose. The activity- $p_H$  curve is said to be almost identical with that of raffinase on the alkaline side of the optimum. [Cf. *B.*, 1924, Dec. 26.]

F. M. H.

**Properties of a Highly Active Invertase Preparation.** K. MYRBÄCK (*Arkiv Kemi, Min., Geol.*, 1924, 9, No. 2, 1—6).—A highly purified stable invertase ( $I_f=240$ ) was prepared (cf. *B.*, 1924, Dec. 26) and was found to have no significant optical activity. Its acidity (cf. Michaelis, *Biochem. Z.*, 1915, 65, 360) was half that of an albumin preparation but its basicity was about equal to that of the albumin (cf. Euler and Josephson, *A.*, 1923, i, 721). The equivalent concentration of the invertase was found to be  $1.64 \times 10^{-3}$  in 1% solution, corresponding with an invertase equivalent of about 6000;  $k_b=3 \times 10^{-10}$ .

F. M. H.

**Polysaccharides. XXVII. Lichenase.** P. KARRER and M. STAUB (*Helv. Chim. Acta*, 1924, 7, 916—928; cf. this vol., i, 471).—Lichenase occurs in Plata-barley from the first to the eleventh day of germination. Its amount increases a little after the first day and then remains constant. It is present in nearly constant amount in spinach seeds both before and during germination. During the first few days of germination, the lichenase of maize is distributed equally between the embryo and the endosperm. Subsequently a greater proportion is found in the embryo. Green *Triticum repens* contains lichenase. The enzyme has been found in the intestine of a rabbit (cf. Tschermak, *Biochem. Z.*, 1912, 45, 452), but all previous attempts failed to reveal it in the alimentary canal of any other vertebrate. It is now shown to be present in the stomach of the pig and of the cow, but not in the rennet-bag of the latter animal. Whether it originates in these places or is introduced along with the food is not certain. Lichenase is not present in the stomach of a calf which has been fed entirely on milk.

The effect of additions on the enzymic hydrolysis of lichenin was studied at  $p_H$  3.94—7.1. Dextrose, lævulose, galactose, maltose, sucrose, cellobiose, and gentiobiose inhibit the action; sodium chloride is inactive; the effect of egg-albumin varies with  $p_H$ , but is greatest in feebly acid solution.

Snail-lichenase after dialysis for many days contains no enzymes acting on starch, inulin, maltose, lactose,  $\beta$ -methylglucoside, or ethyl  $\beta$ -methylglucosidosalicylate, and invertase is present only in traces. On the other hand, the enzyme decomposes not only lichenin, but also cellobiose and gentiobiose. The decomposition of gentiobiose supports the theory that cellulose contains glucose residues attached by 1 : 6-glucosidic linkings. W. E. E.

**Diastatic Power of the Juice of Different Varieties of Potatoes.** A. JOSZT and B. STARCZEWSKI (*Rozpraw biol. z zakresu rolnictwa, hodowli i med. wet.*, 1922; from *Chem. Zentr.*, 1924, i, 2784).—Removal of nitrogenous substances from the juice of potatoes is not completely effected by heating, or by treatment with lead acetate, animal charcoal, or colloidal ferric hydroxide. To accomplish this it is necessary to add 1% ammonium sulphate after heating the juice for 10 minutes at 100°. Considerable differences are shown in diastatic power, but no marked relationship was found between the acidity of the juice, the starch concentration, and the degree of germination. G. W. R.

**Influence of Hydrogen-ion Concentration on the Action of certain Amylases.** J. T. GROLL (*Arch. Néerland. Physiol.*, 1924, 9, 520—538).—Differentiation between various amylase preparations has been studied by comparing the types of curves obtained by plotting the time of hydrolysis of starch against the  $p_H$  of the buffered medium (methods are those of the author; cf. *ibid.*, 1918, 2, 516; 1922, 6, 445). The amylase of ox-blood acts best in an alkaline medium,  $p_H$  8. The amylases of different organs or secretions of the same animal may vary considerably (in man, that of saliva and pancreas; cow, that of milk, blood, and pancreas), or be nearly the same (in man, pancreas and urine). In the same organs of different animals, a similar variation is found; e.g., the amylase of human pancreas differs considerably from those of ox and pig pancreas which are very similar. H. J. C.

**Allelocatalysis and the Growth of Yeast.** G. L. PESKETT (*Biochem. J.*, 1924, 18, 866—871).—Living yeast-cells grown in bacteria-free media in hanging-drop preparations, multiply in proportion to the number of cells present. The phenomenon of "allelocatalysis," i.e., the mutual acceleration of reproductive rate by contiguous organisms, observed by Robertson (*ibid.*, 1921, 15, 612) in the case of certain infusoria does not hold true in this case.

S. S. Z.

**Cannizzaro's Reaction in the Mechanism of Alcoholic Fermentation.** C. SCHWEIZER and H. GEILINGER (*Bull. Assoc. Chim. Sucr.*, 1924, 42, 20—31).—The acetic acid and alcohol produced by the action of pressed yeast on acetaldehyde are formed in equivalent amounts, as required by Cannizzaro's reaction, only when oxygen is completely excluded from the reaction mixture.

E. S.

**Specific Action of Plant Proteases.** A. V. BLAGOVESCHENSKI (*Biochem. J.*, 1924, **18**, 795—799).—From experiments on the proteases of *Cannabis sativa*, *Phaseolus Mungo*, *Brassica rapa*, *Lupinus luteus*, *Hibiscus esculentus*, and *Dolichos melanophthalmus*, DC. the author concludes that the enzyme from every plant splits its own globulin more actively than the globulins of other plants.

S. S. Z.

**Behaviour of Dried Enzymes on Exposure to Heat. III. Pancreatic Enzymes.** C. ARTOM (*Arch. Farm. speriment. aff.*, 1924, **38**, 105—132).—Both the enzymes in the pancreas of the dog and those in the pancreatic juice itself, when dried at 10—30°, withstand higher temperatures in the dry state than after re-solution in water. This protective effect of drying is, however, considerably less marked in the latter than in the former of the two cases. These results correspond with those previously obtained with intestinal enzymes.

T. H. P.

**Ammonia Production by Animal Tissues *in vitro*. I. Use of Mixed Tissue Extracts.** J. M. LUCK (*Biochem. J.*, 1924, **18**, 814—824).—A series of experiments with mixed and single tissues is described. Free ammonia is liberated from trypsin-digested caseinogen by the liver and kidney, and very slightly by intestinal mucosa. It is considered to be due to deamidation and not to deamination. Urea was formed by preparations of the liver, intestinal mucosa, and kidney. Marked ammonia production was observed in mixtures of gastric mucosa and liver preparations. No appreciable deamination by either gastric mucosa or liver or other single tissue preparation could be demonstrated. Definite deamidation was effected by the liver, gastric mucosa, kidney, intestinal mucosa, and most liver mixtures. The liver and the liver-mixtures synthesise an amide-like substance. No residual amide nitrogen could be found after the action of a gastric mucosa–liver mixture on totally hydrolysed gelatin.

S. S. Z.

**Ammonia Production by Animal Tissues *in vitro*. II. Demonstration of Urease in the Animal Body.** J. M. LUCK (*Biochem. J.*, 1924, **18**, 825—828).—From experiments on a number of animals, it is concluded that the animal body contains urease. The gastric mucosa of the carnivora gave the most active preparations. The distribution of the enzyme in the stomachs of the ruminants is definite. The enzyme is present in the abomasum where peptic digestion takes place. No urease could be found in the gastric mucosa of the rodents.

S. S. Z.

**Irregularities in Lactic Acid Fermentation.** C. RICHET and H. CARDOT (*Ann. Inst. Pasteur*, 1924, **38**, 842—847).—It is shown that the irregularities observed by the authors in lactic acid fermentation in the presence of mercuric chloride as an antiseptic are dependent on the dilution of the inocula, being more marked at dilution 30,000 than at 300, whilst at a dilution of 300,000 the mercury-treated cultures do not ferment (cf. Lumière, A., 1923, i, 353).

J. P.

**Regularity of Lactic Acid Fermentation.** A. LUMIÈRE (*Ann. Inst. Pasteur*, 1924, **38**, 848—850).—Polemical in reply to Richet and Cardot (preceding abstract). J. P.

**Influence of Media containing Bile on the Chemical Composition of *Bacillus subtilis*.** A. BERTHELOT and E. OSSART (*Bull. Soc. Chim. biol.*, 1924, **6**, 770—772).—Cultures of *Bacillus subtilis* grown in media containing bile and afterwards dried, yield on acid hydrolysis a much smaller proportion of reducing substance (dextrose) than do cultures grown in the absence of bile. J. P.

**Bacterial Nutrition. II.** H. R. WHITEHEAD (*Biochem. J.*, 1924, **18**, 829—832).—When broth is autoclaved some substances necessary for streptococcal growth are destroyed. These substances are contained in the fraction of the broth precipitable by phosphotungstic acid. This fraction alone, however, is not sufficient. Glycine, alanine, leucine, tyrosine, tryptophan, histidine, aspartic and glutamic acids do not remove this deficiency in the same way as does the filtrate after precipitation with phosphotungstic acid. Caseinogen broth was submitted to fractionation by Dakin's butyl alcohol extraction method, and it was found that the fractions soluble in butyl alcohol, in butyl and in ethyl alcohol, and the fraction insoluble in butyl alcohol did not promote streptococcal growth alone. Complete growth was obtained only when all the three fractions were reunited, although partial growth could be obtained with any two fractions. The fraction insoluble in butyl alcohol was active in high concentration. This was most probably due to incomplete extraction. S. S. Z.

**Relation between the Chemical Composition of Peptones and Hydrogen Sulphide Production by Bacteria.** F. W. TILLEY (*J. Bact.*, 1924, **8**, 287—295).—Commercial peptones contain unoxidised, partly oxidised, and oxidised sulphur compounds. No hydrogen sulphide is liberated by bacteria from the last named, but freely from the others. Hydrogen sulphide is produced from cystine in abundance. CHEMICAL ABSTRACTS.

**Fermentation of Salts of Organic Acids as an Aid to the Differentiation of Bacterial Types.** H. C. BROWN, J. T. DUNCAN, and T. HENRY (*J. Hygiene*, 1924, **23**, 1—22).—The production of gas and change of reaction produced by bacteria in organic salt media are irregular and cannot be used as criteria for the differentiation of bacterial types. Suitable data can be obtained, however, because the decomposition of the salts of certain organic acids having insoluble lead salts can be demonstrated by adding lead acetate to the media after incubation (only formic of the simple monobasic and dibasic aliphatic acids is readily attacked; monohydroxy-carboxylic acids are also stable but tartaric and citric acids are easily decomposed). Using the sodium salts of citric, *d*-, *l*-, and *r*-tartaric, fumaric, and mucic acids, seven different groupings of the common *Salmonella* types have been obtained (the usual sugar reactions give only four). The method has been applied to other groups of bacteria. Citric acid on bacterial decomposition by

*B. suipestifer* yields acetic and succinic acids and carbon dioxide; a reaction mechanism is suggested. Fumaric acid yields succinic acid. These organic salt fermentations cannot be used to replace the sugar reactions in general use. H. J. C.

**Production of Organic Compounds of Sulphur in Bacterial Cultures with Special Reference to Glutathione.** J. W. McLEOD and J. GORDON (*Biochem. J.*, 1924, **18**, 937—940).—A distinct nitroprusside reaction was observed in 24—48-hour cultures of a number of anaërobes: *Bacillus paratyphosus* B and most allied species, *Cholera vibrio*, *B. typhosus*, *B. pyocyaneus*, and some strains of *B. coli* and *B. proteus*. No such reaction could be detected in cultures of *Staphylococcus*, *Streptococcus*, *Pneumococcus*, *Gonococcus*, *Meningococcus*, *B. influenzae*, *B. Morax-Axenfeld*, *B. paratyphosus* A, or the dysentery bacilli. The thermostable substance reacting with nitroprusside is oxidised glutathione or some related compound originally present in the medium and reduced by the organisms in the course of their development. S. S. Z.

**Selective Bactericidal Action.** E. A. COOPER and G. E. FORSTNER (*Biochem. J.*, 1924, **18**, 941—947).—The chemical germicides, namely those that react with the constituents of protoplasm, have a more powerful action on *Bacillus coli* than on *B. pyocyaneus*. Formaldehyde forms an exception in this respect, attacking both organisms equally. Germicides, on the other hand, such as the aliphatic alcohols, phenol, etc., which exert a physico-chemical action on bacteria are more active towards *B. pyocyaneus* than towards *B. coli*, and their germicidal action in this case resembles that of heat. S. S. Z.

**Chemotherapeutic Experiments with Chaulmoogra and Allied Preparations. IV. Growth-inhibiting Effect of Organic Compounds towards Acid-fast Bacilli. V. Mechanism of Growth-inhibiting Effect of Chaulmoogra and Other Vegetable Oils.** O. SCHÖBL (*Philippine J. Sci.*, 1924, **25**, 123—134, 135—150).—IV.—In general, water-soluble organic antiseptics inhibit the growth *in vitro* of *Bacillus tuberculosis*, whereas fat solvents do not. The sodium, copper, and nickel salts of fatty acids are antiseptic; the zinc, strontium, lead, and uranium salts are inactive. The presence in a compound of an aliphatic double bond, a benzene nucleus, one or more phenolic groups, or an alkyl group attached to a benzene nucleus all tend to increase its antiseptic activity. The amino group in aromatic compounds has no influence if it is attached to the benzene ring but greatly increases the activity if it is in the side chain. Terpenes are less active than their related straight-chain compounds.

V.—Although the degree of unsaturation of vegetable oils does not run parallel with their power to inhibit or to promote the growth of acid-fast bacteria, yet complete hydrogenation abolishes their activity. In terms of Ehrlich's theory the author suggests that all the oils which have any effect on the growth of bacteria have a "haptophore" group by virtue of their unsaturation, and that the

nature of their effect depends on whether the rest of the molecule is a "toxophore" as in the case of chaulmoogra oil or a "nutriphore" as in the case of the growth-stimulating oils. The "nutriphore" in the latter case is the glycerol part of the molecule, the fatty acids being without effect. Some evidence was obtained of acquired tolerance on the part of the bacteria towards chaulmoogra oil.

C. R. H.

**Extraction and Purification of Insulin.** L. BANTI (*Arch. Farm. speriment. aff.*, 1924, **38**, 176—184).—Marked improvement in the yield of insulin obtained from pancreas is attained by addition of a relatively high proportion of acid to the alcohol used for the extraction, and by the employment of a procedure which gives highly concentrated aqueous solutions of insulin without evaporation in a vacuum. [Cf. *B.*, 1924, Dec. 26.]

T. H. P.

**Duality of Insulin.** L. AMBARD, F. SCHMIDT, and M. ARNOVLYEVITCH (*Compt. rend. Soc. Biol.*, 1924, **90**, 790—792; from *Chem. Zentr.*, 1924, i, 2794).—Two insulin hormones are distinguished: one concerned in the oxidation of sugar to carbon dioxide and water, and the other polymerising sugar to glycogen. An equilibrium appears to exist between the two hormones whereby an increase in the one is associated with a decrease in the other.

G. W. R.

**Efficiency of Various Sugars and their Derivatives in Relieving the Symptoms caused by Insulin in Mice.** P. T. HERRING, J. C. IRVINE, and J. J. R. MACLEOD (*Biochem. J.*, 1924, **18**, 1023—1042).—Complete positive results were obtained with dextrose and mannose. Maltose was also permanently efficacious, but its action was slower. Temporary disappearance of symptoms was obtained with levulose, galactose, and tetra-acetylfructose. Lactose, 2:3:5:6-tetramethylglucose, 2:3:5-trimethylglucose, sucrose,  $\alpha$ - and  $\beta$ -methylglucosides, tetramethyl- $\beta$ -methylglucoside, tetramethyl- $\gamma$ -methylglucoside, glucose-monoacetone, salicin, man-nitol, dulcitol, and  $\beta$ -glucosan had no action at all. The relation of chemical structure and some physiological considerations are discussed.

S. S. Z.

**Concentration-Action Curve of Insulin Preparations, and Anti-Insulin.** S. G. DE JONGH (*Biochem. J.*, 1924, **18**, 833—838).—An anti-insulin substance was observed in some Dutch preparations which showed the phenomenon of double convulsant doses and differed in their behaviour in the case of rabbits and of diabetics. The concentration curve of insulin with regard to sugar seems to be a straight line, that of the anti-insulin an adsorption curve.

S. S. Z.

**Extraction and Properties of an Ovarian Hormone.** E. A. DOISY, J. O. RALLS, E. ALLEN, and C. G. JOHNSTON (*J. Biol. Chem.*, 1924, **61**, 711—727).—Fresh liquor folliculi was mixed with alcohol and the solution evaporated to dryness after removal of the proteins; the residue was extracted with alcohol and the solution treated with

acetone to remove phospholipins, this process being repeated several times; finally the dry residue from the alcoholic extracts was taken up in ether. Amounts of the order of a few mg. of the dry residue from this ethereal solution, when injected into ovariectomised rats, were found to induce the full oestrous cycle in these animals. The active substance is soluble in ether, alcohol, chloroform, light petroleum, or acetone, but insoluble in water. It is thermostable and moderately resistant to both acid and alkaline hydrolysis; it is not affected by tryptic digestion. Preparations with similar properties were obtained from placenta and from whole ovaries, but the yield of active substance was much smaller; no active preparations could be made from corpora lutea. C. R. H.

**Durability of Vitamin-A of Cod-liver Oil.** E. POULSSON (*Biochem. J.*, 1924, **18**, 919—920).—A sample of cod-liver oil 23 years old in daily doses of 3—5 mg. promoted growth in rats deficient in vitamin-A. S. S. Z.

**Stability of the Vitamin-A of Cod-liver Oil Towards the Hardening Process.** S. S. ZILVA (*Biochem. J.*, 1924, **18**, 881—882).—If anaërobic conditions are observed, cod-liver oil can be hardened at a temperature of 150° and deodorised without any appreciable loss in the vitamin-A content. S. S. Z.

**Investigation of Barley, Malt, and Beer for Vitamins-B and -C.** A. HARDEN and S. S. ZILVA (*Biochem. J.*, 1924, **18**, 1129—1132).—The vitamin-B of barley is not affected by the malting process and is frequently present in the finished malt, but is absent from the culms. The antiscorbutic vitamin appears in the steeped grain and is present in the green malt but absent from kilned malt. The beer examined by the authors (India Pale Ale) was free from both vitamins-B and -C. S. S. Z.

**Fractionation of Bios and Comparison of Bios with Vitamins-B and -C.** G. H. W. LUCAS (*J. Physical Chem.*, 1924, **28**, 1180—1200).—The bios contained in malt combings and in rice-polishings can be fractionated by precipitation in alcoholic solution with barium hydroxide into bios I and II, neither of which has by itself any great influence on the rate of reproduction of *Saccharomyces cerevisiae*, race F, but together enormously increase the crop of yeast. A top yeast is described, however, which is much less dependent on bios than race F. Bios I and II cannot replace the vitamins in preventing polyneuritis in pigeons or scurvy in guinea-pigs or in maintaining the growth of rats. The growth-producing vitamin can be extracted from rice-polishings by treatment with pepsin. The chemical treatment employed in the fractionation of bios destroys the growth-promoting vitamin. M. B. D.

**Action of Nitrous Acid on the Antineuritic Substance in Yeast.** R. A. PETERS (*Biochem. J.*, 1924, **18**, 858—865).—Primary and many secondary amines are not responsible for the antineuritic activity of acid extracts of yeasts, since such extracts retain their activity after being treated with nitrites. Histamine

sometimes cures polyneuritis in pigeons; this confirms Abderhalden's observations. Daily doses of this drug do not, however, delay the onset of the disease. S. S. Z.

**Dietetic Value of Barley, Malt, and Malted Liquors as Determined by their Vitamin Content.** H. W. SOUTHGATE (*Biochem. J.*, 1924, **18**, 769—776).—Barley and malt, tested on rats, have been found to contain water-soluble-*B* in considerable and equal amounts. Malt has also been shown to possess antineuritic properties in the case of pigeons fed on a basal diet free from vitamin-*B*. Beer independent of its yeast content contains vitamin-*B*, but to a much less extent than that the corresponding amount of malt used in its manufacture. Vitamins-*A* and -*C* are not present in appreciable quantities in barley or its derivatives. S. S. Z.

**Nutritive Properties of Milk. III. Effectiveness of the X-Substance in Preventing Sterility in Rats on Milk Rations High in Fat.** H. A. MATTILL, J. S. CARMAN, and M. M. CLAYTON (*J. Biol. Chem.*, 1924, **61**, 729—740).—Rats of both sexes fail to reproduce on a milk diet of high fat content; the addition of nucleoprotein to such a diet has no effect, but reproductive power is retained if wheat embryo in added to the food; preliminary ethereal extraction of the wheat embryo, however, deprives the latter of its curative power. This observation, together with the fact that addition of green lettuce leaves to the diet will also prevent sterility, indicates that the missing factor is the substance designated "X" by Evans (*J. Metabol. Res.*, 1923, **3**, 233). C. R. H.

**Extraction and Determination of Lipochromes from Animal and Plant Tissues.** K. H. COWARD (*Biochem. J.*, 1924, **18**, 1114—1122).—The only quantitative method of extraction is saponification in an atmosphere of nitrogen with aqueous potassium hydroxide of not higher strength than 20%. Cvet's observation on the existence of four xanthophylls has been confirmed by employing his chromatographic method (fractional filtration of the pigments through a column of chalk). This method has also been found suitable for separating carotin and lycopin from a mixture of the two pigments. A curve for use with the Hellige colorimeter is given for the determination of carotin. S. S. Z.

**Lipochromes of Etiolated Wheat Seedlings.** K. H. COWARD (*Biochem. J.*, 1924, **18**, 1123—1126).—The pigments of etiolated wheat seedlings are carotin and the four xanthophylls isolated by Cvet from green leaves. It is impossible to obtain quantitative figures for the four xanthophylls by Cvet's chromatographic method. S. S. Z.

**Yellow Pigments of Australian Acacias.** J. M. PETRIE (*Biochem. J.*, 1924, **18**, 957—964).—The water-soluble yellow pigment of *Acacia linifolia*, *A. decurrens*, and *A. longifolia* is a glucoside which on hydrolysis yields flavonol, kaempferol, and rhamnose. Free flavonol is absent. The yellow flavonol obtained on hydrolysis



can be transformed by reduction with nascent hydrogen into a red solution resembling that of anthocyanins. The acacia tannins are composed of phloroglucinol and protocathechuic and gallic acids, and deposit on hydrolysis large amounts of the red phlobaphen anhydrides. The flavonol is present in quantities of about 0.06% of the fresh flower, carotin and xanthophyll from 0.14 to 0.3%. S. S. Z.

### Grape Pigments. III. Anthocyanins of Seibel Grapes.

R. J. ANDERSON (*J. Biol. Chem.*, 1924, **61**, 685—694; cf. this vol., i, 1152).—The pigment occurring in the skins of the hybrid Seibel grapes was isolated as the *picrate*, red needles, and converted into the *chloride*,  $C_{23}H_{25}O_{12}Cl$ , prisms ( $+3H_2O$ ), m. p.  $160^\circ$  (sintering at  $158^\circ$ ); on hydrolysis with hydrochloric acid this yields the *anthocyanidin chloride*,  $C_{17}H_{15}O_7Cl$ , prisms ( $+1.5H_2O$ ), m. p. above  $260^\circ$  [*picrate* ( $+H_2O$ )]. Glucosazone was isolated from the filtrate after the hydrolysis. Methoxyl determinations indicated that the anthocyanidin was a mixture of the mono- and di-methyl ethers of delphinidin, containing a preponderance of the dimethyl ether. Delphinidin iodide was isolated from the solution after removal of the methoxyl groups. Details are given of the absorption spectra of the chlorides of the anthocyanin and anthocyanidin. C. R. H.

**Sitosterol.** R. J. ANDERSON and F. P. NABENHAUER (*J. Amer. Chem. Soc.*, 1924, **46**, 2113—2118).—A sample of sitosterol obtained from the bottom fraction of maize-gluten sterols as previously described (this vol., i, 924) was acetylated and brominated by Windaus and Hauth's method (A., 1907, i, 921). On debromination with zinc dust and acetic acid in alcoholic solution followed by hydrolysis with alcoholic potassium hydroxide, a sitosterol was obtained which on recrystallisation had m. p.  $138$ — $139^\circ$ ,  $[\alpha]_D^{20}$  — $36.69^\circ$ ; acetyl derivative, m. p.  $130$ — $131^\circ$ ,  $[\alpha]_D^{20}$  — $40.20^\circ$ . Sitosterol from wheat bran and from crude maize oil similarly purified yielded products having m. p.  $140$ — $141^\circ$ ,  $[\alpha]_D^{20}$  — $34.90^\circ$  (acetyl derivative, m. p.  $130$ — $131^\circ$ ), and m. p.  $138$ — $139^\circ$ ,  $[\alpha]_D^{20}$  — $34.87^\circ$  (acetyl derivative, m. p.  $128$ — $130^\circ$ ,  $[\alpha]_D^{20}$  — $38.81^\circ$ ), respectively, and it is concluded that sitosterol as usually prepared is contaminated with small amounts of dihydrositosterol. The approximate composition of a mixture of the two sterols can be calculated from the formulæ  $S = (25.82 - R)/0.6246$  and  $P = (36.64 + R)/0.6246$ , where  $S$  and  $P$  represent the percentages of sitosterol and dihydrositosterol respectively, and  $R$  is the specific rotation of the mixture in chloroform, the values  $-36.64^\circ$  and  $+25.82^\circ$  being chosen for the specific rotations of the respective pure sterols. R. B.

**Non-volatile Acids of the Peach.** E. K. NELSON (*J. Amer. Chem. Soc.*, 1924, **46**, 2337—2338).—Fractionation by the ester-hydrazide method shows that the non-volatile acids of the peach consist chiefly of *l*-malic acid and citric acid in approximately equal proportions. The m. p.  $145^\circ$  is recorded for citric acid trihydrazide (cf. Curtius, A., 1917, i, 635; Franzen and Helwert, A., 1923, i, 637). R. B.

**Non-volatile Acids of the Dried Apricot.** E. K. NELSON (*J. Amer. Chem. Soc.*, 1924, **46**, 2506—2507; cf. preceding abstract).—The non-volatile acids of the dried apricot, identified by esterification, fractionation, and conversion into the hydrazides, consist of *l*-malic and citric acids in the proportion 2.5 : 1, with traces of an unidentified acid, possibly oxalic acid. F. G. W.

**Acetaldehyde: A Normal Constituent of the Tannin-rich Contents of the "Inclusion" Cells in the Mesocarp of certain Fruits.** C. GRIEBEL (*Z. Unters. Nahr. Genussm.*, 1924, **48**, 218—220).—In a previous paper (this vol., ii, 791) the presence of small amounts of acetaldehyde was demonstrated in certain fruits. The so-called inclusion cells (A., 1919, i, 427) were found to contain acetaldehyde readily liberated from the cell by distillation with 2% tartaric acid. The contents of the inclusion cell of *Ceratonia siliqua*, L, separated by mechanical means, gave a considerable amount of acetaldehyde on distillation with water alone, a further yield being obtained by distillation with acid. The acetaldehyde is considered to be responsible for the coagulation and consequent disappearance of the rough taste of the tannins during the process of ripening. G. S. W.

**Ripening Process of Bananas.** C. GRIEBEL (*Z. Unters. Nahr. Genussm.*, 1924, **48**, 211—227).—During the ripening of bananas the tannin-rich cell contents of the latex tubes present in the pith become coagulated and the tannins pass from a soluble to an insoluble condition. Subsequently the latex tubes break down forming the so-called inclusion cells. These cells are found to contain acetaldehyde in an easily liberated condition (cf. preceding abstract). Fruit in which the normal process of ripening has been suppressed by frost is tasteless and odourless, the formation of sugar from starch and the production of amyl acetate having been inhibited; at the same time, the fruit contains tannin in a soluble condition and only traces of acetaldehyde are present. G. S. W.

**Wax from *Fagraea*.** A. J. ULTÉE (*Bull. Jard. Botan. Buitenzorg*, 1924, **6**, [3], 1—3; from *Chem. Zentr.*, 1924, i, 2882).—The fruits of *Fagraea* have beneath the outer integument a layer of white, glutinous substance from which, by coagulation with alcohol, a white, slightly elastic mass was obtained, containing ash 0.23%, protein 0.22%, caoutchouc 5.16%. From the first alcoholic extract crystals, m. p. 79°, were obtained which yielded on hydrolysis lupeol, m. p. 211°, and palmitic acid. Phytosterol was also present. G. W. R.

**Isolation of an Inhibitory Substance from Plants.** W. L. MALLMANN and C. HEMSTREET (*J. Agric. Res.*, 1924, **28**, 599—602).—A substance which inhibits the activity of the cabbage-rot organism was isolated from rotted cabbage plants. The substance was effective against other "soft-rot" organisms, and gave positive results at exceptionally great dilution. It was destroyed by

exposure to a temperature of 63° for 30 minutes, but survived after 20 minutes at 56°. It is not considered to be a product of the soft-rot organism.

A. G. P.

**Action of Bromine on certain Plants.** A. PITINI (*Arch. Farm. sperim. aff.*, 1924, **38**, 164—168).—Decomposition of glucosides contained in plants by the action of bromine (cf. Liotta, A., 1920, i, 587) is the result of a hydrolytic process and takes place either not at all or only partly if the plants are first thoroughly dried. Alkaloids contained in plants are unaffected by bromine only if they are stable towards the halogen hydracid which is formed. T. H. P.

**Absorption of Carbon Dioxide the First Step in Photosynthesis.** H. A. SPOEHR and J. M. MCGEE (*Science*, 1924, **59**, 513—514).—Dried and ground leaf material, to which the same amount of water has been added as was originally contained in the leaves, absorbs carbon dioxide from the air in the dark; the manner of drying the leaves, however, greatly affects their absorptive capacity. *Helianthus* leaves, similarly treated and free from carbon dioxide, absorbed 4.59 mg. of the latter per g. at 25°. Extraction of the dried leaves with cold absolute alcohol greatly, and with water somewhat, reduced the absorptive capacity, but the material extracted by the alcohol absorbed only very small amounts of carbon dioxide. The absorptive capacity of the leaf is also destroyed by heat. Extraction with acetone did not affect the absorptive capacity, but the latter was reduced by 90% by extraction with water saturated with ether at 20° (Chibnall and Schryver's method for protein extraction), the residue absorbing as much carbon dioxide as the original leaf material. It is considered that support is accorded to the theory that the leaf absorbs carbon dioxide from the atmosphere by a mechanism similar to that which in the blood of mammals serves to free the tissues from this gas. The major portion of the carbon dioxide is probably absorbed by the proteins of the leaf; this primary union may be of importance in determining the cause of the asymmetric nature of the synthesis of carbohydrates in the chlorophyllous plant.

A. A. E.

**Water Content, a Factor in Photosynthesis.** R. H. DASTUR (*Ann. Bot.*, 1924, **38**, 779—788).—Inadequate water-supply results in a decline in the photosynthetic activity of leaves and ultimately causes their decay. This factor also accounts for the fact that Willstätter and Stoll were unable to obtain constant values for the assimilation numbers of the leaves of the same species. O. O.

**Chemonastia of *Drosera rotundifolia*.** I. W. MEVIUS (*Biochem. Z.*, 1924, **148**, 548—565).—Solutions of the sodium halides cause inflection of the leaf tentacles of *Drosera rotundifolia*, the duration of which varies with the concentration of the stimulating solution, whilst weak solutions produce a quicker response than concentrated solutions. Sodium nitrate is a more active stimulant, but is also more injurious to the leaves than the halides, whilst sodium sulphate only excites the tentacles in concentrated

solutions. Potassium salts show somewhat parallel results, but here the more concentrated solutions act more quickly. The activity of the anions follows the series:  $\text{NO}_3 > \text{I} > \text{Br} > \text{Cl} > \text{SO}_4$ . The alkaline-earth chlorides warmed at  $51^\circ$  inhibit the inflection of the tentacles, a similar result being obtained with warm 0.25*N*-potassium chloride solution. A chemical stimulus and a heat stimulus do not summate. *Drosera* leaves kept in a strong solution of alkaline-earth salt and then placed in sodium chloride show an immediate infolding of the tentacles. The alkaline-earth salts exert no harmful action on the leaves. J. P.

**Nitrate-reducing Properties of Plants.** V. L. ANDERSON (*Ann. Bot.*, 1924, **38**, 699—706).—Nitrate is frequently found in green plants. Of the plants examined more than 20% contained nitrite. The nitrate-reducing mechanism "atite" (cf. Haas and Hill, this vol., i, 349) was observed in 23 plants. Atite does not appear to be of much significance in the protein metabolism of the plant. O. O.

**Influence of Nitrifying Bacteria on the Growth of Barley.** E. B. FRED (*Soil Sci.*, 1924, **18**, 323—329).—The yield of barley (total dry weight), grown under sterile conditions in sand supplied with nutrient salts and nitrogen as ammonium sulphate, was nearly doubled when pure cultures of nitrifying bacteria were added 2 weeks before planting. The favourable effect on the plants was evident throughout growth, and the presence of nitrates in the inoculated pots and their absence from the others was confirmed by test. The barley contained 0.78% of nitrogen when nitrifying organisms were present and 0.66% in their absence. C. T. G.

**Relation of the Molecular Proportions in the Nutrient Solution to the Growth of Wheat.** M. C. SEWELL (*J. Agric. Res.*, 1924, **28**, 387—393).—Wheat plants were grown in sand cultures with nutrient solutions containing varying proportions of dissolved salts. Grain yields were as good from solutions high in nitrogen and low in potassium and phosphate as from those with less nitrogen but higher proportions of phosphate and potassium salts. A. G. P.

**Antagonism of Hydrogen Ions and Neutral Salt Ions in their Action on the Germination and Growth of Wheat.** H. LUNDEGÅRDH (*Biochem. Z.*, 1924, **149**, 207—215).—Calcium and potassium chlorides and sodium dihydrogen phosphate diminish the toxic effect of increasing hydrogen-ion concentrations on the growth of wheat seedlings, more especially between  $p_H$  4.5 and 6.8. The antagonism between salt and hydrogen ions is also shown in their action on germinating wheat seeds. J. P.

**Nitrogenous Constituents of the Juice of the Alfalfa Plant [Lucerne]. II. Basic Nitrogen.** H. B. VICKERY (*J. Biol. Chem.*, 1924, **61**, 117—127; cf. this vol., i, 1275).—In addition to the asparagine and tyrosine already reported, there have been isolated, from the unhydrolysed juice of the lucerne plant, arginine,

lysine, stachydrine, choline, a purine in the form of its chloride, and a base (unidentified) which gives a picrate melting at 298°. Taken together, the substances so far isolated account for 4.8% of the organic solids and 13.6% of the total nitrogen of the protein-free solution obtained by treating the original juice with alcohol. C. R. H.

**Variation with Temperature of the "Swelling Value" of Amylogen.** A. MAIGE (*Compt. rend. Soc. Biol.*, 1924, **90**, 685—687; from *Chem. Zentr.*, 1924, i, 2784—2785).—In experiments with the embryos of germinating beans, the critical concentration of sugar at which starch is transformed into amyloplasts was found to be increased both by raising and by lowering the temperature.

G. W. R.

**Methylpentosans in Cereals.** G. TESTONI.—(See ii, 790.)

**Determination of Nitrate and Ammonia in Nitrogenous Materials.** O. M. SHEDD (*J. Agric. Res.*, 1924, **28**, 527—539).—The Devarda alloy method of Strowd (*Soil Sci.*, 1920, **10**, 333) is modified by allowing the reduction to take place at ordinary temperatures for 24 hours previous to heating. A control experiment on a portion of the test-liquid without Devarda's alloy is carried out with each determination. The method was used for determining nitrate in tobacco leaves and is suitable for the examination of fertilisers. Where nitrate and ammonia are to be determined in portions of the same solution a preliminary filtration is advised.

A. G. P.

**Determination of Ammonia in Soil.** N. BENGTSSON (*Soil Sci.*, 1924, **18**, 255—278).—By successive extractions of soil with potassium chloride solution (25 g. of soil extracted with, at the most, seven 100 c.c. portions of approximately 4% solution), added ammonia could be recovered quantitatively and determined in the combined filtrates. Very low figures were obtained by this method for the ammonia present in air-dried arable soils, indicating that organic nitrogen compounds are not decomposed. A detailed procedure is given (cf. *B.*, 1924, Dec. 26) which proved entirely satisfactory with all surface soils, but failed in the case of one heavy clay subsoil.

C. T. G.

**Methods of Studying the Strength of Soil Acids.** J. W. TIDMORE and F. W. PARKER (*Soil Sci.*, 1924, **18**, 331—338).—A comparison of the strength (intensity factor) of the soil acids in 25 soils, as determined by the Truog "avidity" method (cf. *A.*, 1916, ii, 404), by the sugar inversion method (cf. Rice and Osugi, *A.*, 1918, i, 520), and by the hydrogen-ion concentration showed good correlation between the results. The methods are based on different principles, and the close agreement between the results obtained may be explained by assuming that the acids of the solid phase undergo hydrolysis producing hydrogen ions, the extent of such hydrolysis depending on the strength of the acids. It is considered that the results support the view that the  $p_H$  of the soil solution is largely determined by the acid silicates of the soil. [Cf. *B.*, 1924, Dec. 26.]

C. T. G.

**Influence of Sulphur Oxidation on Solubility of Soil Minerals.** R. E. STEPHENSON and W. L. POWERS (*Soil Sci.*, 1924, **18**, 317—321).—The application of various amounts of sulphur to soil maintained at optimum moisture content greatly increased the water-soluble calcium and potassium and decreased the water-soluble phosphorus. Nitrification was depressed by the heaviest application and there was an appreciable increase in acidity. Two soils were used, one representative of arid conditions, with  $p_H$  7.0, and the other of humid conditions, with  $p_H$  6.4. Flocculation of the colloidal material of the soils by the products of oxidation of the sulphur was very marked. It is suggested that the increase in the soluble calcium may account to some extent for the response given by leguminous crops, especially lucerne, to light dressings of sulphur on certain soils. C. T. G.

**Absorption of Bases by Soils.** N. M. COMBER and S. J. SAINT (*Soil Sci.*, 1924, **18**, 131—132).—Jones (this vol., i, 820) claims to have shown that beyond a certain point an increase in concentration of a base in solution results in a decrease in the amount absorbed by a soil in contact with the solution. This conclusion is based on determinations of the carbon dioxide evolved on shaking carbonates and hydrogen carbonates of alkali and alkaline-earth metals with soil. In the experiments with normal carbonates, the carbon dioxide given off will form hydrogen carbonate with the remaining carbonate and hence cannot be taken as a measure of the amount of base absorbed. Experiments in which the amount of base absorbed by a soil is calculated both from the carbon dioxide evolved and by titration after filtering show definitely that Jones' conclusions are not justified. C. T. G.

**Resistance of Soils to Acidification.** A. DEMOLON and V. DUPONT (*Compt. rend.*, 1924, **179**, 300—302).—Aqueous extracts of soils from various sources, from which calcium carbonate has been excluded, behave towards both sulphuric and lactic acids as weak buffer solutions. This property is attributed to the humates present. When the soil remains in contact with the aqueous extract, the colloidal clay reacts with sulphuric acid so that the suspension exhibits marked buffer action. H. J. E.

**Microscopical Study of Soil.** S. WINOGRADSKY (*Compt. rend.*, 1924, **179**, 367—371).—A method of soil treatment is described which yields five specimens for examination from each sample. These are stained with erythrosin. From observation of a series of such specimens the following general conclusions are drawn. Normal arable soil contains only cocci in groups; these are surrounded by a gel or membrane and firmly attached to the particles resulting from flocculation of colloid matter. Mineral debris, except in so far as it is colloidal, is free from microbes; this applies particularly to the coarser particles. In the case of soils to which soluble fermentable matter has recently been added, free microbes, distributed in irregular clusters, predominate. These often consist of forms which are not present in normal soil and are not associated

with colloidal particles. A soil which is foul may readily be recognised by the bacterial forms present in the solution even after centrifuging. [Cf. *B.*, 1924, Dec. 26.] H. J. E.

**Secular and Seasonal Changes in the Soil Solution.** J. S. BURD and J. C. MARTIN (*Soil Sci.*, 1924, **18**, 151—167).—The concentration and composition of the soil solutions, obtained by the displacement method, from seven soils have been compared, portions of each soil having been kept for 8 years under different conditions, namely, cropped, fallowed, and air-dried. The displaced solution is taken as a trustworthy measure of the true soil solution (cf. *J. Agric. Sci.*, 1923, **13**, 265) and it is assumed that the air-dried soils have remained unchanged and represent the condition of the soils at the beginning of the 8-year period. The cropped soils all showed a marked decrease in concentration of total solutes and nitrates in the displaced solutions at the end of the period, whilst the fallowed soils, with one exception (a highly productive soil), gave considerably increased concentrations. The concentration of phosphate in the cropped soils is decreased—an unexpected result, since it is known that phosphate tends to form a saturated solution and re-establish equilibrium very rapidly. The concentration of sulphate increased in both cropped and fallowed soils.

With soils in a low state of fertility due to continuous cropping, there is a seasonal decrease in concentration of most of the solutes, but the initial concentration of the soil solution in any given growing season returns to its original magnitude by the beginning of the following season. The results cannot be taken to apply to natural drained soils in which the effect of leaching comes into play, since the experimental soils were kept in vessels allowing no escape of drainage water. C. T. G.

# ABSTRACTS

ISSUED BY THE

## BUREAU OF CHEMICAL ABSTRACTS.

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### A. PURE CHEMISTRY.

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#### PART II.

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#### General and Physical Chemistry.

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**A Burner for Producing Monochromatic Light for Polarimetry, etc.** A. O. JONES (*J. Soc. Chem. Ind.*, 1923, 42, 459—460r).—Gas supplied to a Bunsen burner passes through a steel crucible containing an easily volatile salt, *e.g.*, sodium nitrite, and closed by a screw cap and asbestos washer. The gas inlet- and outlet-tubes support the crucible so that the flame plays on the bottom of the crucible. J. S. G. T.

**Some Approximate Numerical Applications of Bohr's Theory of Spectra.** D. R. HARTREE (*Proc. Camb. Phil. Soc.*, 1923, 21, 625—641).—Bohr's theory of spectra and atomic structure (A., 1922, ii, 363) is applied to the mathematical deduction of a radial electric field such that orbits specified by the application of quantum conditions to the motion of an electron in this field shall have the energies assigned to the different terms in the appropriate optical and X-ray spectra. The results are obtained in a form permitting the numerical calculation of the dimensions of the orbits and the variation of time along them. From these, by making certain assumptions, the X-ray scattering by an atom can be calculated in a form suitable for comparison with the results of Bragg, James, and Bosanquet (A., 1921, ii, 477; 1922, ii, 703). Orbital calculations relating to potassium, ionised calcium, and sodium are tabulated. J. S. G. T.

**Relation of Ultimate Rays and Resonance Rays in Spectra Comprising Several Systems of Series.** F. CROZE (*Compt. rend.*, 1923, 177, 1285—1287).—The resonance rays of elements, the arc spectra of which comprise several systems of series, are only the same as the ultimate rays and the characteristic rays of



the absorption spectra of these elements if their frequencies correspond with combinations between terms belonging to the same system of series. The results of Catalán (A., 1923, ii, 356) and of Kiess and Kiess (A., 1923, ii, 199) and others are discussed, particularly in connexion with chromium, molybdenum, and manganese.

E. E. T.

**Intensity Measurements of Spectral Lines.** J. K. ROBERTSON (*J. Opt. Soc. Amer.*, 1923, 7, 983—995).—Particulars are given of an experimental determination of the relative advantages associated with the measurement of the intensities of spectral lines either by the neutral-tinted glass wedge method developed by Merton and Nicholson (A., 1916, ii, 461; 1917, ii, 433; 1920, ii, 69), or by measuring the densities of the photographic images of the lines.

J. S. G. T.

**Variations in the Structure and Intensity of Band Spectra due to Molecular Influences.** M. TOUSSAINT (*Z. Physik*, 1923, 19, 271—300).—Particulars are given of the effects produced by the presence of argon or iodine vapour on the structures and intensities of the spectra of hydrogen, oxygen, nitrogen, and mixtures of carbon vapour with each of these respective gases, excited either in the positive column or arc discharge.

J. S. G. T.

**Spark Spectra of Metalloids in the Liquid State.** M. CURIE (*Compt. rend.*, 1923, 177, 1021—1023).—Continuous spectra (using highly condensed media) are produced partly because of the non-uniformity of the intermolecular field of force acting on an electron removed from an outer region of an atom as the result of excitation. The presence of hydrogen has been regarded as the cause of continuous spectra obtained with liquids. Spark spectra have now been studied, using platinum electrodes and metalloidal liquids: bromine, oxygen, sulphur, nitrogen, and phosphorus (all in the liquid state). In all cases, continuous spectra were observed. The upper wave-length limit was of the order of  $725\mu\mu$ , the lower limits for bromine, sulphur, phosphorus, oxygen, and nitrogen being, respectively,  $600\mu\mu$ ,  $500\mu\mu$ ,  $475\mu\mu$ ,  $390\mu\mu$ , and  $390\mu\mu$ . The absorption bands of oxygen were observed clearly, the platinum lines indistinctly. Using aluminium electrodes in liquid nitrogen, complete inversion of the rays  $396\mu\mu$  and  $394\mu\mu$  was observed; no fine structure was apparent. The inverted rays correspond with an absorption by certain aluminium centres, no emission following the absorption.

E. E. T.

**Spectral Series in the Oxygen Group.** J. J. HOPFIELD and R. T. BIRGE (*Nature*, 1923, 112, 790—791).—The suggestion that the so-called "singlet" series of oxygen are really of a complex nature is supported; in general, the series spectra of the oxygen group are similar to those of chromium, as far as complexity of terms is concerned. The sulphur triplets  $0P-3D$  and  $0P-4D$  (Hopfield, A., 1923, ii, 708) are in reality  $0P-2S$  and  $0P-3S$ , respectively, whilst those called  $0P-2S$  and  $0P-3S$  remain

unidentified. In addition, the  $\lambda$  5279 narrow triplet of sulphur has been identified as 1S—2P. A. A. E.

**The Vibrational Isotope Effect in the Band Spectrum of Boron Nitride.** R. S. MULLIKEN (*Science*, 1923, **58**, 164—166).—The vibrational frequency for the isotope,  $B^{10}N$ , of boron nitride should be 2.76% greater than for the isotope  $B^{11}N$ , as compared with 0.08% for hydrogen chloride, and possibly 0.04% for lead. Although the abundance ratio (1 : 5 from the atomic weight 10.83) is unfavourable, boron nitride thus presents a favourable case for the observation of differences of spectra. The equation  $\nu = 42885 + 1268.5n' - 10.20n'^2 - 1873n + 11.85n^2$ , where  $n'$  and  $n$  denote, respectively, the initial and final numbers of vibrational quanta possessed by the molecule, gives, in wave-number units in a vacuum, the positions of all the fifty heads of the  $\beta$ -system (cf. Jevons, A., 1915, ii, 33). An examination of the data (Jevons, *loc. cit.*) leads to the conclusion that the  $\beta_1$  and  $\beta_2$  bands belong to the isotope  $B^{10}N$ . The positions of a number of bands which should belong to the  $\beta_1$  system, but appear to be missing, can be calculated by means of the empirical equation,  $\nu = 42871 + 1306.5n' - 10.50n'^2 - 1925n + 12.188n^2$ . The heads of all the missing  $B^{10}N$  bands, except three already observed but not correlated, are shown to be masked by lying just inside the heads of more intense  $B^{11}N$  bands. The maximum displacements between corresponding bands for the two isotopes are as much as 4.5 Å. towards the shorter wavelengths at  $\lambda$  2145, and 34.1 Å. towards the red at  $\lambda$  3256.

Preliminary measurements in the visible portion of the spectrum indicate equally good agreement with theory for the  $\alpha$ - as for the  $\beta$ -system, and a quantitative analogy between the two systems in respect of the relative positions of the  $B^{10}N$  and  $B^{11}N$  bands. In one case, a displacement of 94 Å. (middle of pair  $\lambda$  6462 and 6368 for  $B^{10}N$  and  $B^{11}N$ , respectively) has been observed. A. A. E.

**A Relation between the Spectra of Ionised Potassium and Argon.** H. W. J. DIK and P. ZEEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 498—503).—In continuation of previous work (*ibid.*, 1922, **25**, 67), accurate values of the respective wavelengths of about 150 lines between  $\lambda$  2342.3 and 3514.0 Å. in the spectrum of the electrodeless discharge in potassium vapour have been determined by direct comparison with standard iron lines.

J. S. G. T.

**Band Spectra.** R. MECKE (*Naturwiss.*, **11**, 637; from *Chem. Zentr.*, 1923, iii, 715—716).—The band spectrum of copper hydride is analogous to the cyanogen spectrum. The zero line is given by the formula  $\nu = 23311.1 + n_1(1655.7 - 44.6n_1) - n_2(1903.0 - 36.6n_2)$ . The absorption spectrum of iodine ( $I_2$ ) represents an entirely different type of band spectrum expressed by the formula  $\nu = 16462.72 + n_1(126.52 - 0.852n_1 - 0.0033n_1^2) - n_2(218.43 - 0.571n_2 - 0.0021n_2^2)$ . The formula  $\nu = \nu_0 - n_2(218.4 - 0.57n_2 - 0.002n_2^2)$  is given by Wood for the resonance spectrum of iodine vapour. The agreement of the last two formulæ shows that the absorbing iodine molecule is

responsible for the fluorescence. The fluorescence of iodine vapour is thus probably unconnected with dissociation. G. W. R.

**The Spectra of Metals of the Fifth Group.** A. E. RUARK, F. L. MOHLER, P. D. FOOTE, and R. L. CHENAULT (*Nature*, 1923, **112**, 831).—The absorption spectrum of bismuth and the spectrum of the thermionic discharge have been photographed. Several stages in the excitation of the arc spectrum, and at least two classes of spark lines, have been recognised; sixty-four arc lines have been classified. Some additional classifications of the arc lines of arsenic have been discovered. The ionisation potential must be at least 10.6 volts, whilst the experimental value is 11.5 volts. A. A. E.

**Arc Spectrum of Gold.** V. THORSEN (*Naturwiss.*, **11**, 500—501; from *Chem. Zentr.*, 1923, iii, 731).—With the aid of the Hilger spectrograph, the author has discovered a series of new lines in the gold spectrum which can be arranged with the lines already known into a sharp and a diffuse series, respectively. There are three doublets,  $\lambda$  2476 and 2428,  $\lambda$  7510 and 5837, and  $\lambda$  4811 and 4065, which may, by analogy with the spectra of copper and silver, be denoted by  $1s-2p_i$  ( $i=1.2$ ),  $2p_i-2s$ , and  $2p_i-3d_2$ . G. W. R.

**New Extension of Spark Spectra of Tin and Zinc in the Schumann Region.** L. BLOCH and E. BLOCH (*Compt. rend.*, 1923, **177**, 1025—1028; cf. A., 1920, ii, 719; 1921, ii, 3, 286).—The spectra in question have been re-examined. In addition to the 11 lines already found for tin, 45 new lines have been observed between  $\lambda=1700$  and  $1400 \text{ \AA}$ . In addition to the 34 lines already found for zinc, 73 new lines have been measured. The results are tabulated. E. E. T.

**The High-frequency Lines of Celtium.** A. DAUVILLIER (*Chemistry and Industry*, 1923, **42**, 1182—1183).—Photographs (which are reproduced in the paper) of the high-frequency spectra of certain fractionations of some ytterbium earths obtained by Urbain, show some of the celtium lines. Small errors in the recorded measurements of the lines are attributed to the difficulty of "pointing" them. The possibility, suggested by Coster (A., 1923, ii, 807) of the lines being attributable to substances other than celtium is discussed and considered untenable. J. S. G. T.

**Structure of Molecules and Absorption Spectra of Substances in the Vapour State.** V. HENRI (*Compt. rend.*, 1923, **177**, 1037—1040).—The vapours of sulphur ( $200-1,000^\circ$ ), carbon disulphide, sulphur dioxide, carbonyl chloride, glyoxal, acraldehyde, keten, toluene, aniline, phenol, chlorobenzene, bromobenzene, *p*-xylene, pyridine, and other substances absorb energy in three quanta, corresponding with electronic movements, atomic movements, and molecular rotations. The spectrum consists of several groups of bands (electronic activation), each formed of one or more series of bands (atomic activation), and each band can be resolved into one or several series of closely spaced fine rays (activation of molecular rotation). With ammonia, methylamine, ethyl-

amine, thiophen, furan, pyrrole, diacetyl, crotonaldehyde, benzoic acid, benzaldehyde, acetophenone, methylaniline, naphthalene, diphenylmethane,  $\alpha\beta$ -diphenylethane, benzil, and other compounds, energy is absorbed in two quanta, corresponding with activation of electronic movements and atomic vibrations, the speed of molecular rotation in these cases varying continuously. The spectrum consists of several groups, each composed of series of continuous bands (2—5 Å.), not resolvable into fine rays. In the case of hydrogen sulphide, carbonyl sulphide, ketones, saturated aldehydes, carboxylic acids, saturated esters, olefines, compounds containing two of the preceding groups ( $\cdot\text{CO}\cdot$ ,  $\cdot\text{CO}_2\text{R}$ ,  $\cdot\text{C}\cdot\text{C}\cdot$ ) in the  $\beta$ - or  $\gamma$ -positions, compounds containing these groups in the  $\alpha$ -position and also containing many substituents, compounds containing two benzene nuclei (diphenyl,  $\alpha\alpha$ -diphenylethylene, diphenylamine, azobenzene, etc.) and other compounds, the molecule absorbs energy discontinuously, *i.e.*, in quanta, only in so far as electronic movements are concerned. The absorption spectra consist of several perfectly continuous bands.

The study of the fine structure of absorption bands shows if the molecule is a rigid system (benzene, chlorobenzene, acetaldehyde, etc.) or a plastic one (amines, etc.). In the former case, the existence of a single value for the moment of inertia (benzene) shows the symmetry of the molecule; the existence of two values (chlorobenzene) indicates asymmetry, whilst with acetaldehyde the molecule is seen to be labile or capable of deformation. E. E. T.

**Absorption of Iodine Solutions.** A. CARRELLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1921, [iii], 27, 274—278).—The absorption of solutions of iodine in alcohol, ether, acetic anhydride, carbon disulphide, chloroform, carbon tetrachloride, benzene, toluene, and xylene has been investigated by the method devised by Adinolfi (A., 1920, ii, 720). The absorption is marked and extends over a wide zone, but the maxima are not very prominent, at any rate at the temperatures used, namely, 14—20°. The solutions coloured violet exhibit a minimum of absorption in the red at about  $630\mu\mu$ , the line marking the boundary between the zone in which absorption occurs and the transparent zone then rising towards the region of long waves and thus indicating the presence of a decided absorption in the ultra-red also. Similar phenomena are just perceptible in acetic anhydride solutions of iodine, but are not shown by the other brown iodine solutions. With the solutions in carbon disulphide and in benzene, confirmation is obtained of the gradual displacement of the maximum of absorption with the age of the solution. The results given by benzene, toluene, and xylene solutions show that the introduction of a methyl group into the molecule of the solvent involves displacement of the maximum towards the smaller wave-lengths.

The red solutions exhibit to direct vision absorption increasing from the red to the violet, but, owing to the low sensibility of the eye in the more refractive part of the spectrum, no maximum is observable. The values found are not in accord with Kundt's

law, according to which displacement of the maximum towards the red is accompanied by increase in the refractive index of the solvent.

Photographic investigation reveals the existence of pronounced absorption in the ultra-violet region, even in solutions which appear transparent in the first high-frequency zone. The relative intensity of the absorption varies with the solvent, and nearly all the curves show dissymmetry with respect to the maximum. In the carbon tetrachloride solutions, which exhibit the displacement of the maximum, this dissymmetry is exceptionally marked, the curve indicating transparency in the violet zone and increased absorption in the yellow and extreme red. T. H. P.

**Dispersion of Iodine Solutions.** A. CARELLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1921, [iii], 27, 288—293).—The dispersion of the reddish-brown alcoholic and of the violet carbon disulphide solutions of iodine has been investigated. For the alcoholic solutions the absorption, which extends over the whole spectrum and is somewhat pronounced for the more concentrated solutions, produces no great modification in the form of the curve expressing the dispersion of the pure solvent. The refractive index is increased throughout the spectrum and to a slightly greater degree in the neighbourhood of the zone of absorption; such increase varies, but not linearly, with the concentration. The carbon disulphide solution, exhibiting the maximum absorption at about  $515\mu\mu$ , gives results characteristic of anomalous dispersion with an indication of a bend in the curve for the visible spectrum.

T. H. P.

**The Absorption Spectra of some Organic and Inorganic Salts of Didymium.** J. E. PURVIS (*Proc. Camb. Phil. Soc.*, 1923, 21, 781—785).—Employing the method devised by Liveing and used by Purvis (T., 1915, 107, 966) and using tubes, respectively, 610 mm. and 300 mm. long, the author has investigated the absorption spectrum of didymium phenylacetate, and compared it with the absorption due to equivalent amounts, viz., 0.248 g. didymium oxide per litre, of the acetate, chloride, and nitrate of didymium, respectively, and with that due to phenylacetic acid. The results obtained indicate that in the visible regions of the spectra, there are slight differences in the widths and intensities of the bands of didymium chloride, nitrate, acetate, and phenylacetate; the differences are more apparent in the two latter substances, more especially at  $\lambda\lambda$  596, 590 to 570, and 476. In the ultra-violet, the differences of absorption are much more marked. The large ultra-violet band of didymium phenylacetate is a little wider than that of phenylacetic acid and the line of general absorption is moved a little towards the red end. It is concluded that each of the constituent parts (kation and anion) of the respective salts in solution exercises its own power of absorption to a considerable degree, but the parts do not vibrate independently of each other. Different absorptive powers are probably associated with the constituents, neodymium and praseodymium, of didymium, and the

observed absorptions are attributable to a complex series of vibrations of the electrons, atoms, and molecules of these closely related elements.  
J. S. G. T.

**The Absorption Spectra of Solutions of Benzene and some of its Derivatives.** J. E. PURVIS (*Proc. Camb. Phil. Soc.*, 1923, **21**, 786—788).—In continuation of previous work (T., 1911, **99**, 824; 1915, **107**, 501), the author has investigated the effect of temperature changes on the respective absorption spectra of benzene, toluene, monochlorobenzene, benzonitrile, phenol, and aniline. The absorption tube used was 40 mm. long, the strengths of the alcoholic solutions employed ranged from  $M/5,000$  to  $M/400$ , and observations of absorption were made at 15°, 30°, 45°, and 60°. The results show that an increase of temperature produces a widening of the respective absorption bands, their edges become more diffuse, a slight shift of the bands toward the red end occurs, and they are slightly weaker. The effects generally are similar to those produced by an increase of temperature in the case of the absorption spectra of solutions of inorganic salts.  
J. S. G. T.

**The Extinction Coefficients of Aromatic Hydrocarbons.** L. MARCHLEWSKI and A. MOROZ (*Bull. Soc. chim.*, 1923, **33**, [iv], 1405—1409).—The substances studied were benzene, naphthalene, diphenyl, anthracene, phenanthrene, and chrysene, all in alcoholic solution of 1/10,000 mol. concentration. The results obtained are shown in tabular form and also graphically.  
H. J. E.

**Fluorescence of Organic Substances.** A. CARRELLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1923, [iii], **29**, 97—104).—By means of a special apparatus the author has investigated the fluorescent emission of solutions of various organic compounds of the triphenyl-methane group (cf. Adinolfi, A., 1922, ii, 601), particularly Uranin, Rhodamin B, Erythrosin, and Eosin. When the concentration of these compounds is high and the distances between the absorbing molecules are small, a diminution is produced in the emission in the spectral zone nearest to the position of maximum absorption and an increase in the intensity of the lower frequencies. Thus Stokes's law assumes a character of spectral distribution related to the concentration. The results of experiments made in the ultra-violet region show that, of the vibrators present in the molecule, only those situate in the visible spectrum appear to be connected with the emission band.  
T. H. P.

**Induction of Luminescence by Active Nitrogen.** E. TIEDE and A. SCHLEEDE (*Naturwiss.*, 1923, **11**, 765—766; from *Chem. Zentr.*, 1923, iii, 976).—The production of phosphorescence by active nitrogen described by Lewis (A., 1923, ii, 361) had been discovered by the author in the case of boron nitride, sensitised by flame. The following compounds also show the effect strongly: lithium fluoride, lithium carbonate, beryllium carbonate, beryllium oxide, barium platincyanoide, magnesium carbonate, calcium hexanitride, barium hexanitride, molybdic acid, terephthalic acid, and isophthalic acid. It is noted that all these compounds contain

nitrogen or an element of smaller atomic number. Sulphides and oxides of the second group of the periodic system show little or no effect. Ozone can also induce phosphorescence. The phenomenon is supposed by the author to be due to chemiluminescence, in which the decomposition of the activating substance furnishes the energy for luminescence. G. W. R.

**Chemical and Spectroscopic Properties of Excited Atoms and Reversible Effects of Electron Impacts in Gases.** K. T. COMPTON (*J. Opt. Soc. Amer.*, 1923, 7, 955—971).—The author reviews recent work dealing with the "excitation" of normal atoms by electronic orbital displacements, collisions between electrons and gas molecules, and phenomena associated with transfers of energy not accompanied by the emission of radiation. The suggestions of Franck (A., 1922, ii, 464), and of Cario (*Z. Physik*, 1922, 10, 185) that such transfers may account for the quenching of fluorescence by foreign gases, the excitation of the spectrum of one metal vapour by resonance radiation of another vapour mixed with it, and the dissociation of hydrogen by mercury radiation,  $\lambda$  2536 Å., when mercury vapour is mixed with the hydrogen, are critically reviewed. J. S. G. T.

**Photochemistry of Chlorine.** F. WEIGERT and K. KELLERMANN (*Z. physikal. Chem.*, 1923, 107, 1—40).—In the photochemical combination of hydrogen and chlorine, the first change is a volume change which reverses as soon as the illumination is removed. This change, the so-called Draper effect, has been examined by a new method (A., 1923, ii, 3). It is shown that the Draper effect is due to a warming of the gas and not, as has been often suggested, to a primary splitting of the chlorine molecule into atoms. It has been shown that the amount of the thermal expansion of the chlorine electrolytic gas corresponds with the amount calculated from the amount of hydrogen chloride produced by the photochemical reaction and the heat liberated thereby. It is also found in this connexion, and in confirmation of Mellor's result, that the Draper effect is also brought about by a feeble chlorine electrolytic gas explosion. Electrolytic gas which has been dried by sulphuric acid shows the Draper effect immediately on entry into the illumination vessel. After the addition of liquid water, the effect is not shown so strongly as with the dry gas until it has been shaken with the water for a long time. In the case of spark illumination in the presence of liquid water, the Draper effect produced by the first spark has quite a different form from that produced by the subsequent sparks. After the first momentary expansion of the gas, a second much slower dilation commences, and then only the liquid thread of the manometer takes up a position beyond its original position. This final contraction corresponds with the absorption of the hydrogen chloride by the confining water. After all succeeding sparks, the gas contracts after the first expansion impulse in the normal way. The meaning of the second, slower, expansion with the first spark is probably to be found in the heat of condensation of liquid drops of hydrochloric acid from the water

vapour contained in the gas. The hydrogen chloride produced by the subsequent sparks comes, therefore, only into contact with water vapour at a much lower tension, and is condensed in the confining water which absorbs the heat of condensation. Using the Töpler cloud method, it is shown that with continuous illumination a cloud is produced in sensitive chlorine electrolytic gas immediately on illumination. The cloud is only developed when the gas, chlorine, chlorine electrolytic gas, or bromine vapour is illuminated with light of short wave-length, and the strength of the cloud is parallel with that of the simultaneously observed Budde or Draper effect. The cloud rises rapidly, and this is doubtless a secondary process. The cloud was not observed when the illumination followed the excitation of the gas after half a second. In this time, therefore, the changes of the refractive index brought about by the primary process had spread over the whole gas mixture. When the gas was illuminated by a discharge from a Leyden jar, there was no formation of streaks. When the illumination by a second spark was delayed by  $1/10,000$ — $1/100,000$  second, no streaks were observed despite the fact that the Draper effect was strongly visible. The streaky appearance is only visible when the second illuminating spark is delayed  $1/100$ — $1/20$  second after the first spark. With a shorter delay, the streaks have not had time to form, and with a longer delay they have spread over the whole volume and are no longer visible. It is shown from photographs that the maximum streaky appearance does not coincide with the exciting spark, but is somewhat later, the period between the two being greater for the sensitive gas mixture than for the insensitive mixture. From this, it is concluded that the observed combination of chlorine and hydrogen in light is for the most part a purely chemical process, although the first impulse is furnished by the light. After the first impulse, in the space of about  $1/100$  second, the reaction develops into a purely chemical process in the dark. The dark reaction, however, is made up of a series of successive processes, and the time elapsing before the maximum is reached with the more sensitive gas mixtures shows that in these cases the passage through the series of reactions takes longer than with the less sensitive gas mixtures. A number of photographs illustrating the various stages of the reaction and conditions of the gas mixtures are included in the paper. J. F. S.

**Photographic Sensitiveness of Silver Iodide.** F. E. E. GERMANN and M. C. HYLAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2486—2493).—The reason why emulsions of silver iodide appear to be much less photosensitive than emulsions of silver bromide is considered, and it is shown to be impossible to predict on theoretical grounds whether or no silver iodide should be more photosensitive than silver bromide. Johnson's method of sensitising the apparently non-sensitive silver iodide is described. This consists in treating paper coated with emulsions of silver chloride, bromide, or chlorobromide with a soluble iodide, or by coating the paper with a gelatin or collodion emulsion of silver iodide and



sensitising the emulsion, after drying, with a solution containing an organic sensitiser such as *p*-methylaminophenol sulphate and an inorganic accelerator such as sodium sulphite. A number of experiments have been carried out to ascertain the nature of this sensitisation. It is shown that gelatin, which has a sensitising effect in bromide emulsions, has practically no such effect in iodide emulsions. Potassium iodide has a retarding effect, and emulsions containing an excess of this substance are non-sensitive. An emulsion containing no excess of silver nitrate or potassium iodide has been prepared and found to be sensitive. Washing to remove an excess of iodide does not make the ordinary iodide emulsion sensitive. The amount of moisture in the emulsion has a considerable effect on the sensitiveness. Generally it is found that sensitisation can be effected by treatment with a substance which will react with potassium iodide and so remove it, or remain in the emulsion to combine with any iodine liberated. The non-sensitive emulsions are found to be sensitive when a strongly alkaline developer is used. It is concluded, therefore, that the apparent non-sensitiveness of silver iodide emulsions is due primarily to adsorbed potassium iodide, and secondarily to the absence of a sensitiser, since gelatin does not fill that rôle. Ordinary, apparently non-sensitive, silver iodide emulsions are truly sensitive when a sufficiently strong alkaline developer is used. J. F. S.

**Photochemical Study of Acetylchloroaminobenzene.** J. H. MATHEWS and R. V. WILLIAMSON (*J. Amer. Chem. Soc.*, 1923, **45**, 2574—2584).—The decomposition of acetylchloroaminobenzene under the influence of the light from a quartz mercury-vapour lamp has been investigated in benzene, acetic acid, and alcohol solutions. The solvent is found to have a marked effect on the behaviour of the reaction. When water is added to an alcoholic or glacial acetic acid solution of acetylchloroaminobenzene, the velocity of the photo-decomposition is greatly diminished. It also causes the reaction to proceed as a true photochemical reaction, whereas in the absence of water the reactions in absolute alcohol and glacial acetic acid solutions proceed without the action of light after having been started by the light. J. F. S.

**The Photo-chlorination of Toluene.** G. BOOK and J. EGGERT (*Z. Elektrochem.*, 1923, **29**, 521—527).—Toluene, chlorinated by a stream of chlorine at 105—110°, yields a product consisting almost entirely of benzyl chloride, irrespective of whether the reaction is carried out under the influence of light or in darkness, provided a chlorine "carrier," *e.g.*, ferric chloride, be not present. In the presence of such a "carrier," however, considerable amounts of *o*- and *p*-chlorotoluenes are produced. The reaction between toluene and chlorine in the absence of a carrier is practically suppressed if the temperature is reduced to -80°, and the mixture is effected in darkness. At this temperature, a photochemical reaction between these substances may be stimulated under the incidence and absorption of radiation comprising the orange and light green mercury lines. The initial reaction occurring under these con-

ditions probably comprises the formation of hydrogen chloride together with chlorotoluene or benzyl chloride. This reaction apparently proceeds in discord with Einstein's photochemical law, as about twenty-five chlorine molecules appear to be activated per quantum of absorbed radiation. In general, it was observed that toluene and chlorine reacted with one another in darkness at  $-80^{\circ}$  in the presence of a small amount of iodine. This reaction is not attributable to a sensitising effect produced by the iodine on the components participating in the reaction. J. S. G. T.

**Phototropy.** H. STOBBE (*Ber. Sächs. Ges. Wiss., Math.-Phys. Kl.*, 1922, **74**, 161—250; from *Chem. Zentr.*, 1923, iii, 806—807; cf. Stobbe and Dietzel, A., 1923, i, 39).—A continuation and summary of earlier work of the author on phototropy, which is shown by fulgides, osazones, anils, and some stilbene derivatives. For every phototropic substance there is in the spectrum a region where a darkening in colour occurs and a region where the reverse effect obtains, with a neutral region between. The author supposes that every phototropic substance exists in two forms, conditioned by light and darkness, respectively. The phenomenon is only found in solid substances and is not, except in the case of tetrachloroketonaphthalene, associated with crystalline form.

G. W. R.

**Photoelectric Effect in Metallic Compounds.** G. A. DIMA (*Bul. Şoc. Ştiinţe Cluj*, 1922, **1**, 321—324; from *Chem. Zentr.*, 1923, iii, 718—719).—The results of photoelectric investigations on a number of metallic oxides are reported. Oxides which are reduced with difficulty, such as the oxides of calcium, magnesium, and zinc, have a smaller photoelectric effect than the more easily reduced oxides of lead, copper, and tin. The photoelectric effect with lead oxide and zinc oxide, respectively, increases with the pressure up to a point where structural modification occurs and the effect decreases. Introduction of a hydroxyl group decreases the photoelectric effect. The photoelectric effect of metallic halides increases with the atomic weight of the halogen except in the case of cadmium.

G. W. R.

**Chemical Action Produced by Radon. III. Determination by a Chemical Method of the Mean Effective Path of Alpha Particles in Small Spheres.** S. C. LIND and D. C. BARDWELL (*J. Amer. Chem. Soc.*, 1923, **45**, 2585—2592; cf. A., 1919, ii, 210).—By means of a chemical comparison method, consisting of the measurement of the velocity of combination of electrolytic hydrogen and oxygen under the influence of radium emanation (radon) in equilibrium with Ra-C when confined in an  $\alpha$ -ray bulb placed at the centre of the reaction sphere, and also when mixed with the gas, it was found that the mean effective path of the  $\alpha$ -particles in the gas mixture is  $0.61 \pm 0.01$  times the radius of the sphere. A direct micrometer measurement of the walls of  $\alpha$ -ray bulbs shows them to be about half as thick as indicated by the zinc sulphide screen radiometric method.

J. F. S.

**Chemical Action Produced by Radon. IV. Characteristics of the  $\alpha$ -Ray Bulb as a Source of Ionisation.** D. C. BARDWELL and H. A. DOERNER (*J. Amer. Chem. Soc.*, 1923, **45**, 2593—2599; cf. preceding abstract).—The characteristics of an  $\alpha$ -ray bulb in connexion with its use as a source of ionisation are investigated. It is shown that in order to make the corrections involved in the calculations made in an earlier paper (see preceding abstract) a knowledge of the characteristics of the  $\alpha$ -ray bulb as a radiator, as affected by the tip and neck, by the thickness of the wall and obliquity of passage of the  $\alpha$ -particles through it, and by the diameter of the bulb (reducing it to zero dimensions in order to afford radiation from a point source) is necessary. In addition, the other corrections applying to the outer sphere itself are considered, such as the dead-arm correction and the change of ionisation intensity with the pressure. The recoil atom effect is also used as a correction for the results, to reduce them to the same condition as those obtaining outside the  $\alpha$ -ray bulb, through which recoil atoms cannot penetrate. J. F. S.

**A Possible Interpretation of the Continuous  $\beta$ -Ray Spectrum.** L. MEITNER (*Z. Physik*, 1923, **19**, 307—312).—In continuation of previous work (A., 1923, ii, 675), the author discusses the work of Compton (A., 1921, ii, 366) and of Debye (*Physikal. Z.*, 1923, **24**, 161) on the scattering of homogeneous Röntgen or  $\gamma$ -rays by matter, and considers that a plausible explanation of the continuous  $\beta$ -ray spectrum investigated by Ellis (A., 1922, ii, 466), and the author is afforded by the scattering of primary  $\beta$ -rays ejected from the nucleus with a definite velocity characterising the nucleus. J. S. G. T.

**Diffusion of Radioactive Elements in Metals.** L. WERTENSTEIN and [MLLE] H. DOBROWOLSKA (*J. Phys. Radium*, 1923, **4**, 324—332).—Employing a method based on observing the variation, after an interval of time, in the number of scintillations produced by radiation penetrating through a sheet of the metal, the authors have determined the following values (expressed in sq. cm. per day) for the coefficients of diffusion, at 470°, of radioactive elements in the respective metals: polonium in gold,  $10^{-9}$  (approx.); radium (*B* and *C*): in silver,  $3.77 \times 10^{-7}$ ; in gold,  $8.2 \times 10^{-7}$ ; in platinum,  $3.41 \times 10^{-7}$ . The values obtained for radium (*B* and *C*) are arranged in the inverse order of the respective hardnesses of the metals. It is suggested that the small value found for the coefficient of diffusion of polonium in gold is attributable to the formation of a compound of the two elements. J. S. G. T.

**Problems of Hydrone and Water: the Origin of Electricity in Thunderstorms.** H. E. ARMSTRONG (*Nature*, 1923, **112**, 827).—Polemical (cf. A., 1923, ii, 772; Simpson, A., 1923, ii, 822). A. A. E.

**The Electric Resistance of Pure Metals. XII. Measurements of the Electric Resistance of Indium in the Temperature Field of Liquid Helium.** W. TUYN and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 504—509).—The

resistances of four samples of indium have been determined at temperatures ranging from  $1.87^{\circ}$  (abs.) to  $4.23^{\circ}$  (abs.). A comparison, in the light of the periodic classification, of the results obtained with analogous results for tin, thallium, lead, and mercury, suggests that gold and possibly some other metals do not become super-conducting at any temperature.

J. S. G. T.

**Resistance-Temperature Coefficient of Concentrated Solutions of Potassium in Liquid Ammonia and the Specific Conductivity of Solutions of Potassium in Liquid Ammonia at Intermediate Concentrations.** C. A. KRAUS and W. W. LUCASSE (*J. Amer. Chem. Soc.*, 1923, **45**, 2551—2555).—The resistance-temperature coefficient of concentrated solutions of potassium in liquid ammonia has been measured from a dilution of 6 litres to the saturation point. The change of the temperature coefficient as a function of the concentration is parallel with that previously observed in the case of solutions of sodium in liquid ammonia (A., 1922, ii, 734). At higher concentrations, the temperature coefficient is somewhat greater for solutions of potassium than for solutions of sodium, and the maximum temperature coefficient is found at a somewhat higher concentration. The temperature coefficient has been measured as a function of the temperature at a number of concentrations. It is found to increase as the temperature decreases, and the percentage change of the coefficient is greater at higher concentrations. A number of specific conductivity values for intermediate concentrations at  $-33.5^{\circ}$  are given.

J. F. S.

**Electrical Conductivity of Concentrated Ozone-Oxygen Solutions.** M. BEJA (*Z. Elektrochem.*, 1923, **29**, 478).—The electrical conductivity of a liquid mixture of 70 vol.% ozone and 30 vol.% oxygen has been measured approximately at the temperature of liquid air. The results show that the specific conductivity is about  $10^{-6}$  reciprocal ohm, that is, it is less than the value for water. Consequently, liquid mixtures of ozone and oxygen are to be regarded as non-conductors of electricity.

J. F. S.

**Electrical Conductivity of Vapours of Salts.** G. C. SCHMIDT and R. WALTER (*Ann. Physik*, 1923, [iv], **72**, 565—593; cf. A., 1911, ii, 788; 1913, ii, 747; 1918, ii, 386).—The vapour pressures of mercuric chloride and cadmium iodide have been determined at a series of temperatures, the latter salt in an atmosphere of nitrogen. All other halides of cadmium and the halides of zinc decompose on heating, consequently attempts to determine the vapour pressure could not be made. The following results in mm. of mercury are recorded: mercuric chloride,  $100^{\circ}$ , 0.1099;  $115^{\circ}$ , 0.3293;  $128^{\circ}$ , 0.696;  $140^{\circ}$ , 1.447;  $155^{\circ}$ , 3.346;  $170^{\circ}$ , 7.142;  $180^{\circ}$ , 10.212; cadmium iodide,  $343^{\circ}$ , 0.0582;  $350^{\circ}$ , 0.0860;  $362.4^{\circ}$ , 0.1840;  $372^{\circ}$ , 0.2750;  $385.4^{\circ}$ , 0.4376;  $406.2^{\circ}$ , 0.761;  $426.7^{\circ}$ , 1.343;  $430^{\circ}$ , 1.510;  $450^{\circ}$ , 2.917. The values obtained have been compared with those calculated by means of the Dupré-Hertz formula and by means of

the Nernst formula. The agreement is not particularly good in either case, but that with the Nernst formula is, on the whole, superior to that with the Dupré-Hertz formula. The electrical conductivity of the vapours of the halides of zinc and cadmium, particularly of cadmium iodide, has been measured. It is shown that the values of the conductivity are strongly dependent on the time. In general, the conductivity increases with time, reaches a maximum, and then falls rapidly at first and then slowly. The reduction of the conductivity is not due to the distillation of a foreign substance from the cadmium iodide. The heated salt emits only positive ions, so that here a surface and not a volume ionisation is taking place. When heated on nickel and glass plates, cadmium iodide emits only positive ions, exactly as in the case when it is heated on platinum. The heated oxides of cadmium and zinc as well as the metals themselves at relatively low temperatures do not emit ions or electrons. The distillate from cadmium iodide is always richer in cadmium than the original material, and it becomes increasingly richer the more often the distillation is carried out. Cadmium iodide dissolves iodine and forms the complex  $\text{CdI}_3$ . The influence of time on the conductivity of cadmium iodide is attributed to the decomposition into cadmium-ions and the complex  $\text{CdI}_3$ , which takes place under the influence of the catalytic action of platinum, nickel, and glass. Since the iodine produced by the decomposition of the  $\text{CdI}_3$  poisons the catalyst, the velocity of reaction is reduced and the conductivity is diminished. J. F. S.

**Conductivities of Aqueous Salt Solutions.** A. J. ALLMAND and L. NICKELS (*Nature*, 1923, **112**, 862).—Comparisons have been made of magnitudes ( $\kappa'$ ) representing the conductivity, between electrodes 1 cm. apart, of an amount of the solution containing 1 g. of water. At high concentrations, the relation  $\kappa' = \kappa\eta(1,000 + x)/1,000d$  holds. This value ( $\times 1,000$ ) plotted against the weight molar concentration,  $x/M$ , gives a curve which, in the cases of potassium, sodium, and lithium chlorides, becomes nearly linear after  $x/M$  has exceeded 0.5–1. Thus, if 1,000 g. of water are placed between electrodes 1 cm. apart, and one of the salts in question is gradually added, the increase in conductance of the cell (corrected for viscosity change) brought about by dissolving (*e.g.*) an extra 0.1 g.-equivalent of the salt is nearly independent of the concentration of the solution when a certain limit of concentration has been exceeded. The essential difference between the authors' and Linde's (A., 1923, ii, 287) method of plotting is that the former take the density into the conductance expression. Modification, in this particular, of Linde's curves causes them to approximate in type to those found by the authors. A. A. E.

**Water-jacketed Hydrogen Electrode.** H. S. SIMMS (*J. Amer. Chem. Soc.*, 1923, **45**, 2503–2507).—A water-jacketed hydrogen electrode is described. The electrode is kept at constant temperature by circulating water, from the constant temperature bath, through the jacket by means of an air lift. The cell, which is simple in construction, has a single stopcock, which in various positions

allows the hydrogen to enter the cell, empties the cell, empties the potassium chloride from the salt bridge, and forms the liquid junction. The cell gives accurate readings reproducible to  $p_{\text{H}}$  0.01 with 1—2 c.c. of solution after saturation with hydrogen for three minutes, even with solutions of small electrical conductivity. A calomel cell, also water-jacketed, is described. J. F. S.

**Iron Oxide as Material for Insoluble Anodes.** P. P. FEDOTÉEV [with T. PETRENKO] (*Z. anorg. Chem.*, 1923, **130**, 47—50).—Anodes which are highly resistant to acids and chlorine can be made by heating bar-iron in steam at 1,000—1,100° for eighteen hours. There is formed a layer of oxide in a finely crystalline condition, surrounding a core of metal which gives strength and good conductivity to the anode. The stage of oxidation apparently does not pass beyond  $\text{Fe}_3\text{O}_4$ . Oxidation with air does not give a suitable oxide layer, and a coarsely crystalline metal such as cast iron, or one containing carbon, is not suitable. Anodes prepared as described are not attacked when used for the electrolysis of concentrated sodium chloride solution. E. H. R.

**Arrangement for Electrolysis by Graded Potentials.** A. LASSIEUR (*Compt. rend.*, 1923, **177**, 1114—1116).—A battery is connected to the two ends of a rheostat. A (rotating) cylindrical platinum anode is connected, through an ammeter, to one end of the rheostat, the cathode (cylindrical and concentric with the anode) being connected to the rheostat slider. The latter is also connected through a 25,000 ohm resistance, a millivoltmeter, and a mercury-potassium chloride (or nitrate) electrode to the electrolyte, which is kept stirred. The resistance in the first circuit is slowly increased until separation of metal occurs, at which moment the millivoltmeter records the auxiliary potential corresponding with the particular deposition in question. The auxiliary potential is kept constant by moving the rheostat slider. A bismuth-copper separation is easily effected using this method (cf. Sand, T., 1907, **91**, 373). E. E. T.

**The Effect of Absorption of Carbon Dioxide on the Conductivity of the Sodium Hydroxide Electrolyte Employed in an Open Type of Cell for Producing Hydrogen and Oxygen.** C. F. HOLMBOE (*Z. Elektrochem.*, 1923, **29**, 535—537).—Particulars are given of experiments relating to the decrease of conductivity and increase of decomposition voltage of the solution of sodium hydroxide employed as electrolyte in an electrolytic cell, due to increase of the carbon dioxide content of the electrolyte. Thus, with increase of the sodium carbonate contained in the electrolyte from nil to 9.25 g. per 100 c.c., the specific conductivity of such a cell, employing polished iron electrodes, fell from  $345 \times 10^{-3}$  to  $196 \times 10^{-3}$  ohms<sup>-1</sup> cm.<sup>-1</sup>, whilst the decomposition voltage, in like manner, increased from 1.69 to 1.8 volts. It is suggested that the electrolyte should be renewed when it contains 7.5 g. of sodium carbonate per 100 c.c. J. S. G. T.

**Surface Complications in the Corona Discharge.** F. O. ANDEREGG (*Trans. Amer. Electrochem. Soc.* [Advance copy], 1923, No. 28, 349—360).—It is shown that anomalous results relating to ozone formation and other chemical reactions in the corona discharge, referring more especially to the energy employed in the discharge, are attributable to the complexity of the reactions occurring in the discharge, and to adsorption of some, at least, of the products of these reactions on the walls of the apparatus employed. Thus, in the production of ozone by means of a corona discharge in air, under certain conditions, ozone is formed and then nitrogen pentoxide accumulates. Heavy ions or molecules of low mobility are formed and condense on the walls of the apparatus. These adsorbed substances cause an increase in the density of the discharge. The oxides decompose the ozone and some of the heavy substances evaporate, whereby the conductivity of the discharge is increased. The complexity of the reactions occurring is possibly increased on account of sputtering. J. S. G. T.

**Magnetic Researches. XXII. Determination of Magnetisation [Magnetic Susceptibility] at Very Low Temperatures, and the Susceptibility of Gadolinium Sulphate in the Region of Temperatures attainable with Liquid Hydrogen.** H. R. WOLTJER (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 613—625).—Details are given of the experimental method employed, and the corrections necessary in the determination of specific magnetisation at temperatures attainable by means of liquid helium. The respective values of the magnetic susceptibility of gadolinium sulphate at 20.31° (abs.) and 14.68° (abs.) were found to be  $1.0566 \times 10^{-3}$  and  $1.4663 \times 10^{-3}$ . The corresponding value of the "true" Curie constant is  $2.149 (\pm 0.003) \times 10^{-2}$ . J. S. G. T.

**Magnetic Researches. XXIII. The Magnetisation of Gadolinium Sulphate at Temperatures attainable with Liquid Helium.** H. R. WOLTJER and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 626—634).—Accurate determinations of the specific magnetisation of powdered hydrated gadolinium sulphate at temperatures between 1.31° (abs.) and 4.20 (abs.) indicate that, although the fundamental assumptions of Langevin's theory of magnetisation do not hold, the results agree with Langevin's formula. J. S. G. T.

**Correlation between Boiling Point and Conductivity of Electrolytic Liquids.** G. VON HEVESY (*K. Danske Vidensk. Medd.*, 1921, III, 13, 1—18; from *Chem. Zentr.*, 1923, iii, 472—473).—Substances mainly of molecular structure and in consequence of low conductivity have low boiling points, whilst substances with ionic lattices are good conductors and have high boiling points. Hydrogen chloride is an example of the former class, and sodium chloride of the latter class of substances. This is explained by the author by the close connexion between lattice structure and heat of sublimation, which with the help of Trouton's rule can be applied

to boiling points. The correlation between boiling point and conductivity is exemplified by the mercury and antimony halides. It is concluded that in valency changes or in passing from one member of a homologous group to another, a depression of boiling point implies also a decrease in conductivity. In substances with a purely ionic structure, ionic mobility is a factor, and a correlation between boiling point and conductivity is only to be expected if increase of boiling point runs parallel with decrease in ionic mobility. The low boiling points and low conductivities of the liquid hydrogen halides are supposed to be due to the absence of free hydrogen-ions in their crystal lattices.

G. W. R.

**The Vapour Pressures of some Substances found in Coal-tar.** F. S. MORTIMER and R. V. MURPHY (*Ind. Eng. Chem.*, 1923, **15**, 1140—1142).—The vapour pressures of the following substances, viz., carbazole, phenanthrene, anthracene, fluorene, acenaphthene, and naphthalene, were determined by means of the static isotenoscope method of Smith and Menzies, slightly modified. The pressure in the apparatus was fixed as required, and the melted substance after boiling was allowed to cool slowly until its vapour pressure was in equilibrium with it, as shown by the level of the liquid in the two arms of the U-tube being equal. The temperature corresponding with this vapour pressure was then read. The tabulated results are of considerable accuracy as indicated by the straightness of the  $\log P \cdot 1/T$  curves. The boiling points obtained were naphthalene  $218.0^\circ$ , acenaphthene  $277.3^\circ$ , fluorene  $298.0^\circ$ , phenanthrene  $338.5^\circ$ , anthracene  $342.0^\circ$ , carbazole  $353.0^\circ$ . The phenanthrene employed was purified from anthracene by partial oxidation with chromic and acetic acids. The anthraquinone was reduced to anthranol and removed by washing. The purified phenanthrene had m. p.  $98.0^\circ$ . The latent heats of vaporisation of these compounds are calculated and tabulated, and compared with the results of other investigators.

C. I.

**Fractional Distillation Apparatus.** E. H. NASON (*Ind. Eng. Chem.*, 1923, **15**, 1188).—A simple and robust arrangement for carrying out fractional distillation under reduced pressure consists of an adapter connected to the condenser and having a side branch with stopcock leading to the pump, and a collecting pipette fused to the adapter and closed at the bottom by a three-way cock. To this the receiver is connected and the other branch leads to the air. When a fraction has been collected, this cock is turned and air allowed to enter the receiver, which is then changed. Meanwhile, distillation proceeds continuously, the distillate collecting in the pipette.

**Heat of Formation of Intermetallic Compounds.** W. BILTZ and C. HAASE (*Z. anorg. Chem.*, 1923, **129**, 141—160; cf. A., 1922, ii, 350).—The heats of formation of some intermetallic compounds have been determined from the heats of solution of the component metals and of the compounds in the acid  $\text{HCl}, 8.8\text{H}_2\text{O}$  or a bromine-potassium bromide solution. The values obtained are :  $\text{Na} + 5\text{Cd} = \text{NaCd}_5 + 12.4 \text{ Cal.}$ ;  $\text{Na} + 2\text{Cd} = \text{NaCd}_2 + 8.5 \text{ Cal.}$ ;  $3\text{Al} + \text{Fe} = \text{FeAl}_3$



+25 Cal.;  $2\text{Cu} + 3\text{Cd} = \text{Cu}_2\text{Cd}_3 - 1.3$  Cal.;  $3\text{Cu} + \text{Sb} = \text{Cu}_3\text{Sb} +$  about 2 to 3 Cal.;  $\text{Sb} + \text{Cd} = \text{SbCd} +$  about 3 Cal.;  $2\text{Sb} + 3\text{Cd} = \text{Sb}_2\text{Cd}_3 +$  about 4 Cal. The densities were found to be:  $\text{NaCd}_2$ ,  $d_4^{25}$  5.65;  $\text{NaCd}_3$ ,  $d_4^{25}$  7.07;  $\text{FeAl}_3$ ,  $d_4^{25}$  3.896;  $\text{Cu}_2\text{Cd}_3$ ,  $d_4^{25}$  9.03;  $\text{Cu}_3\text{Sb}$ ,  $d_4^{25}$  8.75;  $\text{SbCd}$ ,  $d_4^{25}$  6.95;  $\text{Sb}_2\text{Cd}_3$ ,  $d_4^{25}$  7.03. In all cases except the last two, the alloy is formed from the components with a contraction in volume. H. H.

**Free Energy and Heat of Formation of Lead Monoxide.** D. F. SMITH and H. K. WOODS (*J. Amer. Chem. Soc.*, 1923, **45**, 2632—2637).—The *E.M.F.* of cells of the type  $\text{H}_2\text{Pt}|\text{Ba}(\text{OH})_2\text{soln.}|\text{PbO}, \text{Pb}$  has been measured at  $25^\circ$  and  $45^\circ$  for solutions of barium hydroxide of concentration 0.0766—0.2242*M*. An apparatus is described by means of which the electrolyte in the cell may be effectually stirred and saturated, thereby decreasing the time required for a cell containing a solid substance to reach equilibrium. The *E.M.F.* measurements give the free energy of  $\text{PbO}(s)$  as  $-45050$  cal. at  $25^\circ$ , when the free energy of liquid water at this temperature is taken as  $-56560$  cal. From the temperature coefficient of the *E.M.F.* of this cell the heat of formation of  $\text{PbO}(s)$  at  $25^\circ$  is calculated to be  $-52360$  cal. when the heat of formation of liquid water at  $25^\circ$  is taken as  $-68270$  cal. Temperature functions for its heat content and free energy have been derived. From the above value for the heat of formation of lead oxide and the value of its entropy of formation derived by Lewis and Randall from the constant-entropy principle, the free energy of  $\text{PbO}(s)$  at  $25^\circ$  is found to be  $-46500$  cal., which is as close to the more accurate experimental value as are most of the free energies calculated in this way. J. F. S.

**Free Energy of Mercurides.** R. H. GERKE (*J. Amer. Chem. Soc.*, 1923, **45**, 2507—2512).—The partial molecular free energy of the electropositive atom in mercurides or a mixed crystal containing mercury has been calculated from the measured value of the *E.M.F.* of a galvanic cell, the electrodes of which consist of the electropositive metal and the liquid amalgam saturated with the mercuride or mixed crystal. The values of the partial molecular free energies of rubidium, potassium, lithium, sodium, and lead in their mercurides have been found to be  $-24800$ ,  $-24200$ ,  $-21900$ ,  $-18046$ , and  $-134$  cal., respectively. The partial molecular free energy of mercury in some mercurides has been calculated from the measured values of the *E.M.F.* of amalgam concentration cells. These values in sodium and lead mercuride were found to be  $-61$  and  $-12$  cal., respectively. The free energies of formation of sodium and lead mercuride are  $-18351$  and  $-280$  cal., respectively. The partial molecular free energies of the constituents of mixed crystals of zinc-mercury, cadmium-mercury, and thallium-mercury have been calculated, the values for mercury being  $-35$ ,  $-77$ , and  $-523$ , respectively, and for the other constituent  $-215$ ,  $-2330$ , and  $-51$  cal., respectively. With the exception of thallium, it has been found in the case of the mercurides and the mixed crystals

considered that the change in free energy is greater for the electro-positive metals than for mercury. J. F. S.

**Heat of Recrystallisation.** J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1923, **129**, 263—264; cf. A., 1922, ii, 623).—Alterthum found very large differences in the energy contents of cold-worked and unworked tin and copper, which he ascribed to heat of recrystallisation. The present author has determined the heats of combustion of unworked and worked tungsten, the latter having a degree of deformation of 99%. He found the difference in his values to be smaller than the experimental error. H. H.

**Heat of Vaporisation and some Equations which Determine the Properties of Non-associated Liquids.** W. KISTIAKOWSKY (*Z. physikal. Chem.*, 1923, **107**, 65—73).—The heat of vaporisation of liquids can be calculated by means of the equation  $Q = RT_s \log_e RT_s$ , where  $T_s$  is the boiling point in absolute degrees. The equation, despite the fact that it contains no empirical coefficient, is shown to give satisfactory results in the case of all non-associated liquids. Since the heat of association can be both negative and positive, it follows that in the calculation of  $Q$  cases arise with associated liquids where the value is less than the observed value and others where it is greater, and a few, for example some of the nitriles, where the two values are alike. The above equation may not be used to calculate the degree of association, so long as the dependence of the change of  $T_s$  on the association is unknown. By means of the above equation, the value of Trouton's coefficient,  $Q/T_s$ , is given by  $1000Q/T_s = 8.75 + 4.571 \log T_s$ , the molecular elevation of the boiling point,  $E_M$ , is given by  $E_M = T_s / \log_e RT_s$ , Crafft's coefficient  $\Delta T d / \Delta P$  is given by  $d \log_e P / d \log_e T = \log_e RT_s$ , Walden's coefficient,  $100Q / \alpha^M M$ , is given by  $\alpha^M M = 0.0116 T_s$ , where  $\alpha^M M$  is the molecular capillary rise. The saturation pressure of unassociated liquids is given by  $\log P = (T - T_s) / T \cdot \log RT_s$ . J. F. S.

**Heats of Solution and of Formation of the Double Chlorides,  $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$ ;  $\text{CuCl}_2 \cdot 2\text{RbCl} \cdot 2\text{H}_2\text{O}$ ;  $\text{CuCl}_2 \cdot 2\text{CsCl} \cdot 2\text{H}_2\text{O}$ ; and of the corresponding Anhydrous Salts.** A. BOUZAT and E. CHAUVENET (*Compt. rend.*, 1923, **177**, 1293—1295).—The salts  $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{RbCl} \cdot 2\text{H}_2\text{O}$  were obtained by evaporating solutions of the component simple salts at  $50^\circ$ , and the corresponding anhydrous salts by heating the hydrates in a current of hydrogen chloride at  $45$ — $70^\circ$ . The salt  $\text{CuCl}_2 \cdot 2\text{CsCl} \cdot 2\text{H}_2\text{O}$ , which loses its water at the ordinary temperature, was prepared by evaporating its aqueous solution at  $10$ — $12^\circ$ , whilst at  $40^\circ$  the anhydrous salt resulted, either as bright yellow or as brownish-red crystals (giving the same heats of solution, etc.). The heats of solution (determined over the temperature range  $9$ — $21^\circ$ ) found are as follows:  $\text{CuCl}_2 \cdot 2\text{KCl}$ ,  $-1.85 + 0.15$  ( $t-15^\circ$ ) cal.; dihydrate,  $-6.88 + 0.17$  ( $t-15^\circ$ ) cal.;  $\text{CuCl}_2 \cdot 2\text{RbCl}$ ,  $-3.57 + 0.17$  ( $t-15^\circ$ ) cal.; dihydrate,  $-11.14 + 0.17$  ( $t-15^\circ$ ) cal.;  $\text{CuCl}_2 \cdot 2\text{CsCl}$ ,  $-5.24 + 0.14$  ( $t-15^\circ$ ) cal.; dihydrate,  $-9.80$  cal. at  $12^\circ$ . It is seen that

whilst for the anhydrous salts the heat of solution of the rubidium salt is roughly the mean of those of the potassium and caesium salts, no such relation holds with the hydrates. The following results were obtained for the heats of formation:  $\text{CuCl}_2 \cdot 2\text{KCl} + 3.95$  cal. (dihydrate,  $+1.91$  cal.);  $\text{CuCl}_2 \cdot 2\text{RbCl} + 5.57$  cal. (dihydrate,  $+4.45$  cal.);  $\text{CuCl}_2 \cdot 2\text{CsCl} + 6.88$  cal. (dihydrate,  $+0.94$  cal.). Here again, the anhydrous rubidium salt has a mean figure with respect to the other salts.

The results are regarded as being less in favour of the presence of water of constitution than of water of crystallisation. E. E. T.

**The Theoretical Heat of Dissolution of Hydrated Salts (Copper Sulphate).** F. ISHIKAWA (*J. Chem. Soc. Japan*, 1923, 44, 708—725).—H. von Steinwehr (A., 1920, ii, 589) has deduced the following formulæ for the theoretical heat of dissolution of hydrated salts:  $Q = m - c/m \cdot T \cdot [(dE/dT)_A - (dE/dT)_B] \cdot 46105$  cal. (1) and  $Q = m - c/m \cdot T \cdot dE/dm \cdot dm/dT \cdot 46105$  cal. (2). To provide experimental proof, the author has determined the heat of dissolution of copper sulphate by measuring the *E.M.F.* of a series of the cell: Copper amalgam| $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  + satd. solution of the sulphate| $\text{Hg}_2\text{SO}_4$ |Hg. The *E.M.F.* of a cell (A) containing the solution and the solid salt was expressed:  $E = 0.34672 - 0.000647(t - 25) - 0.00000198(t - 25)^2$ , and  $(dE/dT)_A = -0.000647$  volt/degree. For a cell (B) containing the saturated solution only:  $E = 0.34655 - 0.00038(t - 25)$ , and  $(dE/dT)_B = -0.00038$  volt/degree. For determination of  $(dE/dC)_x$ , *E.M.F.* of cells containing solutions of the salt of different concentration were determined:  $E = 0.36687 - 0.001088C$  ( $C$  = number of g. of the anhydrous copper sulphate in 100 g. of the solution), and  $dE/dC = -0.001088$  volt/%. The solubilities of copper sulphate in water were minutely determined: 17.298 g. of the salt dissolves in 100 g. of the solution at  $20.0^\circ (\pm 0.01^\circ)$ ; 17.886 g. at  $22.5^\circ$ ; 18.515 g. at  $25.0^\circ$ ; 19.128 g. at  $27.5^\circ$ ; 19.781 g. at  $30.0^\circ$ ; 20.427 g. at  $32.5^\circ$ ; and 21.085 g. at  $35^\circ$ ; therefore  $C = 12.9192 + 0.19911t + 0.00097956t^2$ ;  $(dC/dT)_{25} = +0.24809$  g./degree and molecular number of water which dissolves 1 mol. of the anhydrous salt at  $25^\circ$  is  $m = 38.995$ . From these results, the theoretical heats of dissolution were calculated from (1)  $Q = -3199$  cal. and from (2)  $Q = -3234$  cal. respectively. K. K.

**The "b" Term of Van der Waals's Equation.** W. HERZ (*Z. Elektrochem.*, 1923, 29, 527—529).—The author has compared the value of  $b_k$  (calculated from the equation  $b_k = RT_k/8p_k$ ) in van der Waals's equation with the value of the critical molecular volume,  $M/d_k$ , the symbols  $b$ ,  $R$ ,  $T$ ,  $p$ ,  $M$  and  $d$  having the customary significance and the subscript,  $k$ , referring to the critical state. In fifty-eight out of seventy-two substances investigated, the value of  $b_k/(M/d_k)$  lies between 2.0 and 2.4, whilst the highest value, 3.31, occurs in the case of carbonyl sulphide, and the lowest value, 1.46, is associated with hydrogen chloride. Eight compounds affording abnormally low values of the ratio, viz., 1.46 to 1.99, are characterised by the formation of associated liquids. Abnormally high values of the ratio characterise substances having a very low critical

temperature, thus neon, 2.60; hydrogen and helium, 2.65. The value of  $b_k$  for neon, when compared with the corresponding values for other members of the series of rare gases, appears to be anomalous. Examples are given illustrating that in the case of analogous compounds of elements arranged in the same vertical row of the periodic classification, *e.g.*, water, hydrogen sulphide, and hydrogen selenide, the value of  $b_k$  increases as the atomic weight of the element concerned increases. Nitrous and nitric oxides are characterised by very approximately the same value of  $b_k$ , viz. 44.31 and 44.34, respectively. In homologous series, the value of  $b_k$  increases with increase of molecular weight, but the increase of  $b_k$  due to the introduction of the  $\text{CH}_2$  group is not constant in any series examined. The author finds that  $b_0$  and  $M/d_0$ , the subscript referring to the absolute zero of temperature and the value  $b_0$  being calculated by means of van Laar's relation  $b_0 = b_k / (0.038 \sqrt{T_k + 1})$ , are approximately equal. In a homologous series of organic compounds,  $M/d_0$  increases a little more rapidly than  $b_0$  with increasing molecular weight.

J. S. G. T.

**Some Conclusions from van der Waals's Equation.** M. CENTNERSZWER (*Z. physikal. Chem.*, 1923, 107, 81—96).—A theoretical paper in which it is shown that every substance at zero pressure has three characteristic volumes, of which one is equal to infinity and the other two are either both real or both imaginary. Every substance has a limiting temperature at which the pressure curve touches the abscissa axis in a point. Above this limiting temperature every substance has only a real volume at zero pressure, but below the temperature it has three volumes. Volumes smaller than the  $b$  constant of van der Waals's equation are only conceivable at negative pressures. These conclusions have been examined by means of existing data for carbon dioxide, sulphur dioxide, and hydrogen chloride. The characteristic quantities for zero pressure are given for ten organic substances.

J. F. S.

**Fluidity Relationships in the System Nitric Acid, Sulphuric Acid, and Water.** E. C. BINGHAM and S. B. STONE (*J. Physical Chem.*, 1923, 27, 701—738).—The fluidities of forty-five binary and ternary mixtures of nitric acid, sulphuric acid, and water have been measured at 10°, 20°, and 40°. Several cases of both negative and positive curvature of the fluidity-volume concentration curves have been observed. The evidence favours the view that negative curvature is due to some form of dissociation, whilst positive curvature is brought about by solvation. The concentration of the mixture showing the maximum deviation from the linear fluidity-volume concentration curve is independent of the temperature, provided that only one solvate is formed, and in such favourable cases it is believed that this concentration may be utilised for finding the composition of the solvate. Concentrations of equal fluidity, *isorrhies*, differing by intervals of ten absolute units, have been calculated for each of the three temperatures and plotted on triangular diagrams.

J. F. S.

**Surface Energy of Several Salts.** M. L. DUNDON (*J. Amer. Chem. Soc.*, 1923, **45**, 2658—2666).—A value for the surface energy has been calculated from the increased solubility of small particles of six salts. The values obtained are lead iodide, 130, gypsum, 370, silver chromate, 575, lead fluoride, 900, strontium sulphate, 1,400, barium sulphate, 1,250, and calcium fluoride, 3,000. It is shown that a rough proportionality exists between surface energy and hardness, and the inverse proportion between surface energy and molecular volume, predicted by the Ostwald-Freundlich formula, has been indicated. It has been observed that fine particles may have their solubility diminished by an electrical charge or adsorption effect on the surface.  
J. F. S.

**Surface Tension.** W. HERZ (*Z. anorg. Chem.*, 1923, **129**, 265—266).—The surface tensions,  $\gamma_0$ , at absolute zero, for a number of non-associated organic liquids are calculated from the Ramsay-Shields-Eötvös formula, and compared with  $\gamma_s$ , the surface tensions at the boiling point.  $\gamma_0/\gamma_s$  has a value varying from 3 to 4.

H. H.

**Growth of Freely Suspended Gas Bubbles in Solutions Saturated with the same Gas.** R. FRICKE and W. BLENCKE (*Z. physikal. Chem.*, 1923, **107**, 136—139).—A continuation of previous work (*ibid.*, 1923, **104**, 363). It is shown that, in vessels which have been thoroughly cleansed with dichromate and sulphuric acid, a saturated aqueous solution of carbon dioxide evolves very few bubbles, but in a vessel which has been washed only with water there is a rapid evolution of gas. The present experiments were made with somewhat larger bubbles of gas than the earlier experiments, and it is shown that the ratio  $\Delta r(\text{calc.})/\Delta r(\text{found})$  is smaller than the value previously obtained. The relationship between the length of path and the growth of the bubble previously found is confirmed. A number of experiments with water saturated with air are described.  
J. F. S.

**Kinetic Theory of Gibbs' Principle on Adsorption.** K. F. HERZFELD (*Z. physikal. Chem.*, 1923, **107**, 74—80).—A theoretical paper in which the significance of Gibbs' principle in connexion with the force of attraction is developed, and an upper limit for the possible elevation of the surface tension of solutions is deduced.

J. F. S.

**Adsorption Isotherms.** D. REICHNSTEIN [in part with P. BERNAYS] (*Z. physikal. Chem.*, 1923, **107**, 119—136).—A theoretical paper in which it is shown that the mechanistic treatment of the problem of adsorption as put forward by Langmuir (*A.*, 1916, ii, 417) is incapable of giving an explanation of the principle of displacement as put forward by the author in connexion with adsorption (*A.*, 1913, ii, 843). Adsorption isotherms can be deduced from the phenomena by means of the principle of displacement and an extended form of Henry's law. An adsorption theorem is developed, namely, the concentrations of two substances in the adsorption space are in the relationship of their trans-masses,

where the term "trans-mass" is defined as that fictitious concentration in the adsorption space which would be present if Henry's law were true for the conditions obtaining there. If the general expression for the adsorption isotherm,  $dx/dz=l_4(a-x)$  is formally brought into agreement with the principle of displacement, the relationship  $l_4=l_3/(l_1s+l_2\theta+l_3z)$  is obtained. The integration of the differential equation so obtained gives a relationship which is identical with the above adsorption isotherm. J. F. S.

**Adsorption of Mixed Gases by Charcoal. I. Carbon Dioxide and Nitrous Oxide.** L. B. RICHARDSON and J. C. WOODHOUSE (*J. Amer. Chem. Soc.*, 1923, **45**, 2638—2653).—The adsorption isotherms of carbon dioxide and nitrous oxide, independently and in mixtures of the two, containing approximately 75, 50, and 25% of carbon dioxide have been determined at 0° and at pressures up to 2,800 mm. At each point of reference on the three isotherms, the amounts of carbon dioxide and nitrous oxide adsorbed have been determined by analysis. The total amount of the mixture adsorbed can be calculated from the independent adsorption isotherms of the individual gases. The ratio of the degree of adsorption of the two gases varies with the pressure. Only at the highest pressures is it found to be in inverse ratio to the molecular volumes of the adsorbed substances in the liquid form. Calculations from other work make it probable that a similar ratio holds at very low pressures. It is shown that a gas admitted to another already adsorbed by charcoal replaces it rapidly at first, then with increasing slowness and that replacement never goes so far as to give an amount of the second gas adsorbed equal to that which would be adsorbed from a mixture of the same composition mixed before being admitted to the charcoal. A considerable lag in the adsorption isotherm obtained from carbon dioxide leaving charcoal compared with that obtained when the gas was entering it was detected. The maximum amount of lag was 5%. J. F. S.

**The Adsorptive Power of Metallic Hydroxides. I.** H. VON EULER and R. NILSSON (*Z. physiol. Chem.*, 1923, **131**, 107—115).—A saturated solution of lanthanum hydroxide prepared from lanthanum sulphate by the action of potassium hydroxide contains approximately 2 mg. per litre and has a  $p_H$  6.55. A saturated solution of aluminium hydroxide contains 10—18 mg. per litre and has a  $p_H$  6.11 to  $p_H$  7.0—7.6, the exact figures varying according to the method of preparation of the hydroxide. Although lanthanum is more strongly basic than aluminium hydroxide, it adsorbs saccharase less well, at least at  $p_H$  6.0—6.4. W. O. K.

**Theory of the Capillary Layer of a Liquid in Contact with its Saturated Vapour.** G. BAKKER (*Z. physikal. Chem.*, 1923, **107**, 97—110).—A mathematical paper in which it is shown that by a comparison of the results obtained from the results of the thermodynamic theory on the one hand with the results from a continuously extended substance by use of the potential function  $-f \cdot e^{-\tau A}/r$ , on the other, the thickness of the capillary layer in the

latter theory can be expressed by  $\zeta=6\lambda$  to  $6.5\lambda$ . This value is in good agreement with the way in which the force between two unit masses decreases with their distance apart. The mean value of  $\zeta$ , above, gives for the thickness of the capillary layer  $\zeta=16H/a(\rho_1-\rho_2)^2$ , where  $H$  is the surface tension,  $\rho_1$  and  $\rho_2$  are the densities of the liquid and vapour, respectively, and  $a$  is the coefficient of the expression for cohesion (the so-called molecular pressure). The value of  $\zeta$  calculated by the above equation is in excellent keeping with the formula  $H=\frac{1}{2}a\zeta[(\rho_1-\rho_2)/R]^2$ , where  $R$  is the number of molecular layers in the capillary layer. If for an isothermal change the differential equation of the energy has the form  $Td\eta=d\epsilon+p_T dv$ , in which  $p_T$  is regarded as the work factor of the isothermally developed work in the capillary layer, then the condition that this is so is given by  $(r^3+2r_2^3)dr_1^3=(r^3+2r_1^3)dr_2^3$ , where  $r$  is the radius of partial surface, and  $r_1$  and  $r_2$  are the radii of the inner and outer boundary surfaces of the capillary layer. The calculation shows further that  $\zeta$  changes only slightly with the curvature at a definite temperature.

J. F. S.

**Osmotic Pressure of Electrolytes.** N. BJERRUM (*Z. anorg. Chem.*, 1923, 129, 323—340).—An expression connecting the inter-ionic force with the osmotic pressure of an electrolyte with univalent ions is deduced and used to explain small individual differences in the osmotic properties of different salts. From this formula and determinations of freezing points, some ionic dimensions of the alkali halides are calculated and found to agree with those calculated from crystal measurements except in the case of sodium and lithium salts, which must therefore have hydrated ions in solution. In the case of complex ions (chlorate, bromate, nitrate, and iodate), it is suggested that the charge is situated, not at the centre of the ion, but near the surface.

H. H.

**Theory of Atmolysis.** J. SAMESHIMA (*J. Chem. Soc. Japan*, 1923, 44, 671—690).—The author has calculated the separation velocity in the case of a mixture of ideal gases being atmolyzed under ideal conditions. For a two-component system, the following relations were deduced:  $t=c(1/a-1/b)+1/b-x/a-1-c/b \cdot c^{-b/a} \cdot x^{b/a}$ , or  $t=(1-c)(1/b-1/a)+1/a-y/b-c/a \cdot (1-c)^{-a/b} \cdot y^{a/b}$  and  $y=(1-c)c^{-b/a} \cdot x^{b/a}$ ; where  $a(b)$ =volume of the pure first (second) gas which flows through a porous plate during unit time;  $c$ =volume of the first gas in one volume of the first mixed gas;  $t$ =the time from the beginning of atmolysis;  $x(y)$ =volume of the first (second) gas in the remainder after time  $t$ .

For  $n$  components system:  $t=(c/a+c_2/a_2+c_3/a_3+\dots+c_n/a_n)-(x_1/a_1+1/a_2 \cdot c_2c_1^{-a_2/a_1} \cdot x_1^{a_2/a_1}+1/a_3 \cdot c_3c_1^{-a_3/a_1} \cdot x_1^{a_3/a_1} \dots +1/a_n \cdot c_nc_1^{-a_n/a_1} \cdot x_1^{a_n/a_1})$  etc. and  $x_2=c_2c_1^{-a_2/a_1} \cdot x_1^{a_2/a_1}$ ;  $x_3=c_3c_1^{-a_3/a_1} \cdot x_1^{a_3/a_1}$ ;  $x_4=c_4c_1^{-a_4/a_1} \cdot x_1^{a_4/a_1}$ ;  $x_n=c_nc_1^{-a_n/a_1} \cdot x_1^{a_n/a_1}$ ; where,  $a$ =volume of each pure gas which flows through a porous plate during unit time;  $c$ =volume of each gas in one volume of the first mixed gas;  $t$ =the time from the beginning of atmolysis;  $x$ =volume of each gas in the remainder after time  $t$ ; and the subscript figures show

those concerning the 1st, 2nd, 3rd, . . .  $n$ th components. The relation between the composition of the gases and  $t$  and that between the composition and volume of the gases were shown with diagrams.  
K. K.

**Chemical Changes at the Glide Planes and Cleavage Planes of Crystals.** G. TAMMANN (*Z. anorg. Chem.*, 1923, **130**, 87—92).—In mixed crystals of certain metals, the limiting composition for resistance to chemical agents is modified in the direction of a higher proportion of the noble metal by cold working or polishing. This is attributed to changes in the lattice structure at glide planes, whereby the atoms of the less noble metal become more exposed. An illustration of such changes occurring at a cleavage plane is afforded by the case of mica. Fresh cleavage planes of mica condense moisture uniformly and discharge an electroscope, whilst old cleavage planes condense water in drops and do not discharge the electroscope. It was supposed at one time that the ageing of the mica surface was due to atmospheric pollution. If that were the case, washing with water should restore the surface, but it is found, on the contrary, that ageing can be rapidly induced by wetting the cleavage plane. It is suggested that the change which accompanies ageing is an aggregation effect of the surface particles brought about by the condensation and evaporation of water. In confirmation of this view, it is shown experimentally that water applied to a fresh mica cleavage surface dissolves a layer 2·4 times as thick as one molecular layer, whilst a second application of water to the surface removes very much less. The chemical changes occurring at cleavage and fracture surfaces are probably important factors in the metamorphosis of rocks.  
E. H. R.

### Equilibrium between Reducing Gases and Metallic Oxides.

**I. (1) Carbon Monoxide and Tin Oxide. (2) Carbon Monoxide and Zinc Oxide.** T. MAEDA (*Rikwagaku Kenkyujo Ihô*, 1923, **2**, 350—361).—The equilibrium which can be obtained in the reduction of stannic and zinc oxides with carbon monoxide has been studied. For obtaining equilibrium, carbon monoxide was gradually passed over stannic oxide, contained in an alundum boat in a porcelain tube, at a definite velocity, the reaction temperature being 700—950°. At this temperature, stannous oxide is unstable and is decomposed as follows:  $2\text{SnO} \rightarrow \text{SnO}_2 + \text{Sn}$ . The equilibrium,  $\text{SnO}_2 + 2\text{CO} = \text{Sn} + 2\text{CO}_2$ , was established, in which the equilibrium constant is given by  $\log K = -641.8/T + 1.084$ . For  $\text{SnO}_2 + 2\text{CO} = \text{Sn} + 2\text{CO}_2$ , the heat of reaction at 800° is -5,870 cal., and for  $\text{Sn (liquid)} + \text{O}_2 = \text{SnO}_2$  at 800° it is -130,260 cal. The oxygen pressure given by  $\text{SnO}_2$  at 927° is  $4.47 \times 10^{-15}$ . By the same process, carbon monoxide was passed over zinc oxide, but the reaction was not definitely examined, the reducing efficiency of the monoxide being very much less than that in the former case. The volume percentages in the resulting gases were 4.5, 6.0, and 6.59% at 741°, 827°, and 859°, respectively. The oxygen pressure of zinc oxide at 827° was about  $1.6 \times 10^{-20}$ .  
K. K.



**Equilibrium of Iodine and Sulphur in Carbon Disulphide Solution.** J. MORI (*J. Chem. Soc. Japan*, 1923, **44**, 730—738; cf. Amadori, A., 1922, ii, 561).—The equilibrium of iodine and sulphur in carbon disulphide solution was studied at 10° and 18°. No mixed crystals of the two elements in the solid phase were found in the range of the author's investigations.

K. K.

**Equilibria in Systems involving Calcium, Hydrogen, and Nitrogen.** C. A. KRAUS and C. B. HURD (*J. Amer. Chem. Soc.*, 1923, **45**, 2559—2574).—The action of ammonia on calcium and barium nitrides has been investigated, and it is found that, contrary to the statement of Mentrel (*Diss.*, Nancy, 1902), no absorption of ammonia by these nitrides could be observed. Calcium hydride, when heated with nitrogen, yields an end-product containing less than 10% of hydrogen, and calcium nitride, when treated in the same way, yields a product containing approximately 16% of hydrogen. The dissociation pressure of calcium hydride has been determined at a series of temperatures, and the following values, expressed in cm. of mercury, have been obtained. 985°, 57.50; 921°, 18.26; 892°, 10.80; 871.2°, 8.40; 843.6°, 4.82; 769.2°, 0.93, and 734.0°, 0.42. The results indicate the existence of a definite equilibrium involving hydrogen and calcium hydride. The third phase is uncertain, but the conditions of the experiments together with the observations of earlier investigators render it probable that a sub-hydride of calcium exists. An attempt is made to measure the dissociation pressure of calcium nitride at temperatures somewhat above 1,000°. Reproducible results were obtained for the pressure of the order  $0.3-5.5 \times 10^{-4}$  cm. over the range 958—1,049°. These results are consistent with an energy change accompanying the reaction of 113,250 cal., which agrees well with the heat of formation of calcium nitride at the ordinary temperature, as determined by Guntz and Bassett (A., 1905, ii, 300). It is pointed out that in all probability calcium could not have been present as a third phase in this equilibrium. In a system consisting initially of a mixture of calcium, calcium hydride, and calcium nitride, an equilibrium was found to exist at temperatures in the neighbourhood of 1,000°. Only hydrogen was present in the vapour phase. After continued heating at 870°, the hydrogen was ultimately absorbed completely.

J. F. S.

**Theory of the Liesgang "Rhythmic" Precipitation.** R. FRICKE [with H. KLEEBECK and E. FRIELING] (*Z. physikal. Chem.*, 1923, **107**, 41—64).—A theoretical paper in which it is shown that, by applying Fricke's diffusion equation to the conditions obtaining in the formation of rhythmic precipitates, and taking account of the influence of the precipitation on the fall of diffusion, not only can the formation of rhythmic precipitates be understood and explained, but also the details of the form and conditions of formation can be predicted. The conclusions drawn in the consideration are illustrated by descriptions of experiments on the formation of

copper ferrocyanide, thallous iodide, lead chromate, and silver chromate in jellies, and lead chromate in the absence of jelly.

J. F. S.

**Micelles and Colloidal Ions.** J. W. McBAIN (*Nature*, 1923, **112**, 865).—All movement in an electric field can be summed up in a single formula which applies equally to ions, diaphragms, gels, suspensions, micelles, etc., and governs the movement of any such charged constituent relative to the solvent. There is a gradual transition from uncharged or isoelectric colloidal particles, through those which are very slightly charged, such as the neutral micelle in soap solution or the particles in a gold sol, to those which are more highly charged, like the ionic micelle of soaps, and then to the true ions which are fully charged. The term "micelle" is more appropriate than "colloidal ion" and "colloidal molecule" for the aggregate of soap ions containing substantial proportions of undissociated soap and the aggregate of hydrated neutral soap, respectively.

A. A. E.

**Colloids of the Second Order.** C. JABŁOZYŃSKI (in collaboration with M. FORDONSKI, R. FRANKOWSKI, J. LISIECKI, and (MLLE) KLEIN) (*Bull. Soc. chim.*, 1923, **33**, [iv], 1392—1405).—The author distinguishes between colloids of the first and second order, the former including such substances as metals and metallic sulphides insoluble in water, whilst the latter comprises those substances which are more or less soluble. The stabilising action of gelatin on colloidal halides of silver (cf. Lottermoser, A., 1904, ii, 31) is adduced in support of this view. It is not possible to make a complete distinction between the two orders, because solubility differences exert considerable influence. But in all colloids of the second order a dominant part is played by the effect of the growth of the larger particles at the expense of the smaller, and the greater the solubility of the substance the further its colloidal solution is from the type of the first order. Colloids of the second order are regarded as forming a class intermediate between colloidal solutions of truly insoluble substances and true solutions.

H. J. E.

**Colloidal Phenomena in Paints Prepared with Polymerised Oils.** C. COFFIGNIER (*Bull. Soc. chim.*, 1923, **33**, [iv], 1558—1560).—Similar phenomena to those previously described (A., 1923, ii, 137) occur in the case of paints prepared solely with polymerised ("boiled") oils. Experiments show that a similar explanation applies, the amount of swelling being correlated with the free acid of the polymerised oil.

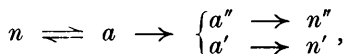
H. J. E.

**A Simple Continuously Acting Washing Apparatus for the Purification of Colloidal Gels.** H. G. BUNGENBURG DE JONG (*Rec. trav. chim.*, 1923, **42**, 1074—1076).—The gel to be washed is placed in a Büchner funnel, on the perforated plate, on which rests a second Büchner funnel, fitting easily into the first funnel. Air-free water is allowed to syphon upwards through this arrangement, which

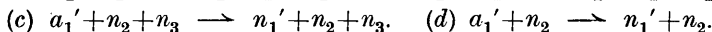
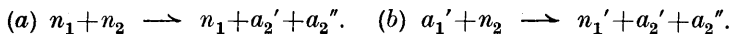
can, if necessary, be immersed in a thermostat. The ash-content of agar-agar may be greatly reduced using this apparatus.

E. E. T.

**Velocity of Chemical Reactions.** J. A. CHRISTIANSEN and H. A. KRAMERS (*Z. physikal. Chem.*, 1923, **104**, 451-469).—A study of the mechanism of activation in unimolecular reactions. The dissociation of a gas molecule  $n$ , according to the equation  $n \rightarrow n' + n''$ , is discussed. Assuming that  $n$  passes into the active condition  $a$ , which then decomposes to give  $n'$  and  $n''$ , it is shown that the velocity constant  $k' = A \cdot p_a \cdot e^{-(\epsilon_a - \epsilon_n)/RT} / p_n$ , where  $A$  is the probability per second that an active molecule decomposes,  $\epsilon_a - \epsilon_n$  is the energy of activation, and  $p_a$  and  $p_n$  represent the statistical weight of the corresponding states. For the ordinary temperature and heats of activation of 10,000 to 30,000 calories, it is shown that the number of molecules activated by radiation cannot be essentially greater than  $10^8 e^{-Q/RT} C_n$ , whereas activation by collision at 1 atm. pressure and 300–500° Abs. is approximately  $10^{10} e^{-Q/RT} C_n$ , so that at small pressures the activation by radiation may not be neglected. This mechanism of a unimolecular reaction is, however, unsatisfactory, for the sum of the molecules activated both by collision and radiation is much too small to account for the measured velocities of unimolecular reactions. An alternative scheme, in which the assumption of  $a'$  and  $a''$  as active states of  $n'$  and  $n''$  is made, is put forward



and this leads to the same equation for  $k'$ , but only on the assumption that a collision between  $n$  and  $a'$  always gives rise to  $a' \rightarrow n'$ . When the probability of this step is less than unity the unimolecular law is not obeyed, and when  $\alpha=0$  the reaction becomes bimolecular. This method of formulation leads, however, to a value for  $1/A$ , the mean period of life of an active molecule, of the order  $10^{-13}$ – $10^{-14}$  second. This time is approximately that taken by the loosely bound electrons in the molecule to complete one circuit of their orbits. It is shorter than the time of collision between two molecules, and hence deactivation cannot proceed by the above mechanism. It is suggested that the reaction takes place in the following elementary reactions, which entails giving up the view that an activated molecule exists as a definite intermediate product, spontaneously undergoing change into  $a'$  and  $a''$ . Thus:



The principal difference between uni- and multi-molecular reactions disappears, and it is suggested that thermal reactions are caused by collisions and hence in basis are bi- or ter-molecular. The decomposition of nitrogen pentoxide, which has been shown to follow the unimolecular law, is discussed from this point of view. A list of data on unimolecular reactions is given,

W. E. G.

**Velocity of Dissolution of Magnesium by Acids.** M. CENTNERSZWER (*Rec. trav. chim.*, 1923, **42**, 1065—1073; cf. A., 1923, ii, 627).—In the dissolution of magnesium in unstirred dilute hydrochloric acid, there is a definite period of induction, which, however, is only noticeable with the more dilute solutions (e.g.,  $N/32$ ). The period of induction is little affected by temperature, but is greatly increased by dilution. The velocity of dissolution of magnesium in  $N/4$ - or  $N/8$ -hydrochloric acid is multiplied by 1.18 for a rise of  $10^\circ$  in temperature, a fact that supports the diffusion theory of dissolution. The diffusion-layer, calculated from a study of the temperature-coefficient of dissolution (in  $N/4$ - or  $N/8$ -acid), varies in thickness from 33—63 $\mu$ , according to the speed of agitation and the temperature. The reaction constant of dissolution of magnesium in unstirred  $N/4$ -acid shows only a slight tendency to increase with the volume of acid used, and even this small increase is probably due to secondary and not to volume effects. E. E. T.

**Catalytic Decomposition of Hydrogen Peroxide by Ferric Salts.** II. V. L. BOHNSON and A. C. ROBERTSON (*J. Amer. Chem. Soc.*, 1923, **45**, 2493—2503; cf. A., 1921, ii, 250).—A continuation of previous work (*loc. cit.*) on the catalytic decomposition of hydrogen peroxide by ferric salts. The existence of an intermediate compound,  $H_2FeO_4$ , as previously suggested, has been confirmed by a spectroscopic examination of the reaction mixture. The free energy of formation of the ferrate-ion,  $FeO_4^{2-}$ , is shown to lie in the neighbourhood of -140,000 cal. Free-energy relationships show that the ferrous-ferric-ion intermediate reactions postulated by von Bertalan are improbable (A., 1920, ii, 614). The catalytic effect of ferrous-ions is shown to be due solely to the fact that they are oxidised first to ferric salts. The molecules of ferric salt, as well as the ions, appear to exert catalytic activity. It is possible that there are two molecular forms of differing activity. The temperature coefficient of the reaction shows the critical increment of the reaction to be 23,960 cal., the frequency of the active radiation  $2.5 \times 10^{14}$ , and its wave-length 1.2 $\mu$ . J. F. S.

**Promoter Action in Homogeneous Catalysis.** I. **Copper Salts as Promoters in the Iron Salt Catalysis of Hydrogen Peroxide.** V. L. BOHNSON and A. C. ROBERTSON (*J. Amer. Chem. Soc.*, 1923, **45**, 2512—2522).—A number of experiments are described on the influence of copper salts on the catalysis of the decomposition of hydrogen peroxide by ferric salts. It is shown that a small amount of a copper salt greatly accelerates the decomposition of hydrogen peroxide by iron salts in acid solution. Other metallic salts do not appear to possess this promoter action. For a given concentration of iron salt, either sulphate or chloride, there is a maximum rate of reaction with about 1 millimol. per litre of added copper salt. This maximum effective concentration of the copper salt appears to be independent of the concentration of the iron salt. The extent of promoter action as measured by the "promotion factor," which is the ratio of the maximum rate to the normal rate for iron alone, is independent of the temperature and the concen-

tration of acid. The extent of promoter action is much greater for ferric sulphate than for ferric chloride, although the maximum rate obtained in each case is the same. The promotion factors for the two systems approach each other as the concentration of iron approaches zero. These facts are best explained by the following assumptions in connexion with the mechanism of promoter action. The iron salt is the primary catalyst by virtue of its ability to form an intermediate compound. The copper salt is a secondary catalyst, accelerating both the formation and subsequent decomposition of the intermediate compound. The effect of the secondary catalyst is dependent on its concentration only for very small quantities, a maximum effective concentration being noticeable. The mechanism of the secondary catalysis is not explained. J. F. S.

**The Interaction of Ferric Salts and Sulphurous Acid, and its Catalysis.** J. PINNOW (*Z. Elektrochem.*, 1923, **29**, 547—552).—Low hydrogen-ion concentration is favourable to interaction between a ferric salt, *e.g.*, ferric chloride, and a sulphite, *e.g.*, sodium sulphite. *p*-Benzoquinone, quinol, and their respective sulphonic acids function as carrier-catalysts in the oxidation of a sulphite to sulphate by means of a ferric salt, and their effects increase with increase in their respective amounts present. In acid solution, their catalytic action is less pronounced. The increased yield of sulphate in the presence of *p*-benzoquinone is not in accord with the suggestion of Mees and Sheppard (*Z. Phot.*, 1904, **2**, 5) that a dithionate is formed from benzoquinone and a sulphite. The authors find that benzoquinone is converted into its sulphonic acid. The regeneration of quinol or its sulphonic acids by means of sulphurous acid, and its subsequent oxidation to benzoquinone, can be effected only in acid solution. The process is therefore inapplicable to spent photographic developing solutions on account of their alkaline reaction. The catalytic action of *p*-benzoquinone may be demonstrated by the colour changes occurring in the solution. J. S. G. T.

**Oxide Equilibria in Catalysis.** J. M. WEISS, C. R. DOWNS, and R. M. BURNS (*Ind. Eng. Chem.*, 1923, **15**, 965—967).—Experiments were made to determine, in the oxidation of benzene to maleic acid by oxygen in presence of vanadium oxides, the influence of the experimental conditions on the final composition of the oxide catalyst. It was hoped in this way to throw some light on the mechanism of such oxidations. At 400°, the catalyst finished as a mixture of  $V_2O_5$  and  $V_2O_4$ , the proportion of the former increasing rapidly as the ratio of oxygen to benzene in the reacting gases increased. Even when the catalyst started as a mixture of  $V_2O_3$  and  $V_2O_4$ , its final composition appeared to depend only on the ratio of oxygen to benzene. It is suggested that catalytic action depends on an oscillation between  $V_2O_5$  and  $V_2O_4$ , the dissociation of the former supplying activated oxygen. At temperatures higher than 400°, for any given ratio of air to benzene the proportion of  $V_2O_5$  progressively decreases, but complete combustion also increases at the expense of the partial oxidation products. At lower tem-

peratures, the reverse is true. Complete combustion is therefore not dependent on the ratio of  $V_2O_5$  to  $V_2O_4$ , but on some other factor, such as the activation of the reacting substances. The nature of the chemical products of combustion is a function of some property of the catalyst other than mere activation of oxygen by dissociation of the oxide. There may be some specific relation between the structure and dimensions of the metallic atom and the structure and dimensions of the molecule of the organic compound. In this connexion, it is observed that, whereas in the case of benzene the only catalyst capable of bringing about a partial combustion is a vanadium oxide, more complex molecules, such as naphthalene and anthracene, are susceptible to a variety of catalysts. Some mixtures of oxides will bring about partial combustion of benzene, although the constituent oxides have not this property.

E. H. R.

**Catalytic Activity of Tin.** O. W. BROWN and C. O. HENKE (*J. Physical Chem.*, 1923, 27, 739—760).—The catalytic activity of tin in the reduction of nitrobenzene, *o*-nitrotoluene, and *o*-nitroanisole by hydrogen has been investigated. Of all the forms of tin catalyst investigated, that made from stannous hydroxide, prepared by the action of sodium carbonate on a solution of stannous chloride, was the most efficient. Oxidation of the hydroxide, prior to reduction to the metal, increased the efficiency of the resulting catalyst; the lower the temperature of oxidation, within the limits examined (150—300°), the better the resulting catalyst. The lower the temperature of reduction of the oxide within the limits of the experiments (350—237°) the better is the resulting catalyst. A tin catalyst in the form of rather coarse lumps is better than the powdered form. The behaviour of the catalyst in iron and glass tubes is very different, a higher temperature being necessary in glass tubes than in iron for the same results. Tin permits of a larger variation of temperature than many other catalysts. Probably 275—294° is the best temperature for the production of aniline when a glass tube is used. The best rates of flow of nitrobenzene and hydrogen with the tin catalyst compare closely with those for the copper catalyst (A., 1922, ii, 833). When *o*-nitrotoluene and *o*-nitroanisole were used instead of nitrobenzene, yields of 94% and 93% were obtained of *o*-toluidine and *o*-anisidine, respectively. Experiments carried out in a larger apparatus gave yields of 99% of aniline and 98—99% of toluidine. J. F. S.

**Atomic Structure and the Reflection of X-Rays by Crystals.** D. R. HARTREE (*Phil. Mag.*, 1923, [vi], 46, 1091—1111).—The mathematical analysis developed in a previous paper (this vol., ii, 1) is applied in more detail to the problem of the intensity of the reflection of X-rays by crystals, and is further developed in connexion with an inquiry into the extent to which it is possible to obtain, from data relating to X-ray reflection, evidence regarding orientations of the orbits in the atom, and the relative phases of the electrons in the different orbits. The formulæ deduced are compared with the experimental results obtained by Bragg, James,

and Bosanquet in the case of the reflection of X-rays by rock-salt (A., 1921, ii, 477; 1922, ii, 184). The maximum calculated values of the radii of the sodium- and chlorine-ions are, respectively, 0.65 Å. and 1.22 Å., compared with Bragg's respective values, 1.8 Å. and 1.06 Å. Whilst fair agreement is found between calculated and experimental values of the orbital dimensions in the case of the sodium-ion, observed values in the case of the chlorine-ion are much smaller than the experimental values. As the contribution to the reflection by an electron in a given position with respect to the nucleus is the same, whatever atom the electron belongs to, it appears that X-ray reflection data can afford no evidence of relative orbital orientations or of relative electronic phases in the orbits.

J. S. G. T.

**Atomic Arrangement of Crystalline Elements.** J. BECKENKAMP (*Naturwiss.*, **11**, 667; from *Chem. Zentr.*, iii, 705).—The fine structure of elements is attributed to the combined influence of nuclear electrons and valency electrons. The nucleus has the tendency towards a tetrahedral grouping (face-centred, hexagonally close packed). The attraction of a valency electron to the nucleus is electrostatic, whilst the attraction normal to the plane of the electron orbit is magnetic. One valency electron between two nuclei exerts an attraction, whilst two valency electrons between two nuclei exert a repulsion. When the effect of the nuclei predominates, the tendency is for a face-centred lattice (gold). Where the electrostatic effect predominates, the arrangement varies from group to group according to the valency, for example, space-centred (alkali metals), hexagonal close packed (beryllium), face-centred (aluminium), and the diamond type. The magnetic polarity has the tendency to bring the lattice lines falling in its direction into the closest possible arrangement.

G. W. R.

**The Arrangement of Atoms and Valency in Crystals.** J. BECKENKAMP (*Z. anorg. Chem.*, 1923, **130**, 69—86).—The author advances the theory that the distances between atoms in molecules and crystals are determined primarily by waves emanating from the atomic nuclei, secondarily by the electrostatic and electrodynamic forces of the outer electrons. Radiations are assumed to be set up by the oscillation of the protons ("Uratome") of the nucleus about one or more fixed points, and it is shown that the wavelength  $R_x$  of the radiation is proportional to  $m/A_x$ , where  $m$  is the number of oscillation centres and  $A_x$  the atomic weight. The waves from the different oscillation centres will interfere, giving rise to a number of node-points surrounding the atom, the sharpness of which will diminish as their distance from the centre of gravity increases. Neighbouring atoms of the same kind will adjust themselves to bring their systems of nodes into coincidence; as  $A_x$  increases,  $R_x$  diminishes. It is shown that, for a large number of elements, which combine with oxygen, the ratio  $R_x:R_O$  is a numerically simple one; thus  $R_{Mg}:R_O=2:3.04$ ;  $R_{Al}:R_O=\tan 30^\circ:0.98$ ;  $R_{Si}:R_O=\tan 30^\circ:1.103$ ;  $R_P:R_O=1:1.94$ ;  $R_S:R_O=1:2.004$ , when  $m=1$  in each case. When a lighter element

combines with a heavier, its node-point coinciding with the centre of gravity of the heavier element, if the value of  $R$  for the lighter element is smaller than that of the heavier, the lighter element will be drawn somewhat nearer to the heavier. Like atoms will arrange themselves in straight lines, at the corners of an equilateral triangle, or at the corners of a tetrahedron, giving rise to a number of fundamental types of symmetry, which are described.

Electron orbits are assumed to lie in octahedral planes, and the electrodynamic forces of the electrons have the effect of magnetic axes perpendicular to the orbits. The electrons tend to arrange themselves in astatic pairs or groups. Should one octant have one more electron than the other seven, the free odd electron constitutes a valency; if two octants have such a free electron, the atom is bivalent, and so on. The strength of the free valency will diminish with increasing atomic weight. Variable valency in an atom is attributed to different arrangements of the outer electrons in astatic groups; the case of iron is discussed in some detail. The electron systems of the atoms of the rare gases must be completely astatic. Single valency electrons can be more easily detached from the atom by electrical forces the greater the surface of the atom; hence gold, silver, and copper, which possess only a single valency electron, are the best conductors. The valency electrons of combined atoms must be assumed to form astatic groups. The node-points of certain atoms may perhaps be identified with the co-ordination positions of Werner's theory. The possible modes of adaptation of the atoms in crystals to the conflicting forces, thermal, electrostatic, and electrodynamic, are discussed.

E. H. R.

**The Polarisation of Double Bonds.** (SIR) J. J. THOMSON (*Nature*, 1923, **112**, 826; cf. A., 1923, ii, 682; Lapworth and Robinson, A., 1923, ii, 849).—It is held that a difference must exist between the action of an external electric field on singly- and that on doubly-bonded atoms. The electron octets round  $C_1$  and  $C_2$  in the system  $C_2=C_1$  have four electrons in common; some of the shared electrons moving from left to right under the influence of an external electric field may be so far displaced from  $C_2$  towards  $C_1$  that they can no longer be regarded as shared. Two so displaced will cause  $C_1$  to be saturated, and reduce the  $C_2$  octet to a sextet (involving unsaturation and chemical activity), whilst the remaining two electrons form a single linking. In the system  $C_2-C_1$ , however, only two electrons are held in common; displacement of one from the  $C_2$  octet, leaving only one binding electron, would presumably involve ready formation of oppositely charged ions, neither of the carbon atoms becoming chemically active while in combination.

Further, the objection that evidences of polarity would be restricted to the ends of a chain is valid only when the chain is entirely uniform. On the basis of the author's theory, an argument is developed to justify the contention that the interaction of vinyl chloride and hydrogen chloride would be expected to yield the compound  $CH_3 \cdot CHCl_2$ .

A. A. E.



**The Bohr Atom and Covalency.** N. V. SIDGWICK (*Chemistry and Industry*, 1923, **42**, 1203—1206).—The author replies to Smith's adverse criticism (*A.*, 1923, ii, 844) of Bohr's atomic theory, and its extension by the present author to non-polar compounds (*T.*, 1923, **123**, 725). It is pointed out, inter alia, that the dynamics of orbits in which more than one nucleus is concerned are such as to necessitate the subject of non-polar linkings being approached from the chemical side. The application of electronic ideas to chemistry enables all questions of structure, whether organic or inorganic, to be regarded from a single point of view. Smith's treatment of the relation between ionisable and non-ionisable links is opposed to Werner's view. The idea of effective atomic number follows from the conception of the existence of two kinds of valency, and is not a new assumption. Smith's misconception of the rule relating the covalency to the position of the atom in the periodic table is referred to; the rule is explained at length and its application illustrated by reference, inter alia, to substances the respective formulæ of which, according to Smith, contradict the rule. Misinterpretation of the theory is possible owing to omission to take ionisation or probable structural modifications into account. The composition and structure of a molecule must be determined from its properties in the liquid state before these can be used to support or overthrow any theories of valency. A consideration of some of the physical properties of basic beryllium acetate leads the author to regard the structural formula suggested by Bragg and Morgan for this substance (this vol., i, 7) as untenable; an alternative structure, characterised by a different distribution of the electrons, is more in accord with these properties.  
J. S. G. T.

**The Properties of Chemical Compounds and the Arrangement of the Electronic Orbits in their Molecules.** C. A. KNORR (*Z. anorg. Chem.*, 1923, **129**, 109—140).—A theoretical discussion of the possible electronic orbits in the molecules of chemical compounds, and the effect of different orbits on their properties. The discussion is qualitative only, and the results obtained are generally in accord with those deduced from the Langmuir theory.  
H. H.

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### Inorganic Chemistry.

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**Electrolytic Production of Active Hydrogen.** Y. VENKATARAMAIAH and B. S. V. R. RAO (*J. Sci. Assoc. Vizianagaram*, 1923, **1**, 45—46; cf. A., 1923, ii, 235, 482; Wendt and Landauer, A., 1922, ii, 369; Grubb, A., 1923, ii, 403).—By electrolysing dilute sulphuric acid with a current of 3 to 15 amperes in a cell with platinum electrodes, one being a perforated tube of length 30 mm., internal diameter 1.0 mm., and external diameter 1.5 mm., while a current of nitrogen is passed through the perforated electrode

into the solution, ammonia is formed. In another form of apparatus, the permeability of iron to nascent hydrogen at the ordinary temperature is utilised; a small quantity of triatomic hydrogen present in the atomic hydrogen reacts with sulphur and forms hydrogen sulphide.

A. A. E.

**Revision of the Atomic Weight of Bromine by the Complete Synthesis of Silver Bromide.** O. HÖNIGSCHMID and E. ZINTL (*Annalen*, 1923, **433**, 201—230).—The stoichiometrical relationship between silver and the halogens has hitherto always been found in modern work on atomic weights, by measuring the ratio  $\text{Ag} : \text{AgHal}$ . The results now communicated are therefore novel, since, in addition to the ratio  $\text{Br} : \text{AgBr}$ , the ratio  $\text{Br} : \text{Ag}$  is determined directly.

An apparatus, constructed entirely of glass, is described, by means of which specially purified bromine is distilled, under reduced pressure, into glass bulbs, in which it is weighed. It is then reduced by means of ammoniacal ammonium arsenite solution, an excess of which does not matter, and the solution treated with a weighed quantity of silver, dissolved in nitric acid. Equivalence of the bromine and silver is determined nephelometrically; also, the silver bromide is weighed.

As the mean of ten determinations of the ratio  $\text{Br} : \text{Ag}$ , and nine of the ratio  $\text{Br} : \text{AgBr}$ , the atomic weight of bromine is found to be 79.916, on the basis  $\text{Ag} = 107.880$ .

It is agreed with Baxter (A., 1922, ii, 377) that, contrary to the results of Guye and Germann (A., 1914, ii, 727), the purity of atomic weight silver is fully adequate.

W. S. N.

**Hypobromous Acid and the Determination of Hypobromous Acid and Bromic Acid.** E. BILMANN and E. RIMBERT (*Bull. Soc. chim.*, 1923, **33**, [iv], 1465—1473).—Hypobromous acid may be prepared by the action of bromine water on silver nitrate solution or on silver oxide, the equations given being  $\text{Br}_2 + \text{AgNO}_3 + \text{H}_2\text{O} \rightarrow \text{HBrO} + \text{AgBr} + \text{HNO}_3$  and  $2\text{Br}_2 + \text{Ag}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HBrO} + 2\text{AgBr}$ , and the acid is then distilled under reduced pressure at 30—35°. Various experimental difficulties and the methods of obviating them are discussed. Both reactions are reversible; this may be shown by removal of free bromine on passing a current of air through the mixture when it becomes clear by solution of the precipitated silver bromide. Hypobromous acid, even after distillation, always contains bromic acid, although the latter is not volatile under the conditions of distillation. The bromic acid may be determined by adding excess of phenol, which removes the hypobromous acid, then titrating with sodium thiosulphate after addition of dilute sulphuric acid and potassium iodide. If the titration is carried out without the addition of phenol, the total of hypobromous and bromic acids is obtained and from this the former is estimated by difference.

H. J. E.

**Mechanism of Oxidation Processes. VI.** H. WIELAND (*Annalen*, 1923, **434**, 185—203).—I. [With A. WINGLER and H. RAU.] The Activation of Oxygen by Metallic Copper.—When

dilute aqueous solutions of carboxylic acids (acetic, pyruvic, succinic, malic, benzoic, or better, oxalic, lactic, malonic, fumaric and citric) are shaken with copper powder in an atmosphere of oxygen, the latter is rapidly absorbed (with oxalic acid,  $3\text{Cu}$  absorbs  $2\text{O}_2$ ) and the acids are converted into carbon dioxide; the metal passes into solution, and the action, which is therefore not a catalytic one, ceases when dissolution is complete. Neutral substances (alcohol, dextrose, etc.) are only oxidised when acid is present, since the autoxidation of copper depends on its dissolution to form a salt and the metal cannot, therefore, alone, activate molecular oxygen. The sodium salts of the above acids, for example, are not oxidised by copper and oxygen.

As is shown by experiments conducted in an atmosphere of nitrogen, the hydrogen acceptor, molecular oxygen, may be replaced by *p*-benzoquinone, Methylene-blue, or potassium persulphate. The copper dissolves, and equivalent reduction (to quinol, etc.) occurs, but there is no oxidation when copper passes into solution in absence of molecular oxygen.

An oxidation process similar to that observed with copper and oxygen occurs with cuprous salts and hydrogen peroxide. Similar  $\text{CO}_2\text{:O}_2$  relations are observed (potassium cyanide acts as a strong anticatalyst). An ice-cold suspension of cuprous chloride with hydrogen peroxide gives a strongly oxidising brownish-yellow precipitate, probably identical with Moser's copper peroxide (A., 1914, ii, 467), which, since it is formed by the direct combination of cupric oxide and hydrogen peroxide, is probably  $\text{OH}\cdot\text{Cu}\cdot\text{O}\cdot\text{O}\cdot\text{Cu}\cdot\text{OH}$ . With acids, it affords a cupric salt and hydrogen peroxide, and its oxidising properties are simply those of the latter substance. It plays no part in the autoxidations under discussion, in which the active intermediary is probably produced ( $\text{R}$  = acid radical) thus:  $\text{CuR} + \text{HO}\cdot\text{OH} \rightarrow \text{R}\cdot\text{CuH}\cdot\text{O}\cdot\text{OH} \rightarrow \text{R}\cdot\text{H} + \text{Cu}\cdot\text{O}\cdot\text{OH}$  or  $\text{O}\cdot\text{Cu}\cdot\text{OH}$  (again, possibly, a basic salt  $\text{R}\cdot\text{Cu}\cdot\text{O}$  functions as the intermediary).

Cuprous salts, like copper, also activate molecular oxygen. Cuprous chloride (2 mols.) effects, similarly, the reduction of 1 mol. of *p*-benzoquinone, in presence of aqueous oxalic acid, in absence of oxygen:  $2\text{CuCl} + 2\text{ClH} + \text{O}\cdot\text{O}$  (or  $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}$ )  $\rightarrow 2\text{CuCl}_2 + \text{HO}\cdot\text{OH}$  (or  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ ). Hydrogen peroxide so formed during an autoxidation cannot, however, be detected, since it is at once destroyed (cf. Traube, A., 1882, 795), but both with copper and with cuprous salts a cuprous-hydrogen peroxide intermediary complex is responsible for the autoxidations observed.

II. [With A. WINGLER.]—The Oxidation of Phosphorous Acid.—Aqueous solutions of phosphorous acid do not absorb oxygen, but do so in presence of palladium black, phosphoric acid resulting. For oxygen may be substituted *p*-benzoquinone, etc., oxygen being excluded. Charcoal does not act like palladium.

Bromine does not react in dry ethereal solutions with anhydrous phosphorous acid, nor does dry palladium black cause absorption of oxygen in dry ether, whereas, on admitting traces of water, both reactions proceed rapidly. Similarly, palladium black, *p*-benzoquinone, and phosphorous acid do not interact in absence of water.

It is therefore concluded that the reducing action of phosphorous acid is due, not to its absorption of oxygen, but to the loss of hydrogen from a *hydrate*, which is the active form:  $\text{O:PH(OH)}_2 \rightarrow \text{PH(OH)}_4 \rightarrow 2\text{H} + \text{O:P(OH)}_3$  (cf. Mitchell, T., 1923, **123**, 629, etc.).  
E. E. T.

**Diffusion of Sulphur Vapour in Air at the Ordinary Temperature.** CHAVASTELON (*Compt. rend.*, 1923, **177**, 1040—1041, 1217—1218).—If small pieces of rhombic sulphur are kept in contact with, or very near to, sheets of silver, copper, or lead, a circular sulphide film forms on the metal round the sulphur. Temperature, time, and presence or absence of light affect the result slightly. The effect is due to sulphur possessing an appreciable vapour pressure at the ordinary temperature. Silver, lead, or copper wire was wound round a quartz tube closed at one end, and containing sulphur. The whole was placed (open end inwards) inside a similar but larger tube. With dry air inside the apparatus, which was kept closed, no metallic sulphide formed at the ordinary temperature during nineteen months' exposure to light. With moist air, a faint tarnishing was noticed.  
E. E. T.

**Pyrosulphates and Acid Sulphates.** L. CAMBI and G. BOZZA (*Ann. Chim. Applicata*, 1923, **13**, 221—238).—None of the methods proposed for the preparation of pyrosulphates yields the pure salts with the exception of the direct synthesis from anhydrous sulphates and sulphur trioxide. Dehydration of the hydrogen sulphates does not proceed to completion, even under reduced pressure or in a current of sulphur trioxide.

Sodium pyrosulphate solidifies in lustrous, translucent, white crystals, m. p.  $400.9^\circ$ ,  $d_4^{25}$  2.658, begins to exhibit evident dissociation at about  $460^\circ$ , and in moist air is rapidly converted into concentrated sodium hydrogen sulphate solution. The system  $\text{Na}_2\text{H}_2\text{S}_2\text{O}_8$ — $\text{Na}_2\text{S}_2\text{O}_7$ , with which supercooling is common, forms an eutectic containing 6.8 mol.% of the pyrosulphate at  $182.7^\circ$ . Sodium hydrogen sulphate has m. p.  $185.7^\circ$  (cf. Kendall and Landon, A., 1921, ii, 45). The pure pyrosulphate and also all the mixtures containing it in greater proportion than 10% are greenish-yellow in the liquid state. The dissociation of sodium hydrogen sulphate has been investigated by measuring the pressure of the water vapour emitted at different temperatures; this pressure is very slight at  $180^\circ$ , and becomes equal to 1 atmosphere at a little above  $320^\circ$ .

Potassium pyrosulphate crystallises in transparent, colourless prisms, m. p.  $414.2^\circ$ ,  $d_4^{25}$  2.512, and absorbs moisture from the air only very slowly. The solid undergoes a polymorphic transformation at  $315^\circ$ , assuming an opaque, porcelain-like appearance, and a second transformation may be detected thermally at  $225^\circ$ ; both changes are frequently accompanied by marked supercooling, and usually proceed slowly. The eutectic temperature for the system  $\text{K}_2\text{H}_2\text{S}_2\text{O}_8$ — $\text{K}_2\text{S}_2\text{O}_7$  is  $201.2^\circ$ , and the corresponding composition 14 mol.% of the pyrosulphate. The polymorphic transformations of the pyrosulphate in the mixtures generally escape the thermal

analysis owing to the sluggishness with which they occur at low temperatures.

The divergent results for the system  $\text{Na}_2\text{SO}_4\text{--H}_2\text{SO}_4$  obtained by Pascal and Ero (A., 1919, ii, 154) and by Kendall and Landon (*loc. cit.*) depend on the fact that the former authors fused the mixtures in open tubes and followed the crystallisation during the cooling, whilst the latter melted the mixtures in sealed tubes. The curve of unstable crystallisation at 0—25 mol.% of  $\text{Na}_2\text{SO}_4$  is observed (cf. Kendall and Landon) and the transition point between the compounds  $\text{Na}_2\text{SO}_4\cdot 2\text{H}_2\text{SO}_4$  and  $2\text{Na}_2\text{SO}_4\cdot 9\text{H}_2\text{SO}_4$  fixed at  $54\cdot 6^\circ$ . In the range 25—60 mol.% of  $\text{Na}_2\text{SO}_4$ , anomalies are manifested owing to dehydration of the sodium hydrogen sulphates occurring in the mixtures melting at the higher temperatures. The non-existence of any compound of sodium pyrosulphate with sodium hydrogen sulphate and the existence of the compounds  $2\text{Na}_2\text{SO}_4\cdot 9\text{H}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4\cdot 2\text{H}_2\text{SO}_4$ , and  $\text{Na}_2\text{SO}_4\cdot \text{H}_2\text{SO}_4$  are confirmed.

The results obtained for the system  $\text{K}_2\text{SO}_4\text{--H}_2\text{SO}_4$  differ little from those of Kendall and Landon (*loc. cit.*). Less dehydration occurs than with the sodium sulphate system, but anomalies occur at temperatures above  $120^\circ$ . The results indicate potassium hydrogen sulphate to be tetramorphous (cf. Bridgman, *Proc. Nat. Acad. Sci.*, 1916, 52, 124). The double salts,  $\text{K}_2\text{SO}_4\cdot 3\text{H}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4\cdot \text{H}_2\text{SO}_4$  are formed.

The results obtained with the system  $(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{SO}_4$  coincide with those of Kendall and Landon.

T. H. P.

**The Preparation of Pure Ammonia.** L. MOSER and R. HERZNER (*Monatsh.*, 1923, 44, 115—122).—Pure magnesium and calcium nitrides readily yield pure ammonia if allowed to fall gradually into gas-free water. On account of the highly exothermal nature of the reaction, decomposition of the gas always occurs if water is allowed to fall on the nitride. The only impurity present in the gas obtained by allowing the nitride to fall slowly into water is hydrogen, traces of which are formed from the traces of metal always present in the nitride. Commercial ammonium salts always contain organic matter, the carbon dioxide obtained by oxidation corresponding with 0.39—0.62% of carbon in the samples examined. By oxidation with nitric acid or permanganate at high temperatures, the organic matter may be completely destroyed, and pure ammonia obtained from the residues.

Ammonia from technical salts may be completely freed from pyridine and other organic impurities by being passed over prepared wood charcoal.

S. I. L.

**Decomposition of Nitric Oxide by Heating with Metals.** E. MÜLLER and H. BARCK (*Z. anorg. Chem.*, 1923, 129, 309—320).—The action of metals on nitric oxide at high temperatures is studied. Copper at  $500^\circ$  decomposes 99.7% of the gas but the action at lower temperatures depends on the purity of the metal. Silver is without action up to  $700^\circ$ ; iron, if reduced in hydrogen, is better than copper for decomposing nitric oxide, whilst brass is without action at  $600^\circ$ , and decomposes only 29% at  $700^\circ$ . Tin has no action up to  $400^\circ$ ,

but then commences to act rapidly, forming a nitride, which may be completely decomposed at 600°. Zinc has no action below 350°; at 600°, the action is slow, but the decomposition is complete. Bismuth decomposes 74% at 400°, forming bismuth trioxide. Magnesium and calcium decompose the gas at 500° with the formation of metallic oxide and nitride. Aluminium has little action below 600°. Manganese decomposes 68% of the gas at 400°, all of it at 500°, manganese nitride being formed. Chromium has no action below 700°, and ferrochrome (60% Cr) only 19% at 650°. Lead peroxide absorbs nitric oxide at laboratory temperature, forming lead nitrite. On heating, the gas is liberated, but at 200°, oxygen is liberated as well, and nitrogen peroxide is formed. Litharge is practically without action on nitric oxide, even at 650°. Red lead has no action on nitric oxide at laboratory temperature, but at 200° absorbs it almost completely, forming lead nitride (? nitrite). Vanadium trioxide decomposes the gas completely at 500°, forming vanadium tetroxide.

H. H.

**The Intermittent Glow of Phosphorus.** K. R. KRISHNA IYER (*Chem. News*, 1923, 127, 321).—The author states that the phenomena of intermittent luminosity and the propagation of luminous pulses exhibited by phosphorus contained in an exhausted vessel into which air is allowed to leak (Lord Rayleigh, A., 1921, ii, 546; 1923, ii, 755) may be produced in an open vessel containing traces of inhibitors, *e.g.*, naphthalene, carbon disulphide, turpentine, and light petroleum. A simple method of exhibiting the effect as a lecture experiment is described.

J. S. G. T.

**Hexametaphosphates.** P. PASCAL (*Compt. rend.*, 1923, 177, 1298—1300).—Hexametaphosphate is the name usually given to the product of the action of heat (with subsequent rapid cooling) of an acid pyrophosphate or metal dihydrogen phosphate. If the rapid cooling is omitted, trimetaphosphate is also formed, and some colloidal products. Hexametaphosphates are also supposed to result from the interaction of alkali sulphides and the metaphosphates of heavy metals. The products, however, are mixtures of trimetaphosphates, hexametaphosphates, and colloidal metaphosphates.

To obtain a pure alkali hexametaphosphate, a pure trimetaphosphate is fused (at 700°) in a platinum crucible and the latter then rapidly placed in cold water. The vitreous product is free from colloidal material and from trimetaphosphate.

Tri- and hexa-metaphosphates are interconverted at a definite temperature ( $607^{\circ} \pm 2^{\circ}$  for the sodium salts). The hexametaphosphate is the form stable at high temperatures. Interconversion is almost instantaneous at one definite temperature, being slower as the temperature falls, until at the ordinary temperature no change occurs. The identity of the melting points of the two sodium salts (638°) is thus explained, as are also the details necessary for obtaining "Graham's soluble salt."

After their formation, hexametaphosphates undergo slight

changes (complete in sixteen hours at  $648^{\circ}$  or in six hours at  $835^{\circ}$ ). The viscosity of their solutions increases slightly, owing to the formation of a little colloidal salt (1.8% and 1.2% at  $648^{\circ}$  and  $835^{\circ}$ , respectively).

The hexametaphosphates are distinguished by the formation of complex salts of the types:  $M_4[Fe(PO_3)_6]$ ,  $M_3[Fe(PO_3)_6]$ , and  $M_4[UO_2(PO_3)_6]$ . Thus, an excess of an alkali hexametaphosphate decolorises ferric thiocyanate, and prevents the formation of a colour when uranyl salts and ferrocyanides are mixed. E. E. T.

**The Vapour Pressure of Arsenious Oxide.** P. SMELLIE (*J. Soc. Chem. Ind.*, 1923, 42, 466—468T).—Experiments were made to extend the work of Schwes (A., 1920, ii, 247) on the vapour pressure of arsenic in sulphuric acid solution. Using the same method as Schwes, but taking special precautions to prevent sulphuric acid being carried over mechanically, much lower results were obtained than those recorded by Schwes. At  $60$ — $64^{\circ}$ , the vapour pressure found was  $2.7$  to  $9 \times 10^{-7}$  mm. of mercury. Using a similar method, the vapour pressure of pure arsenious oxide was found to be: at  $60$ — $61^{\circ}$ ,  $2.4 \times 10^{-7}$ ; at  $81$ — $86^{\circ}$ ,  $2.5 \times 10^{-5}$ ; at  $101$ — $105^{\circ}$ ,  $4.6 \times 10^{-4}$ ; at  $117$ — $124^{\circ}$ ,  $1.9 \times 10^{-3}$ ; at  $119$ — $126^{\circ}$ ,  $2.2 \times 10^{-3}$ ; at  $149$ — $152^{\circ}$ ,  $2.6 \times 10^{-2}$  mm. To obtain hydrochloric acid free from arsenic for the Marsh test, it is recommended to dilute the acid to  $d$  1.10, and boil it gently with precipitated copper for several hours, using a reflux condenser. The copper is prepared from pure granulated zinc and cuprous chloride dissolved in hydrochloric acid. The acid is then distilled over fresh precipitated copper and stored in Jena glass vessels. It is also recommended to use electrolytic hydrogen for the Marsh test. E. H. R.

**Optical Properties of Graphite and Graphitic Oxide.** P. GAUBERT (*Compt. rend.*, 1923, 177, 1123—1125).—Very thin graphite laminae result when a lamina (obtained by cleavage) is rubbed between two microscope slides. The laminae are transparent (if sufficiently thin), green in transmitted light, give complete extinction between crossed Nicols, and in convergent light give a black cross, without coloured rings. The crystals are optically negative and have a refractive index between 1.93 and 2.07.

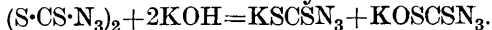
Graphitic oxide (green), obtained by treating graphite laminae with fuming nitric acid and potassium chlorate, has a crystalline structure (crystals, optically negative; black cross distinct). The oxide is stable while it contains a little nitric acid, but after washing with water becomes brown, grey, or yellow, when it also deflagrates on heating, giving pyrographitic acid, *i.e.*, graphite. The dried oxide has a refractive index of 1.93—2. E. E. T.

**Azido-carbondisulphide. I. Formation, Preparation, and General Properties.** A. W. BROWNE, A. B. HOEL, G. B. L. SMITH, and F. H. SWEZEY [with Microscopical Studies by C. W. MASON] (*J. Amer. Chem. Soc.*, 1923, 45, 2541—2550).—The action of oxidising agents on a 3% aqueous solution of potassium azido-



dithiocarbonate (A., 1922, ii, 847) has been investigated; in each case a 1% solution of the oxidising agent was used with 5 c.c. of the azido-salt (cf. Sommer, A., 1916, ii, 29). It is found that hydrogen peroxide, after producing a green colour, gives a precipitate of *azido-carbondisulphide*  $(\text{S}\cdot\text{CS}\cdot\text{N}_3)_2$ ; ozonised oxygen, potassium chlorate, potassium chromate, potassium persulphate, mercuric chloride, ferric chloride (acidified), stannic chloride, acidified potassium permanganate, solid manganese dioxide, cerium dioxide, sodium nitrite, chlorine, bromine, and iodine all produce the same substance in greater or lesser yields. It can also be prepared by the electrolysis of a 20% solution of potassium azido-dithiocarbonate between a rotating platinum anode of 30 sq. cm. total area and a stationary platinum cathode enclosed in a parchment thimble with an anode current density of 18.6 amperes/dcm.<sup>2</sup>, when relatively large yields are obtained. The best method of preparation consists in taking 5 c.c. of the clear concentrated solution of potassium azido-dithiocarbonate, obtained by filtering the liquid resulting from the interaction of 6 g. of potassium azide and 6 g. of carbon disulphide in 25 c.c. of water. This is diluted to 55 c.c. with water and treated drop by drop with a normal solution of iodine in potassium iodide and continually stirred until the precipitation of azido-carbondisulphide is complete. An excess of iodine must be avoided. The precipitate is washed with water, dried by suction, and transferred to porous plates by a bone spatula, pressure and tapping being avoided, and placed in a desiccator over phosphoric oxide at 10° or lower.

It is a white, crystalline solid, soluble to the extent of 3 parts in 10,000 of water at 25°; it is very unstable and particularly sensitive to impact and heat, more so than potassium azido-dithiocarbonate. It explodes with the liberation of heat, and with more smoke and less flame than the azido-dithiocarbonate. It undergoes spontaneous decomposition at the ordinary temperature, giving nitrogen, sulphur, and a polythiocyanogen  $(\text{S}\cdot\text{CS}\cdot\text{N}_3)_2 = 2\text{N}_2 + 2\text{S} + (\text{SCN})_2$ . Examination of the rate of decomposition shows that the spontaneous decomposition probably takes place in the two stages  $(\text{SCSN}_3)_2 = \text{N}_2 + \text{S} + \text{SCSN}_3\cdot\text{SCN}$ ;  $\text{SCSN}_3\cdot\text{SCN} = \text{S} + \text{N}_2 + (\text{SCN})_2$ . In the spontaneous decomposition, the colour changes to dark orange, passing through various yellow shades. The crystals are tetragonal or orthorhombic and have a refractive index about 1.8. It is soluble in the commoner organic solvents, but decomposes slowly in them. Dilute sulphuric acid (1 : 6) has little action on azido-carbondisulphide until the temperature is raised above 40°, but more concentrated acid decomposes it at all temperatures; hydrochloric and nitric acids both decompose it. It reacts with potassium hydroxide in much the same manner as a halogen to form the potassium salts of azido-dithiocarbonic acid and azido-oxydithiocarbonate,



It reduces potassium permanganate, potassium iodate, and potassium iodide. On the basis of the reactions of azido-carbondisulphide the authors adopt the formula  $\text{N}:\text{N}:\text{N}\cdot\text{CS}\cdot\text{S}\cdot\text{CS}\cdot\text{N}:\text{N}:\text{N}$  suggested by Sommer.

J. F. S.

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**Azido-dithiocarbonic Acid. I. Formation, Preparation, and Properties.** G. B. L. SMITH and F. WILCOXON [with A. W. BROWNE and with Microscopical Studies by C. W. MASON] (*J. Amer. Chem. Soc.*, 1923, **45**, 2604—2613).—Azido-dithiocarbonic acid,  $\text{HS}\cdot\text{CS}\cdot\text{N}_3$ , a new halogenoid hydracid, has been prepared by treatment of concentrated solutions of the sodium salt with concentrated hydrochloric acid. It is a white or very pale yellow, crystalline solid; it crystallises in the monoclinic system, has a strong double refraction, and is readily soluble in non-aqueous solvents. It has the characteristic properties of a strong acid, and its strength approaches that of hydrochloric acid. It is easily oxidised by various oxidising agents, yielding the free halogenoid,  $(\text{S}\cdot\text{CS}\cdot\text{N}_3)_2$ . In the solid form, the acid is very sensitive to both shock and to heat. It undergoes spontaneous decomposition at the ordinary temperature, in keeping with the laws of unimolecular change. In the dry state, this reaction is catalysed by an intermediate product or by the thiocyanic acid formed, but not in aqueous solution. The decomposition may be represented by the equation  $\text{HS}\cdot\text{CS}\cdot\text{N}_3 = \text{HSCN} + \text{S} + \text{N}_2$ . The solid product formed consists of polymerised thiocyanic acid and free sulphur. J. F. S.

**Diffusibility of Helium through Crystalline Septa.** A. PIUTTI and E. BOGGIO-LERA (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1923, [iii], **29**, 111—115; cf. A., 1923, ii, 20).—At  $480^\circ$ , helium is unable to traverse plates of lævo- or dextrorotatory quartz cut either parallel or perpendicular to the optic axis and having the thickness 0.3—1 mm., although the gas is able to penetrate ordinary or quartz glass at this temperature (cf. Williams and Ferguson, A., 1922, ii, 841). T. H. P.

**The Separation of Radium and Barium.** V. CHLOPINE (*Bull. Soc. chim.*, 1923, [iv], **33**, 1547—1551).—The values obtained by Engel (A., 1894, ii, 40) and by Masson (T., 1911, **99**, 1132) for the solubility of barium chloride in hydrochloric acid of various concentrations were used as the basis of a method of separating the chlorides of radium and barium from one another. Gaseous hydrogen chloride is passed into a solution containing the mixed chlorides until the optimum concentration of the acid has been attained. This value depends on the "coefficient of enrichment," which is the ratio of the percentage of total radium precipitated to the percentage of total barium precipitated. This coefficient is a regular function of the percentage of the barium salt precipitated, and varies from 3.7 to 1.3, with a corresponding precipitation of 7—8% to 55—57% of the total barium present. The presence of other chlorides, with the exception of that of lead, does not interfere with the efficiency of the method, which may therefore be carried out without preliminary purification of the mixed chlorides. H. J. E.

**Solubility of Potassium Perchlorate in Salt Solutions and the Corresponding Activity Relations.** R. M. BOZORTH (*J. Amer. Chem. Soc.*, 1923, **45**, 2653—2657).—The solubility of potassium perchlorate has been determined in 0.1*N*, 0.3*N*, and 0.6*N*

solutions of potassium chloride, nitrate, and sulphate, sodium chloride, nitrate, perchlorate, and sulphate, and barium chloride and nitrate. The individual effects of the separate ions on the activity coefficient product of the potassium- and perchlorate-ions have been compared, and at the concentrations involved (0.25—0.75*N*) have been found to be markedly specific and additive.

J. F. S.

**The Third Form of the Ammonia-soda Process.** P. P. FEDOTÉEV and A. KOLOSSOV (*Z. anorg. Chem.*, 1923, **130**, 39—45; cf. A., 1914, ii, 268).—A third form of the ammonia-soda process involves the reaction between sodium sulphate and ammonium hydrogen carbonate, which is complicated by the existence of the double salt,  $\text{NaNH}_4\text{SO}_4\cdot\text{aq}$ , now shown to crystallise with  $3\text{H}_2\text{O}$ . The equilibrium conditions for this salt pair have been studied at  $35^\circ$  under a pressure of 3 atm. of carbon dioxide. Measurements were made of the solubility of ammonium sulphate in sodium sulphate solution and of sodium sulphate in ammonium sulphate solution (these at  $15^\circ$  as well as  $35^\circ$ ), of ammonium hydrogen carbonate in ammonium sulphate, and vice versa, of sodium hydrogen carbonate in ammonium hydrogen carbonate, and of sodium hydrogen carbonate in sodium sulphate solution. Three solutions are possible, saturated simultaneously with three salts, namely: (1)  $\text{NaHCO}_3$ ,  $\text{NH}_4\cdot\text{HCO}_3$ , and  $(\text{NH}_4)_2\text{SO}_4$ ; (2)  $\text{NaHCO}_3$ ,  $\text{NaNH}_4\text{SO}_4\cdot 3\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ; (3)  $\text{NaHCO}_3$ ,  $\text{NaNH}_4\text{SO}_4\cdot 3\text{H}_2\text{O}$ , and  $\text{Na}_2\text{SO}_4$ . The solubility of sodium sulphate in ammonia solutions at  $35^\circ$  was also determined. The disadvantage of this form of the ammonia-soda process is the low solubility of sodium sulphate in ammonia solutions.

E. H. R.

**A Cæsium Cupric Mercuric Chloride,  $\text{Cs}_2\text{CuHgCl}_6$ ; the Failure to Prepare Cs—Cu—Cd or Cs—Cu—Zn Chlorides; and the Varying Complexity of certain Triple Salts.** H. L. WELLS (*Amer. J. Sci.*, 1923, **6**, 521—525).—The addition of strong hydrochloric acid to mixed solutions of cæsium, cupric, and mercuric chlorides, with subsequent concentration and cooling, causes the separation of the triple salt,  $\text{Cs}_2\text{CuHgCl}_6$ , in the form of black cubes, which when broken show a pale brownish-red colour, and thus appear to be strongly dichroic or pleochroic. Triple chlorides of cæsium and copper with cadmium or zinc could not be obtained.

A comparison of the formulæ of various triple salts of the metals of groups I and II shows that ammonium and the alkali metals of lower atomic weight than that of cæsium tend to form more complex triple salts than cæsium itself; this may be attributed to the more electro-positive character of cæsium, which gives it a greater combining power.

S. I. L.

**Preparation of Pure Silver Antimonide.** E. J. WEEKS and W. V. LLOYD (*Chem. News*, 1923, **127**, 362).—When stibine, prepared as previously described (T., 1923, **123**, 456), is washed, dried, and passed into a cold *N*/2-solution of silver nitrate, pure silver antimonide is deposited.

J. S. G. T.

**Solubility and Surface Energy of Calcium Sulphate.** M. L. DUNDON and E. MACK, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 2479—2485).—Some of Hulett's experiments (A., 1901, ii, 493; 1904, ii, 321) on the variation of solubility with the size of the particles have been repeated and further experiments have been carried out with calcium sulphate of different sizes of particles, with the object of obtaining trustworthy values of the surface energy. The method of working consisted in adding finely powdered calcium sulphate to a saturated solution at 25° in equilibrium with large crystals and measuring the increase in concentration and the return to the original concentration by conductivity measurements. On adding particles of average size  $0.3\mu$  to a solution in equilibrium with particles 20—50 $\mu$  long, the electrical conductivity rose from  $2208 \times 10^{-6}$  to  $2616 \times 10^{-6}$  in a minute; after two days it had returned to  $2276 \times 10^{-6}$ , and after six days to  $2213 \times 10^{-6}$ . This represents an increased concentration of 24%. It was found that grinding gypsum and precipitated calcium sulphate causes them to lose water, and since the particles added in the above experiment contained only 12% of water instead of 21.1%, it is possible that some of the increased solubility is due to this cause. The concentration can be increased if the dehydrated salt is added to the saturated solution without any previous fine powdering. Thus a solution saturated as above rose in conductivity to  $2450 \times 10^{-6}$  in one day and to  $2520 \times 10^{-6}$  in two days on adding dehydrated crystals of the same sort as those with which the original solution was in equilibrium. Calculations from the results obtained with particles of calcium sulphate 0.2 and 0.5 $\mu$  in diameter give a value 370 ergs/cm.<sup>2</sup> for the surface energy of the dihydrate of calcium sulphate.

J. F. S.

**Action of Silica and Alumina on Calcium Sulphate.** (MLLE) G. MARCHAL (*Compt. rend.*, 1923, **177**, 1300—1302).—Using a method similar to that employed previously (cf. A., 1923, ii, 139), the author has studied the reactions: (1)  $\text{CaSO}_4 + \text{SiO}_2 = \text{CaSiO}_3 + \text{SO}_2 + 0.5\text{O}_2$  and (2)  $\text{CaSO}_4 + \text{Al}_2\text{O}_3 = \text{CaAl}_2\text{O}_4 + \text{SO}_2 + 0.5\text{O}_2$ , by measuring the equilibrium pressures at different temperatures (the systems being univariant). The first reaction begins at 870°, the second at 940—950°, both being studied up to 1,280°. Both are very rapid: thus if gas is removed at 1,230°, equilibrium is restored in a few seconds. For the first reaction, the total gas pressure becomes 760 mm. at 1,273°, for the second at 1,363° (extrapolation value).

E. E. T.

**New Reaction producing Strontium.** C. MATIGNON (*Compt. rend.*, 1923, **177**, 1116—1118).—The method previously used for the preparation of barium (A., 1913, ii, 504) has been successfully applied to the case of strontium, which is obtained in a pure state by heating silicon (2.5 parts) with strontium oxide (20 parts) in an exhausted iron tube at 1,250° for three hours (2.1 grams of strontium were actually obtained). Ferro-silicon, if sufficiently rich in silicon, may be used instead of silicon.

E. E. T.

**The Technical Electrolysis of Fused Carnallite.** P. P. FEDOTÉEV [with N. WORONIN] (*Z. anorg. Chem.*, 1923, **130**, 25—38).—A study of the conditions favourable for the preparation of magnesium by the electrolysis of carnallite. [Cf. *B.*, 19.]

E. H. R.

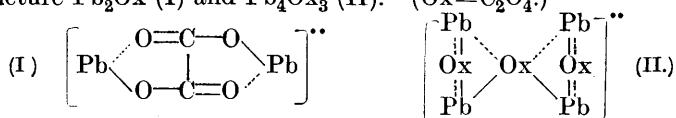
**The Preparation of Zinc by Electrolysis of Sulphate Solutions.** P. P. FEDOTÉEV and W. W. STENDER (*Z. anorg. Chem.*, 1923, **130**, 51—62).—This paper records the results of a study of the influence of different factors (concentration of electrolyte, concentration of acid, current density, temperature and impurities) on the efficiency of the electrolysis of zinc sulphate. [Cf. *B.*, 18.]

E. H. R.

**Zinc Halide Ammines.** W. BILTZ and C. MESSERKNECHT (*Z. anorg. Chem.*, 1923, **129**, 161—175).—Compounds of the zinc halides with ammonia have been prepared and their vapour tensions determined. From these measurements, the isothermals have been plotted. The halides all form monoammines, diammines, tetra-ammines, and hexa-ammines, whilst the chloride in addition forms a deca-ammine. By plotting the heats of formation of the ammines against the valency of the halide, it is found that for the hexa-ammines, and tetra-ammines the heats of formation are in the order  $\text{Cl} < \text{Br} < \text{I}$ , whilst for the diammines and monoammines, the reverse is the case.

H. H.

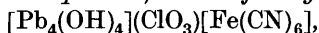
**Lead Acetato-(Oxalato-)complexes and Basic Lead Salts.** R. WEINLAND and F. PAUL (*Z. anorg. Chem.*, 1923, **129**, 243—262; cf. *A.*, 1922, i, 981; ii, 767).—By means of replacement reactions carried out with the lead acetatoperchlorates previously prepared, some other salts have been obtained, notably the dithionate, picrate, nitrate, and bromate. Further, it has been found possible to prepare lead oxalato-salts in a similar way, having kations of the structure  $\text{Pb}_2\text{Ox}$  (I) and  $\text{Pb}_4\text{Ox}_3$  (II). ( $\text{Ox} = \text{C}_2\text{O}_4$ .)



Basic lead salts have also been prepared: these are considered to be aquo-salts of the types  $\left[ \text{Pb} \begin{array}{c} \diagup \text{OH} \diagdown \\ | \quad | \\ \text{OH} \end{array} \text{Pb} \right] (\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$  and  $\left[ \text{Pb} \left( \begin{array}{c} \diagup \text{OH} \diagdown \\ | \quad | \\ \text{OH} \end{array} \text{Pb} \right)_2 \right] (\text{ClO}_3)_2$ . Of these, many examples, including dithionates, nickelicyanides, and a nitroprusside have been prepared. Other basic salts have been prepared, derived from the kation  $[\text{Pb}_3(\text{OH})_4]^{**}$  by elimination of water to give  $[\text{Pb}_3(\text{OH})_2\text{O}]^{**}$  or  $\left[ \text{Pb}=\text{O}-\text{Pb} \begin{array}{c} \diagup \text{OH} \diagdown \\ | \quad | \\ \text{OH} \end{array} \text{Pb} \right]^{**}$ . Salts with tervalent ions (III)  $\left[ \text{Pb} \begin{array}{c} \diagup \text{OH} \diagdown \\ | \quad | \\ \text{OH} \end{array} \text{Pb}-\text{OH}-\text{Pb} \begin{array}{c} \diagup \text{OH} \diagdown \\ | \quad | \\ \text{OH} \end{array} \text{Pb} \right]^{***}$  or  $[\text{Pb}_4(\text{OH})_5]^{***}$  and (IV)  $\left[ \left( \text{Pb} \begin{array}{c} \diagup \text{OH} \diagdown \\ | \quad | \\ \text{OH} \end{array} \right)_2 \text{Pb}-\text{OH}-\text{Pb} \left( \begin{array}{c} \diagup \text{OH} \diagdown \\ | \quad | \\ \text{OH} \end{array} \text{Pb} \right)_2 \right]^{***}$  or  $[\text{Pb}_6(\text{OH})_9]^{***}$  are

also described. Finally are described salts containing the phosphito-plumbo-kations (V)  $\left[ \text{Pb} \cdots \text{O} = \text{PH} \begin{array}{c} \text{O} - \text{Pb} \\ \text{O} - \text{Pb} \end{array} \right]^{+++}$  and (VI)  $\left[ \text{Pb} \cdots \text{O} = \text{PH} \begin{array}{c} \text{O} \\ \text{O} \end{array} \text{Pb} \right]^{++}$ .

The following salts are new: *diacetatodiplumbo-dithionate*,  $[\text{Pb}_2(\text{OAc})_2]\text{S}_2\text{O}_6$ , irregular, greasy platelets; *picrate*, lemon-yellow, long tablets; *bromate*, irregular, very thin platelets; *diacetatotriplumbo-nitrate*,  $[\text{Pb}_3(\text{OAc})_2](\text{NO}_3)_4$ , granular, crystalline masses. *Oxalatodiplumbo-perchlorate*,  $[\text{Pb}_2\text{Ox}](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ , long, thin tablets; *nitrate*, thick, irregular platelets ( $2\text{H}_2\text{O}$ ); *trioxalatotetraplumbo-perchlorate*,  $[\text{Pb}_4\text{Ox}_2](\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ , prismatic, six-sided crystals; *dioldiplumbo-chlorate*,  $[\text{Pb}_2(\text{OH})_2](\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ , large, greasy, well-defined prisms, *dithionate* ( $1\text{H}_2\text{O}$ ), irregular, pearly plates, *bromide* (anhy.), whitish, microcrystalline powder, *nitroprusside* ( $2\text{H}_2\text{O}$ ), red cubes, *nickelicyanide* (anhy.), microcrystalline, pale yellow powder, *bromate* (anhy.). *Tetroltriplumbo-chlorate*,  $[\text{Pb}_3(\text{OH})_4](\text{ClO}_3)_2$ , sharp, spiky crystals, *dithionate* ( $0.5\text{H}_2\text{O}$ ), rods and truncated prisms, *bromide* (anhy.), microcrystalline powder, darkening in the light, *nickelicyanide* (anhy.), irregular platelets, *bromate* (anhy.), light orange needles, *basic bromate*,  $[\text{Pb}_5(\text{OH})_6](\text{BrO}_3)_4$ , lustrous, irregular six-sided platelets. *Dioloxtotriplumbo-bromate*,  $\text{Pb}(\text{BrO}_3)_2 \cdot 2\text{PbO} \cdot \text{H}_2\text{O}$ , yellow, microcrystalline powder, *trioxotetraplumbo-dichromate*,  $4\text{PbO} \cdot 2\text{CrO}_3$ , fiery red powder, *dioxotriplumbo-dichromate*,  $3\text{PbO} \cdot 2\text{CrO}_3$ , deep orange-red powder, *basic nitrite* ( $0.5\text{H}_2\text{O}$ ), orange-yellow, tufted prisms. *Di(dioldiplumbo)chlorate ferricyanide*,



exists in a brown and black form, the *bromateferricyanide* ( $1\text{H}_2\text{O}$ ) forms reddish-brown, irregular tablets, the *hypophosphiteferricyanide* (anhy.), bright yellowish-green powder. *Di(dioldiplumbo)tetroltriplumbo-tribromate ferricyanide*,  $[\text{Pb}_7(\text{OH})_8](\text{BrO}_3)_3[\text{Fe}(\text{CN})_6]$ , bright yellow, irregular platelets, *dioldiplumbotetroltriplumbo-nitrateferricyanide*,  $[\text{Pb}_5(\text{OH})_6]\text{NO}_3[\text{Fe}(\text{CN})_6]$ , minute cubes. *Dioldiplumbo-μ-oldioldiplumbo-ferricyanide*,  $[\text{Pb}_4(\text{OH})_4](\text{H}_2\text{PO}_2)[\text{Fe}(\text{CN})_6]$ , olive-green and red forms. *Tetroltriplumbo-μ-oltetroltriplumbo-ferricyanide*, dirty violet powder, *olacetatodiplumbo-chlorate*, *dioldiacetatotriplumbo-chlorate*, *phosphitotriplumbo-bromide*, *phosphitodiplumbo-chloride*, *lead chlorate monohydrate*, and *dileadthiocyanate monohydrate*.

H. H.

**Metallisation of Organisms.** N. D. ZELINSKI (*Compt. rend.*, 1923, 177, 1041—1043).—A bee, placed in a platinum boat, and lightly covered with cupric oxide, was heated in a glass tube in a current of carbon dioxide. On removing the excess of cupric oxide, a copper replica of the bee was obtained, the minutest details of the structure being preserved. Beneath the metal was a coke-like mass, containing nitrogen and hydrogen. The metallised bee contained 48.84% of copper. Vegetable products, *e.g.*, leaves, undergo similar metallisation. The effect is ascribed to the volatility of cupric oxide (cf. following abstract). E. E. T.

**Transportation of Copper in the Gaseous State and Copper Carbonyl.** G. BERTRAND (*Compt. rend.*, 1923, **177**, 997—999).—Zelinski's results in connexion with the effect of heat on organisms which have previously been covered with cupric oxide (preceding abstract) are most readily explained on the assumption that *copper carbonyl* is formed, being decomposed almost immediately, but being sufficiently stable to account for the alleged volatility of copper oxide. Ignition of animal or vegetable matter, not containing copper, using copper or brass gas burners, causes the introduction of traces of copper into the ash obtained, this result being observed in absence of halogen compounds. If carbon dioxide is passed over heated cupric oxide in a glass tube, no unusual effect is observed, but if, before passing over the cupric oxide, the gas first passes over red hot carbon, a red, mirror-like deposit of copper is produced, presumably owing to the intermediate formation of copper carbonyl. E. E. T.

**Formation of Sulphides, Selenides, and Tellurides of certain Metals. I. Copper Compounds.** F. GARELLI (*Atti R. Accad. Sci. Torino*, 1923, **58**, 193—200).—The author confirms the observation made by Wicke (*Annalen*, 1852, **82**, 145), who found that a piece of sulphur, wrapped in clean copper wire and immersed in saturated copper sulphate solution at the ordinary temperature, gradually becomes coated with indigo-coloured, crystalline copper sulphide. The copper sulphate solution, which need not be saturated, does not change in composition during the reaction. Very pure cupric sulphide may be prepared in considerable quantities by adding copper, together with rather more than the atomic proportion of sulphur, to neutral, aqueous cupric sulphate or nitrate kept boiling by means of a current of steam. If the proportion of sulphur added is halved, pure cuprous sulphide is obtained.

In a similar manner, by the interaction of copper and selenium in copper sulphate solution, the selenides  $\text{Cu}_2\text{Se}$ ,  $\text{CuSe}$ , and  $\text{Cu}_3\text{Se}_2$  may be obtained in pure condition. The copper telluride,  $\text{Cu}_4\text{Te}$ , may be prepared similarly. T. H. P.

**Basic Copper Sulphate.** F. S. WILLIAMSON (*J. Physical Chem.*, 1923, **27**, 789—797).—The formation of basic sulphates of copper has been investigated by adding various definite molecular quantities of sodium hydroxide to copper sulphate solution and analysing the precipitates. The results of Pickering (*A.*, 1883, 853) have been confirmed, namely, that the precipitate obtained by adding varying amounts of sodium hydroxide, not exceeding 1.5 mols. per mol. of copper sulphate, is practically constant in composition. This precipitate has the composition  $\text{CuSO}_4 \cdot 3\text{CuO} \cdot 4\text{H}_2\text{O}$ , which may be written  $(\text{CuO}_2\text{H}_2)_3\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . By precipitating with alkali as in the above case, the compound  $\text{CuSO}_4 \cdot 2\text{CuO} \cdot 2\text{H}_2\text{O}$  is not obtained as postulated by Stearn and Young (*Phil. Mag.*, 1843, [3], **23**, 501). Since copper sulphate will peptise hydrated copper oxide and be carried down by it, there is no certainty that the basic salts may not contain adsorbed copper sulphate. J. F. S.

**Absorption of Halogens by Mercurous Salts.** K. G. NAIK and M. D. AVASARE (*J. Amer. Chem. Soc.*, 1923, **45**, 2769—2770).—Mercurous chloride, sulphate, and nitrate are treated with an alcoholic solution of iodine or bromine in excess. Mercurous chloride yields mercuric iodochloride,  $\text{HgICl}$ , and mercuric bromochloride,  $\text{HgBrCl}$ . The sulphate yields di-iodomercuric sulphate,  $(\text{IHg})_2\text{SO}_4$ , and a perbromide,  $(\text{BrHg})_2\text{SO}_4\cdot\text{Br}_2$ . The latter reacts with dry chlorine to give dichloromercuric sulphate,  $(\text{ClHg})_2\text{SO}_4$ . The nitrate gives a periodide,  $(\text{IHgNO}_3)_2\cdot\text{I}_2$ , and a perbromide,  $(\text{BrHgNO}_3)_2\cdot\text{Br}_2$ . The periodide, when treated with chlorine, gives a perchloride,  $(\text{ClHgNO}_3)_2\cdot\text{Cl}_2$ . W. S. N.

**Separation of Rare Earths by Basic Precipitation. VI.** W. PRANDTL and J. RAUCHENBERGER (*Z. anorg. Chem.*, 1923, **129**, 176—180; cf. A., 1922, ii, 769).—The influence of mercuric cyanide and of nickel nitrate on the precipitation of the rare earth oxides from solutions of their nitrates by means of ammonia has been studied. The authors conclude that, although these and other salts tend to keep the rare earths, especially lanthanum, in solution in the presence of ammonia, the most effective for this purpose is cadmium nitrate. H. H.

**Action of High Temperatures on some Refractory Substances.** C. MATIGNON (*Compt. rend.*, 1923, **177**, 1290—1293).—Various substances have been heated, in the form of pellets, in an electric furnace, in an atmosphere of nitrogen. Sodium aluminate,  $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$  (m. p.  $1,650^\circ$ ), is prepared by heating the appropriate mixture of aluminium oxide and sodium carbonate at  $1,100$ — $1,200^\circ$ , a pure product also being obtained using a slight excess of the oxide. Aluminates of the type  $\text{Al}_2\text{O}_3\cdot(n+1)\text{Na}_2\text{O}$  dissociate below  $1,650^\circ$ ; sodium oxide being lost until the simple aluminate is formed.

Zircon, used in the natural crystalline form, does not melt at  $2,126^\circ$ . At  $1,800^\circ$ , some dissociation occurs, dense white fumes of silicon dioxide being formed at  $1,900^\circ$ . The residue melts at about  $2,600^\circ$ . Zirkite (that is, zircon containing excess of silica and some ferric oxide) does not melt at  $1,950^\circ$ .

Tungstic oxide does not melt at  $2,130^\circ$ . In presence of carbon, it is converted into tungsten and a carbide.

Aluminium nitride ( $\text{AlN}$ ) does not melt at  $2,200^\circ$ . At a higher temperature, it dissociates into its elements, but is, under these conditions, only slowly affected by oxygen. E. E. T.

**Composition of the Precipitate from Partially Alkalinised Alum Solutions.** L. B. MILLER (*U.S. Pub. Health Repts.*, 1923, **38**, 1995—2004; cf. Theriault and Clark, *ibid.*, 181; Williamson, A., 1923, ii, 324).—Varying amounts of sodium hydroxide were added to 0.005 and 0.02*M*. (in aluminium) alum solutions at room temperature, and to the latter at  $100^\circ$ . After precipitates had settled for half an hour, the  $p_{\text{H}}$  value of the liquid was determined colorimetrically. After using a centrifuge, and decanting, the precipitate was treated in a centrifuge with successive 200 c.c. portions of water until nearly free from sulphate-ion. At this



point, dispersion of the precipitate commenced. Bringing the  $p_H$  of the wash-water to that of the solution had little effect on the composition of the precipitate. For additions of sodium hydroxide up to 2.5 mols. per mol. of aluminium at room temperature, the composition of the precipitate was constant, and approximate to  $5Al_2O_3 \cdot 3SO_3$ . Increasing concentration of sulphate-ion over a wide range (by addition of potassium or ammonium sulphate), or increasing concentration of aluminium up to 0.1M had no effect on the composition of a precipitate formed at a definite  $p_H$  value. For  $p_H$  4.0—5.5, the ratio of aluminium to sulphate in the precipitate is constant; at higher  $p_H$  values, the sulphate rapidly disappears. When three or more mols. of sodium hydroxide are added for each mol. of aluminium, the precipitate can be washed free from sulphate. The precipitate appears to consist of two components of nearly equal solubility. For 0.005M-aluminium, the greatest insolubility of the precipitate was found at  $p_H$  6.7—7.0, at which point 2.75 mols. of sodium hydroxide have been added. On both sides of this, however,  $p_H$  5.4—8.5 are zones of great insolubility. Theriault and Clark's (*loc. cit.*) point of greatest flocculation,  $p_H$  5.5 (2.4 mols. of sodium hydroxide added), is the point where precipitation of aluminium first approaches completion, and is in the region where the greatest amount of sulphate is found in the precipitate. In Blum's method for the determination of aluminium, it is essential that sulphate should be absent, or present only in small amount; otherwise, a second precipitation from hydrochloric acid solution is necessary. Chloride is satisfactorily removed by ignition over a Méker burner for ten minutes. Experiments with solutions of aluminium chloride were abandoned on account of the formation of colloidal suspensions not flocculated by the prolonged use of a centrifuge. CHEMICAL ABSTRACTS.

**The Production of Manganese by Electrolysis of Aqueous Solutions of its Salts.** P. P. FEDOTÉEV (*Z. anorg. Chem.*, 1923, **130**, 18—24).—Attempts to obtain pure manganese by electrolysis of manganous chloride or sulphate under different conditions were unsuccessful. Under the most favourable conditions, using a neutral or weakly acid 6.5N solution of the chloride at 5° with a current density of 20 amperes per sq. dcm., the deposit on the copper cathode contained only about 65% of metallic manganese, the remainder being hydroxide. [Cf. *B.*, 19.] E. H. R.

**Formation of Manganese Carbide from Carbon Dioxide and Manganese.** E. MÜLLER and H. BARCK (*Z. anorg. Chem.*, 1923, **129**, 321—322).—When a mixture of carbon dioxide and hydrogen is passed over manganese at 800°, some of the manganese is converted into manganous oxide and some into manganese carbide; the latter yielded methane when treated with water. The gaseous mixture was found to contain carbon monoxide. H. H.

**Polymorphic Transformation of Iron at 370° and the Possibility of Dissolution of Cementite in  $\alpha_1$ -Iron.** G. SIROVICH (*Gazzetta*, 1923, **53**, 674—688).—The existence at 370°

of the point  $A_0$ , corresponding with the polymorphic transformation of  $\alpha_1$ - into  $\alpha_2$ -iron (*La Metall. Ital.*, 1922, **16**, 3) is confirmed by the results of dilatometric measurements, which exhibit anomalous behaviour at that point. Both the  $\alpha_1$ - and the  $\alpha_2$ -modifications of iron possess characteristic coefficients of expansion, so that the conclusions of Le Chatelier, of Charpy and Grenet, and of Driesen with regard to the way in which the coefficient of expansion of iron varies below  $700^\circ$  require revision. The possibility of effecting dissolution of cementite in  $\alpha_1$ -iron by means of maturation, in the field of stability of this iron, on pearlitic steels must be admitted, and such maturation certainly induces in the metal abnormal hardness, which indicates the occurrence of phenomena not yet observed.

T. H. P.

**Ferric Salt as the "Solution Link" in the Stability of Ferric Oxide Hydrosol.** A. W. THOMAS and A. FRIEDEN (*J. Amer. Chem. Soc.*, 1923, **45**, 2522—2532).—Ferric oxide hydrosols prepared from ferric chloride have been investigated with the object of ascertaining the quantitative relationships between the substances constituting the colloid and of determining the amount of electrolyte required to keep the colloidal particles dispersed. It is found that precipitation of the sol is imminent when the ratio  $\text{Fe}_2\text{O}_3/\text{FeCl}_3$  is about 21, and that this value is unaffected by dilution. It is shown that the stability of ferric oxide sol, stabilised by ferric chloride, is due to the solubility, or the solution forces, of the adsorbed ferric chloride in the dispersion medium, rather than to the mutual repulsive forces of the particles presumed to reside in their electrical charges of like sign. The so-called "meta-iron" sol of Péan de St. Gilles (*J. pr. Chem.*, 1855, [1], **66**, 137) is one in which the particles of the dispersed phase are less hydrated than those in Graham's ferric oxide hydrosol.

J. F. S.

**Mechanism of the Mutual Precipitation of certain Hydrosols.** A. W. THOMAS and L. JOHNSON (*J. Amer. Chem. Soc.*, 1923, **45**, 2532—2541).—The mutual precipitation of ferric oxide and silicic acid sols and ferric oxide and arsenic trisulphide sols has been investigated. It is shown that the precipitating ratios depend on the peptising agent. There is chemical equivalence between the peptising agents of ferric oxide hydrosol peptised by ferric chloride and silicic acid sols peptised by sodium silicate, provided the ratio of peptising agent to the dispersed phase falls within a certain range. Outside this range, the precipitation is erratic. Ferric oxide-silicic acid sol precipitations showing chemical equivalence between the peptising agents at maximum precipitation exhibit little variance in precipitation ratios with dilution, whilst those showing a divergence from chemical equivalence approach the chemical equivalence on dilution. The mutual precipitation of ferric oxide-silicic acid sols is due to the removal of the peptising agents by chemical action between them. Qualitative experiment shows that the mutual precipitation of arsenious sulphide hydrosol and ferric oxide hydrosol may be due to the chemical reaction

$S'' + 2Fe''' \rightarrow S + 2Fe''$ . This, however, has not been confirmed quantitatively.

J. F. S.

**Solubility of Nickel Sulphate by the Floating Equilibrium Method.** F. C. VILBRANDT and J. A. BENDER (*Ind. Eng. Chem.*, 1923, **15**, 967—969).—The method for determining solubility described by Dundon and Henderson (*A.*, 1922, ii, 552) was used for measuring the solubility at different temperatures of hydrated nickel sulphates. The new method gives results in good agreement with those obtained by the gravimetric method and is much more rapid. The following results in g. of anhydrous nickel sulphate per 100 g. of water were obtained:  $NiSO_4 \cdot 7H_2O$ :  $-4.25^\circ$ , 27.335;  $-2.0^\circ$ , 23.366;  $0^\circ$ , 26.189;  $6^\circ$ , 30.282;  $15.65^\circ$ , 35.491;  $25^\circ$ , 40.594;  $30^\circ$ , 43.568;  $NiSO_4 \cdot 6H_2O$  (blue):  $31.71^\circ$ , 45.299;  $40^\circ$ , 47.528;  $50^\circ$ , 52.166;  $53.25^\circ$ , 54.041;  $NiSO_4 \cdot 6H_2O$  (green):  $58.21^\circ$ , 55.389;  $60.11^\circ$ , 55.557;  $79.75^\circ$ , 64.476;  $94.22^\circ$ , 72.597.

E. H. R.

**System Chromium-Carbon.** O. RUFF (*Z. Elektrochem.*, 1923, **29**, 469—474).—A criticism of Nischk's paper (*A.*, 1923, ii, 762), in which it is stated that the carbide of chromium richest in chromium has the formula  $Cr_2C$ . In an earlier paper (*A.*, 1918, ii, 399), Ruff and Foehr have shown that a carbide,  $Cr_5C_2$ , exists and can be prepared in quantity. After a discussion of the data furnished in both papers, the author maintains his assertion as to the existence of  $Cr_5C_2$ .

J. F. S.

**Iso- and Hetero-poly-acids. XIX. Molybdi-phosphites and -pyrophosphates. The Structure of Phosphorous Acid.** A. ROSENHEIM and M. SCHAPIRO (*Z. anorg. Chem.*, 1923, **129**, 196—205; cf. this vol., ii, 54; Rosenheim, Weinberg, and Pinsker, *A.*, 1914, ii, 58).—Heteropolymolybdates similar to the heteropolyvanadates have been obtained of the general formulæ  $2R_2O, P_2O_3, 12MoO_3, xH_2O$  (ammonium, potassium, sodium, and lithium) and  $2R_2O, P_2O_3, 5MoO_3, xH_2O$  (potassium, ammonium, and guanidinium) for the phosphites and  $2R_2O, P_2O_5, 12MoO_3, xH_2O$  (sodium and lithium) for the pyrophosphates.

[With A. ITALIENER.]—By measurements of depression of freezing point and elevation of boiling points of aqueous solutions of phosphorous acid, it is concluded that phosphorous acid may be represented as  $H_4(P_2O_6H_2)$  in complete analogy with  $H_4(P_2O_7)$  for pyrophosphoric acid. There is thus a complete series of ions containing phosphorus:  $(PO_4)^{+++}$ ,  $(HPO_3)^{++}$ ,  $(H_2PO_2)^+$ ,  $H_3PO$ , and  $(PH_4)^-$ .  
phosphate
phosphite
hypophosphite
phosphine oxide  
phosphonium

H. H.

**Complex Chlorotungstates.** O. COLLENBERG and K. SANDVED (*Z. anorg. Chem.*, 1923, **130**, 1—17).—The only derivatives of tervalent tungsten known are the potassium salt,  $K_3W_2Cl_9$ , and the corresponding ammonium, rubidium, caesium, and thallium salts prepared from it by double decomposition (*A.*, 1913, ii, 328; 1914, i, 944). It is now shown that in these salts the tungsten is present as part of a complex anion and a number of new com-

pounds have been prepared from the potassium salt by double decomposition with different chlorides. The complex character of the potassium salt was proved qualitatively by ion migration experiments. The freezing point depression in aqueous solutions of the salt  $K_3W_2Cl_9$  indicated that not more than four ions are formed by dissociation of the salt, and conductivity experiments were confirmatory. The complex chlorotungstates are strong reducing agents; solutions of gold, silver, mercury, and copper salts are readily reduced, and powerful oxidising agents oxidise the tervalent tungsten to tungstic acid. With ferric salts, this reaction is quantitative, and can be used for the analysis of the complex salts of tervalent tungsten. The stability of the complex ion,  $W_2Cl_9'''$ , is shown by the fact that the potassium salt interacts with cadmium, copper, and silver salts in presence of strong ammonia to form ammines without precipitation of any tungsten hydroxide.

The following new compounds are generally sparingly soluble in water; their most concentrated aqueous solutions have an intense green colour, becoming yellower on dilution. At lower temperatures, the solutions are fairly stable, more so in presence of hydrochloric acid. The figures in brackets indicate solubility at  $20^\circ$  per 100 c.c. of solution.  $[Cr(NH_3)_6]W_2Cl_9 \cdot 2H_2O$ , dark green, thin, microscopic, rectangular prisms;  $[Co(NH_3)_6]W_2Cl_9 \cdot 6H_2O$  (0.96), bright green, microcrystalline powder.  $[Ag(NH_3)_2]_3W_2Cl_9$  is very unstable towards water and air, losing ammonia and depositing metallic silver.  $Cu(NH_3)_4KW_2Cl_9 \cdot H_2O$  (1.85) forms a finely crystalline powder.  $Cu(NH_3)_4NH_4W_2Cl_9 \cdot H_2O$  (2.4), a green, crystalline powder.  $Cd(NH_3)_4NH_4W_2Cl_9$  (2.17).  $Cd(NH_3)_4KW_2Cl_9$  (1.9). The *pyridine* compound  $(C_5H_5N)_3W_2Cl_9$  (4.7), forms brownish-green, metallic, tabular crystals; the *hexamethylenetetramine* compound,  $(C_6H_{13}N_4)_3W_2Cl_9 \cdot H_2O$  (0.2), is a yellowish-green, crystalline powder; *tetramethylammonium* compound,  $(NMe_4)_3W_2Cl_9$  (1.18), yellowish-brown, microscopic crystals;  $(NEt_4)_3W_2Cl_9$  (relatively high solubility); *trimethylamine* compound,  $(NMe_3)_3W_2Cl_9$ , dark green, thin, pyramidal prisms; *dimethylamine* compound,  $(NH_2Me)_3W_2Cl_9$  (8.25), dark green rhombohedra; *aniline* compound,  $(NH_3Ph)_3W_2Cl_9$  (0.37), greenish-yellow leaflets; *phenyltrimethylammonium* compound,  $(NMe_3Ph)_3W_2Cl_9$  (0.21), a voluminous, greenish-yellow, crystalline powder; *p-tolyltrimethylammonium* compound,  $(C_6H_4Me \cdot NMe_3)_3W_2Cl_9$  (0.48), yellowish-green, striated prisms; *trimethylsulphine* compound,  $(SMe_3)_3W_2Cl_9$  (0.24), a bright green, crystalline powder.

A solution of the free acid,  $H_3W_2Cl_9$ , was obtained by interaction of the thallium salt and hydriodic acid, but the acid could not be isolated. The solubility of the potassium salt,  $K_3W_2Cl_9$ , at  $20^\circ$  is 15.4 g. per 100 c.c. of solution.

E. H. R.

**Solubility of Titanic Acid in Alkali Hydroxides and in Alkali Carbonates. Crystalline Titanium Oxychloride.** V. AUGER (*Compt. rend.*, 1923, **177**, 1302—1304).—The two compounds,  $Na_2TiO_3 \cdot 4H_2O$  and  $K_2TiO_3 \cdot 4H_2O$ , described by Demoly in 1849 are shown not to exist. The approximate solubility of

titanic oxide in alkali hydroxides, etc., has been studied, using either the hydrated oxide or titanic chloride. The results are as follow (figures refer to mg. of  $\text{TiO}_2$  dissolved in 100 c.c. of solution): Sodium hydroxide: 10%, 2—2.5; 36%, 6—10. Potassium hydroxide: 10%, 30—45; 40%, 70—90. Sodium carbonate (saturated) does not dissolve titanic oxide. Sodium hydrogen carbonate (10%), 25. Potassium carbonate: 30%, 2; saturated solution, 30. (All the titanic oxide present in the last three solutions is precipitated on diluting and boiling.) Potassium hydrogen carbonate, saturated solution, 700.

When 1 part of titanic oxide is fused with 40 parts of sodium hydroxide, and the cooled melt extracted with water, the only crystalline material obtained is a hydrate of sodium hydroxide. A little titanic oxide remains in solution, the majority being precipitated even from concentrated solutions. Fusion of titanic oxide with potassium hydroxide, etc., affords a metastable solution of a titanate (containing up to 1,800 mg. of oxide per 100 c.c.), but this deposits most of its titanium (leaving about 100 mg. in solution) in a few hours. Fusion of titanic oxide with sodium carbonate also gives metastable solutions, containing 25—10 mg. of oxide per 100 c.c., all of this being precipitated on keeping. When titanic chloride is added to a mixture of potassium hydrogen carbonate and its aqueous solution, as much as 2,000 mg. per 100 c.c. of titanic oxide remain in solution, 1,300 mg., however, being precipitated in a few hours. A double carbonate is probably present in the more concentrated solutions.

If a solution of titanic chloride in concentrated hydrochloric acid is evaporated in the cold, over sulphuric acid, an *oxychloride*,  $\text{TiO}_2 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ , or  $\text{Ti}(\text{OH})_3\text{Cl} \cdot 2\text{H}_2\text{O}$  is deposited as large, colourless, rhombohedral plates, decomposed in moist air. E. E. T.

**Reduction of Thorium, Zirconium, and Titanium Dioxides.** O. RUFF and H. BRINTZINGER (*Z. anorg. Chem.*, 1923, **129**, 267—275).—The reduction of these oxides by means of metallic calcium and sodium at high temperatures was studied. At 900—950°, sodium alone will not reduce the oxides to any great extent, although calcium gives yields of from 90—100%. The best results were given by a mixture of calcium and sodium containing 30% of the latter. H. H.

**Hafnium or Jargonium.** T. L. WALKER (*Nature*, 1923, **112**, 831).—A suggestion that Sorby's "jargonium" (1869) may have priority over either hafnium or celtium. A. A. E.

**Separation of Hafnium from Zirconium.** G. HEVESY and V. T. JANTZEN (*Chem. News*, 1923, **127**, 353—355).—Detailed accounts are given of the preparation of ammonium zirconium fluoride and ammonium hafnium fluoride from alvite, and of the separation of hafnium from this mineral by the double fluoride method (A., 1923, ii, 570), employing the ammonium double fluorides in place of the potassium double fluorides as previously described. J. S. G. T.

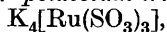
**Iso- and Hetero-poly-acids. XVIII. Vanadioiodates, Vanadioperiodates and a few Vanadiophosphates. The Alkalimetric Determination of Vanadic Acid.** A. ROSENHEIM and K. H. YANG (*Z. anorg. Chem.*, 1923, **129**, 181—195; cf. A., 1922, ii, 47).—By introducing vanadium pentoxide into a boiling aqueous solution of iodic acid, the acids  $V_2O_5 \cdot I_2O_5 \cdot 4H_2O$  and  $V_2O_5 \cdot 2I_2O_5 \cdot 10H_2O$  were obtained according to the amount of iodic acid used. The *potassium*, *ammonium*, and *guanidinium* salts of these acids are described. Similarly, by using alkali periodates and vanadates, the *sodium*, *potassium*, and *ammonium* salts of the type  $3R_2O \cdot 2V_2O_5 \cdot I_2O_7 \cdot xH_2O$  were obtained. By using phosphates and vanadates, if care be taken that the phosphates are sufficiently dilute (2—3 normal), it is possible to obtain salts of the types  $2R_2O \cdot V_2O_5 \cdot P_2O_5 \cdot xH_2O$  and  $R_2O \cdot 2V_2O_5 \cdot P_2O_5 \cdot xH_2O$ . Conductivity measurements were made to ascertain the structures of the various anions.

Vanadic acid is best determined in solution by the addition of excess of sodium hydroxide followed by back titration with sulphuric acid at  $100^\circ$ , using  $\alpha$ -naphtholphthalein as indicator. Iodic acid is also estimated by this method, so that a mixture of the two may be analysed by adopting the above procedure, and then reducing iodate to iodide and determining this with silver. H. H.

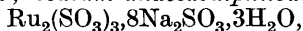
**The Gravimetric Ratio of Antimony to Antimony Tetroxide.** J. KNOP (*Z. anal. Chem.*, 1923, **63**, 181—188).—Pure antimony was treated with nitric acid and subsequently converted into the tetroxide by ignition at  $800$ — $900^\circ$ . The purity of the product was determined by the iodine-thiosulphate method. The results agree with a mean value of 122.04 for the atomic weight of antimony. A. G. P.

**Gold-Chromium Alloys.** R. VOGEL and E. TRILLING (*Z. anorg. Chem.*, 1923, **129**, 276—292).—The temperature-composition diagram for gold-chromium alloys is given in full. Three kinds of mixed crystals are distinguished, one rich in chromium, and two rich in gold. No compounds of definite composition are formed. H. H.

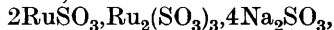
**Chemistry of the Platinum Metals. IV. Alkali-Ruthenium Double Sulphites. II.** H. REMY and C. BREIMEYER (*Z. anorg. Chem.*, 1923, **129**, 215—242; cf. A., 1922, ii, 857).—The preparation of the following new double sulphites of ruthenium and the alkali metals is described: *potassium trisulphitoruthenate*,



dark green needles; *sodium undecasulphitodiruthenate*,



yellowish-white crystals; *sodium ruthenoruthenisulphite*,



dark blue, amorphous powder. In addition, a method of analysis of these salts, involving the determination of the ruthenium as tetroxide and the sulphur as barium sulphate is described.

H. H.

## Mineralogical Chemistry.

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**Bitumen of Judæa. The Sensitivity of Bitumen to Light as a Function of its Degree of Dispersity.** J. ERRERA (*Bull. Soc. chim.*, 1923, **33**, [iv], 1409—1414).—Bitumen which is sensitive to light appears to contain three distinct substances,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -bitumen, of which only the last is sensitive. The author regards bitumen as a "polydispersoid," the sensitive portion being that which is in the form of a disperse colloid. It is the portion with the greatest sulphur content, and this appears to be correlated with polymerisation, molecular and colloidal bitumen being the extremes between which are found intermediates of various degrees of association. Isolation of any one of these probably has a coagulating action. The conclusions are confirmed by evidence from measurements of viscosity and of molecular weight, dialysis, and sensitivity to light. Ultra-filtration is suggested as a method of separating the light-sensitive colloidal bitumen from the molecular portion.

H. J. E.

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## Analytical Chemistry.

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**Application of the Quinhydrone Electrode to Electrometric Acid-base Titrations in the Presence of Air, and the Factors Limiting its Use in Alkaline Solution.** V. K. LA MER and T. R. PARSONS (*J. Biol. Chem.*, 1923, 57, 613—631).—Measurements of the  $p_H$  of solutions of hydrochloric, acetic, and boric acids and of acid potassium phosphate have been made with the quinhydrone electrode, and the results have been compared with those obtained with the hydrogen electrode. In buffered solutions more acid than  $p_H$  8.0, the quinhydrone electrode gives trustworthy results, provided that no rapid oxidising or reducing agents are present. With more alkaline solutions, the results are untrustworthy. This is mainly due to the autoxidation of quinol and to its weak acidic properties. E. S.

**New Methods of Determining Chlorine, Bromine, and Iodine in Organic Compounds. I. Hydrogenation Method.** H. TER MEULEN and J. HESLINGA (*Rec. trav. chim.*, 1923, 42, 1093—1096).—The halogen derivative to be analysed (20—50 mg.) is placed, in a small platinum boat, near the left-hand end of a quartz tube 80 cm. long, the other end of the tube being plugged loosely with cotton wool. A mixture of ammonia and hydrogen is passed through the tube from left to right, and the tube to the right of the boat heated to redness over a distance of about 20 cm. Heating is then commenced to the left of the boat, which, during the course



of about twenty minutes is progressively heated until no further decomposition occurs. The whole of the halogen element present, even in the case of iodine, is converted into ammonium halide, which condenses in the right-hand end of the tube. The latter is washed out with water, the solution acidified with acetic acid, any hydrogen cyanide removed by boiling, and the halogen estimated by Volhard's method.

Explosive substances are mixed with six times their weight of oxalic acid before being analysed, whilst volatile liquids are introduced in small tubes such as are used in ordinary combustions. With a tube partly packed with platinised quartz, very low results are obtained. E. E. T.

**Determination of Dissolved Oxygen in the Presence of Iron Salts.** A. M. BUSWELL and W. U. GALLAHER (*Ind. Eng. Chem.*, 1923, **15**, 1186—1188).—The Winkler method for the determination of dissolved oxygen in water depends on the oxidation of bivalent manganese in alkaline solution, and the liberation of iodine from potassium iodide in acid solution by the oxidised manganese. If iron is present, however, it will be in the ferric state in consequence of the preliminary use of potassium permanganate to oxidise nitrites, etc., and will itself liberate iodine from potassium iodide. Hence too high a value for the dissolved oxygen present is obtained in this case and as the action of ferric iron on the iodide solution is incomplete and depends on the concentration, temperature, and other conditions, no correction can be applied. An investigation of the effect of the presence of iron salts on the Levy-Mohr method, in which the dissolved oxygen is allowed to oxidise ferrous iron in alkaline solution, showed that in this case no error was introduced. C. I.

**Determination of Sulphite and Thiosulphate by Oxidation with Nascent Bromine.** C. MAYR and J. PEYFUSS (*Z. anorg. Chem.*, 1923, **127**, 123—136).—Nascent bromine liberated from an acid bromide-bromate mixture, oxidises sulphurous acid according to the equation:  $\text{SO}_2 + \text{Br}_2 + \text{H}_2\text{O} = \text{SO}_3 + 2\text{HBr}$ ; and thiosulphuric acid according to the equations:  $\text{S}_2\text{O}_2 + \text{H}_2\text{O} + \text{Br}_2 = 2\text{HBr} + \text{SO}_3 + \text{S}$  and  $\text{S} + 4\text{H}_2\text{O} + 3\text{Br}_2 = 6\text{HBr} + \text{H}_2\text{SO}_4$ . Thus  $\text{Na}_2\text{SO}_3 = 2\text{Br}$  and  $\text{Na}_2\text{S}_2\text{O}_3 = 8\text{Br}$ . By using an excess of standard bromide-bromate solution, sulphites may be estimated in the absence of air and excess of bromine used to liberate iodine which may be determined with standard thiosulphate.

Advantage may be taken of the fact that iodine oxidises thiosulphates to dithionates, whilst bromine oxidises them to sulphates, to determine sulphites and thiosulphates in one and the same solution, using the equivalents  $\text{Na}_2\text{SO}_3 = 2\text{I}$  and  $\text{Na}_2\text{S}_2\text{O}_3 = 2\text{I}$ , together with those given above and calculating the amounts of sulphite and thiosulphate from the simultaneous equations so obtained. H. H.

**Determination of Hyposulphite.** BROTHERTON & CO., LTD. (*Chemistry and Industry*, 1923, **42**, 1131).—In an iodometric method proposed for the determination of sodium hyposulphite, the reaction

proceeds according to the equation:  $3\text{Na}_2\text{S}_2\text{O}_4 + 4\text{KIO}_3 + 2\text{KI} = 3\text{I}_2 + 3\text{Na}_2\text{SO}_4 + 3\text{K}_2\text{SO}_4$ . Six g. of potassium iodate and 10 g. of potassium iodide are dissolved in about 500 c.c. of water in a litre flask, 300 c.c. of *N*/10-sodium thiosulphate solution is added, the mixture is diluted to about 950 c.c., and 2 g. of the sample of hyposulphite is added from a weighing bottle. The whole mixture is then diluted to 1,000 c.c., shaken until the hyposulphite is dissolved, and the excess of thiosulphate titrated in an aliquot portion (100 c.c.) with *N*/10-iodine solution. The method cannot be applied to sodium hyposulphite which contains decomposition products or sodium carbonate.

W. P. S.

**Determination of Ammoniacal Nitrogen in certain Nitrogenous Materials and particularly in Proteins and Products of Proteolysis.** J. FROIDEVAUX (*Compt. rend.*, 1923, **177**, 1043—1046).—The method previously described (A., 1922, ii, 454) has been improved. The material is distilled, in presence of aqueous lithium carbonate, keeping the volume of liquid in the distilling flask constant by continued addition of water. The distillate is collected in a series of graduated flasks containing known quantities of standard acid. The distilling flask is heated in a calcium chloride bath kept at 110°. The results are calculated as before, and are satisfactory with proteins, uric acid, amino-acids, and carbamide; special procedure is necessary in the case of some compounds (diphenylamine, oxamide, etc.).

E. E. T.

**Determination of Nitrate Nitrogen in the Presence of Calcium Cyanamide and some of its Derivatives.** K. D. JACOB (*Ind. Eng. Chem.*, 1923, **15**, 1175—1177).—The determination of nitrogen present as nitrate in soil extracts by reduction with Devarda's alloy is interfered with by the presence of cyanamide derivatives. These, however, can be eliminated:—urea by decomposition with urease, and calcium cyanamide, dicyanodiamide and guanyleurea by precipitation with silver sulphate, when an accurate estimation becomes possible. [Cf. B., Jan.]

C. I.

**Determination of the Residual Nitrogen in the Blood.** J. MINICH (*Biochem. Z.*, 1923, **142**, 266—273).—The residual nitrogen of various types of mammalian blood has been determined by Pregl's method after removing the proteins by precipitation with trichloroacetic, phosphomolybdic, phosphotungstic, and metaphosphoric acids, and with uranium acetate. The most consistent results were obtained with the first-mentioned acid, whilst metaphosphoric acid gave the least trustworthy figures, and the other reagents were intermediate between these extremes. No proportionality was observed between the quantity of precipitant used and the residual nitrogen found. Variations in the latter are not solely due to differences in degree of precipitation.

J. P.

**Detection of Small Quantities of Nitric Acid in Poisoning Cases.** C. GHIGLIOTTO (*Ann. Chim. Analyt.*, 1923, **5**, 325).—Tissues that have been in contact with nitric acid are stained blue by treatment with a sulphuric acid solution of diphenylamine.

The lining of the stomach responds to the test if it has been in contact with acid of a greater strength than 0.1%. A. R. P.

**Determination of Organic Phosphorus.** E. J. BAUMANN (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 171—173).—The loss by volatilisation of phosphorus experienced with Bloor's or Bell and Doisy's method is avoided by using 0.2 c.c. of 30% hydrogen peroxide and eight drops of sulphuric acid solution. After removal of most of the water by evaporation on a water-bath, Bell and Doisy's colorimetric method is used for the determination.

CHEMICAL ABSTRACTS.

**Determination of Phosphorus in Organic Materials.** (MILLER) J. GAROLA (*Ann. Chim. Analyt.*, 1923, **5**, 326—328).—The loss of phosphorus during the incineration of organic materials containing it may be avoided by mixing 5 g. of the substance with 0.2 g. of light calcined magnesia and a little water, drying the mixture on a sand-bath, and heating it to dull redness until the residue is free from carbon. It is then dissolved in hydrochloric acid, the solution filtered, and the phosphorus precipitated as magnesium ammonium phosphate by the addition of an ammoniacal solution of ammonium citrate. This process is considerably quicker than the usual Kjeldahl method. A. R. P.

**Determination of Phosphoric Acid by Means of Uranyl Acetate Solution.** G. JANDER and K. REEH (*Z. anorg. Chem.*, 1923, **129**, 302—305).—The phosphate is precipitated as uranyl ammonium salt by the addition of a slight excess of uranyl acetate. The precipitate is filtered, washed, and redissolved in sulphuric acid (about 25%). The solution is heated to incipient ebullition and then reduced with aluminium as previously described (this vol., ii, 65). The quadrivalent uranium is then reoxidised to the sexavalent condition by means of potassium permanganate of known strength, every atom of available oxygen used being equivalent to 1 mol. of uranyl ammonium phosphate. H. H.

**Modification of the Bell-Doisy-Briggs Method for Colorimetric Determination of Phosphoric Acid.** B. SJOLLEMA and H. GIETELING (*Chem. Weekblad*, 1923, **20**, 658—659).—The method (cf. A., 1920, ii, 769; 1922, ii, 718) is now applied to cases such as foodstuffs, urine, etc., in which a preliminary destruction with sulphuric acid is necessary. Comparison is made with a standard phosphoric acid solution to which the reagents used in the destruction (sulphuric acid, potassium and copper sulphates) are added in the same proportions. Since the depth of colour is not proportional to the phosphoric acid present, a correction graph is employed.

S. I. L.

**Separation of Phosphates from Fluorides.** E. MÜLLER and W. WAGNER (*Z. anorg. Chem.*, 1923, **129**, 306—308).—The usual method is to precipitate the neutral phosphate as silver salt, remove excess of silver with sodium chloride, and then precipitate calcium fluoride. The authors criticise the method of neutralising the

solution before adding the silver nitrate. With Methyl-orange as indicator, neutrality is obtained at  $\text{NaH}_2\text{PO}_4$ ; with phenolphthalein, at  $\text{Na}_2\text{HPO}_4$ . As the silver salt is  $\text{Ag}_3\text{PO}_4$ , free hydrogen-ions are liberated during the precipitation, causing solution of the silver phosphate to the extent of 37%. If the solution is neutralised to Methyl-orange after addition of the silver solution, some silver oxide is included in the precipitate. The authors therefore recommend neutralisation with alkali hydroxide, followed by acidification with a very small quantity of nitric acid. H. H.

**Determination of Arsenic in Organic Compounds.** A. KIRCHER and F. VON RUPPERT (*Ber. Deut. pharm. Ges.*, 1923, **33**, 185—186).—It has been suggested by Stollé and Fechtig (A., 1923, ii, 335) that the authors' method for determining arsenic in neosalvarsan (A., 1921, ii, 130) is liable to errors due to the passage of iodine-fixing organic substances into the absorption tube and the loss of arsenic on boiling to remove sulphur dioxide. The concordance of results obtained by the authors' method and that of Stollé and Fechtig proves the above contention to be groundless. W. T. K. B.

**Mixtures Absorbing Carbon Monoxide.** A. PIUTTI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1922, [iii], **28**, 91—96).—The author has investigated the ability to absorb carbon monoxide exhibited by a number of different mixtures, the best results being obtained with cuprous chloride mixed with fine charcoal, granules of pumice, and powdered soda-lime. This mixture is stable in the air and absorbs, per 100 g., 3,960 c.c. of carbon monoxide. T. H. P.

**Determination of Radium in Natural Titano-niobates.** A. KARL and S. LOMBARD (*Compt. rend.*, 1923, **177**, 1036—1037).—The difficulty of obtaining a solution containing the constituents of minerals of the titano-niobate type has led to the following method: The ground mineral is treated with hydrofluoric acid, the product being evaporated to dryness, and fused with potassium hydrogen sulphate until sulphuric anhydride vapours cease to be evolved. The cooled fused mass is mixed with sodium sulphate or even with lithium sulphate as well, to depress the melting point to the minimum obtainable, the whole is raised to a red heat, cooled, broken into pieces, and so transferred to a Pyrex glass tube. By heating at 500—600°, the product becomes completely liquid, and the radium content may be determined in the usual way, the emanation being displaced, using a current of air, and freed, before measurement, from acid fumes, by being passed over soda-lime heated at 150°. E. E. T.

**Gravimetric and Volumetric Determination of Potassium.** W. STREKHER and A. JUNGCK (*Z. anal. Chem.*, 1923, **63**, 161—180).—Comparison is made of a number of methods of determining potassium. Precipitation as potassium cobaltinitrite does not lead to concordant results. The precipitate produced by the addition of sodium cobaltinitrite to potassium salts contains varying proportions of sodium, presumably as the salt  $\text{K}_2\text{NaCo}(\text{NO}_2)_6$ . It is

shown, however, that potassium can be precipitated completely from solution by this means and can be determined in the precipitate by the perchlorate method. Satisfactory results are obtained by reduction of the perchlorate by (1) titanous sulphate, (2) fusion with potassium nitrate and sodium hydroxide, and (3) fusion with hydrazine sulphate and sodium hydroxide, and titration of the chloride produced with silver nitrate. Sodium and potassium can be determined together by determining the mixed chlorides volumetrically, and subsequently precipitating the potassium as perchlorate, which is reduced to chloride and titrated with silver nitrate. Concordant results can be obtained by precipitation of potassium as the hydrogen tartrate and titration with sodium hydroxide. The picric acid method is not of sufficient accuracy owing to the solubility of potassium picrate in the solutions used.

A. G. P.

**Determination of Potassium in Potassium Salts.** MARJAN GÓRSKI (*Przemysł Chemiczny*, 1922, 6, 311—312; from *Chem. Zentr.*, 1923, iv, 488).—Directions are given for the determination of potassium in potassium salts by the perchloric acid method.

G. W. R.

**A New Qualitative Test for Sodium.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, 60, 1251—1255).—The pyroantimonate test for sodium is not very sensitive, and is trustworthy only in the absence of heavy metals and salts of ammonium and the alkaline earths. Magnesium uranyl acetate, which has long been employed for the micro-chemical detection of sodium, may be employed in ordinary qualitative analysis, and in 50% alcohol solution will detect as little as 50 mg. of sodium per litre. The reagent is very suitable when potassium salts are present, and will indicate 0.5% of sodium in a potassium salt; salts of ammonium, lead, zinc, aluminium, magnesium, and the alkaline earths do not interfere, and the reagent may be used directly to detect sodium in them.

S. I. L.

**Determination of Cæsium as Perchlorate.** E. MURMANN (*Oesterr. Chem. Ztg.*, 1923, 26, 164).—About 0.5 g. of cæsium nitrate is dissolved in 50 c.c. of water, an excess of 10% perchloric acid is added, and the mixture is evaporated. The residue of cæsium perchlorate, when cold, is treated with a small quantity of water containing perchloric acid, collected on a weighed filter, washed successively with 50% alcohol (containing a drop of perchloric acid), 95% alcohol, and ether, then dried at 100°, and weighed. Sulphates and potassium, rubidium, barium, and ammonium salts must not be present.

W. P. S.

**New Method of Titrating Silver and Halogen-Ions with Organic Dyes as Indicators.** K. FAJANS and O. HASSEL (*Z. Elektrochem.*, 1923, 29, 495—500).—Very dilute solutions of the alkali salts of fluorescein and its halogen substitution products show characteristic colour changes in the presence of silver halide sols, when the solutions contain an excess of silver-ions. The

colour change is attributed to the association of the dye anion with the excess silver-ions which are adsorbed by the silver halide. By this association, the electron sheaths of the dye anions undergo a similar change to that brought about in the formation of their silver and other salts. The colour change, brought about in the presence of an excess of silver-ions, can in some cases be reversed by an excess of halogen-ions. The halogen-ions in such cases displace the dye anions from the silver halide surface. The ease with which this occurs depends, on the one hand, on the adsorbability of the halogen-ion, and, on the other, on the adsorbability of the dye anion. In the case of the halogen-ions, the adsorbability increases in the order  $I'$ ,  $Br'$ ,  $Cl'$ , and in the case of the dye anions in the order fluorescein, dibromofluorescein, eosin, di-iodofluorescein, and erythrosin. On account of this behaviour, these substances can be used as indicators in the titration of halogen-ions with silver-ions. In the case of chlorides, fluorescein alone may be used, the concentration of indicator should be about  $1/300000M$ , and the titration carried to a red colour. In the case of bromine and iodine, dibromofluorescein and eosin may be used, the concentration of the indicator (eosin) being  $1/30000M$ , the titration being carried to a violet colour. In a mixture of chloride and iodide, the iodide alone can be titrated with eosin as indicator and the sum of the two halogen-ions with fluorescein as indicator. J. F. S.

**Determination of Calcium by the Opacimetric [Nephelometric] Method.** C. CHÉNEVEAU and R. BOUSSU (*Compt. rend.*, 1923, 177, 1296—1298).—A continuation of previous work (A., 1920, ii, 327). It is shown that suspended calcium oxalate precipitates obey, within certain limits, the general optical laws for turbid liquids, and that the determination of calcium by the nephelometric method is always possible, but necessitates careful preliminary experiments. E. E. T.

**Lead. VIII. The Microchemical Detection of Lead.** L. T. FAIRHALL (*J. Biol. Chem.*, 1923, 57, 455—461).—Behrens and Kley's "triple nitrite test," which depends on the formation and recognition of the crystalline hexanitrite of potassium, copper, and lead [ $K_2CuPb(NO_2)_6$ ], is employed. The conditions for carrying out this test on the ash from biological material containing traces of lead have been standardised. Amounts as small as  $1\mu$  g. may be detected. E. S.

**Electro-analytical Determination of Thallium by Means of the Anodic Deposition of Thallic Oxide.** W. DIETERLE (*Z. Elektrochem.*, 1923, 29, 493—495).—Using the method previously described by Gutbier and Dieterle (A., 1923, ii, 880), the author has investigated the determination of thallium by anodic deposition of thallic oxide. The following method is recommended: a solution containing 0.1—0.5 g. of thallous nitrate and 0.1 g. of free nitric acid is placed in a roughened platinum dish, diluted to 100 c.c. with water, and either 10 c.c. of absolute alcohol or 5—10 c.c. of rectified acetone added. The dish is made the anode in the

electrolysis, and the cathode is a disk of platinum of 12 cm.<sup>2</sup> which is rotated at 300 revolutions per minute. The electrolysis is carried out at 60—62° directly from a single lead accumulator. After ten hours, the voltage is raised to 2·5—3·0, and a current of 0·05 ampere passed for a short time. The deposit, which is firm, is washed with water and dried at 160—170°, preferably in an electrically heated oven, but in any case reducing gases must not come into contact with the deposit. When dry, the dish is cooled in a desiccator and weighed rapidly, since the deposit is somewhat hygroscopic. The method is good, the results being associated with an error of  $\pm 0\cdot2\%$ . J. F. S.

**The Quantitative Separation from a Complex Mixture of Very Small Quantities of Copper, Zinc, Nickel, and Cobalt.** G. BERTRAND and M. MOKRAGNATZ (*Bull. Soc. chim.*, 1923, [iv], 33, 1539—1547).—A method of separating traces of copper, zinc, nickel, and cobalt from mixtures is described in detail. It is based on the precipitation of the hydroxides of the metals by ammonia in the presence of calcium hydroxide. In the case of zinc, a crystalline compound of the formula  $(\text{OH}\cdot\text{Zn}\cdot\text{O})_2\text{Ca}, n\text{H}_2\text{O}$  is obtained, but the precipitate given by each of the other metals may be a mixture of the hydroxide of that metal with a calcium compound. Experimental results for comparison of the method with standard procedure are given; these show good agreement. [Cf. *B.*, Jan.] H. J. E.

**The Solubility of Mercuric Sulphide in Ammonia and Its Influence on the Tests for Mercury and Arsenic.** C. GHIGLIOTTO (*Ann. Chim. Analyt.*, 1923, 5, 326).—In toxicological analysis, the organic matter is destroyed by heating with sulphuric acid; this solution, after treatment with hydrogen sulphide for the precipitation of arsenic and mercury, yields a mixture of sulphur and organic sulphur compounds. If the precipitate is extracted with ammonia to dissolve any arsenic, all the mercury will also dissolve owing to the presence of the sulphur and organic sulphides, and on subsequent treatment for arsenic by the Marsh test no mirror will be obtained if mercury is present. Thus neither arsenic nor mercury may be detected. The solution should be again evaporated with sulphuric acid and the heating continued for some time; subsequent treatment according to the usual methods will then give satisfactory separations. A. R. P.

**Determination of Aluminium and its Separation from other Metals.** G. JANDER and B. WEBER (*Z. angew. Chem.*, 1923, 36, 586—590).—The method of determining aluminium in alloys which is based on the sublimation of the chloride in a current of dry hydrogen chloride gas (Jander and Wendehorst, *A.*, 1922, ii, 529) suffers from the disadvantage that traces of magnesium and manganese sublime together with the aluminium chloride. A complete separation of these metals is effected by a series of re-sublimations carried out under carefully controlled conditions in a

slightly modified apparatus, a diagram of which is given. The slight trace of manganese subliming in the first sublimation is easily separated, but the somewhat large quantity of magnesium is only separated after four or five resublimations which are carried out by driving the sublimate on to successive portions of a glass tube lying inside the sublimation tube proper, on which the aluminium chloride is ultimately allowed to deposit. The subliming operation takes about three hours. The improved method affords an accurate means of determining aluminium directly in alloys, and of separating it from the other metals present in much smaller proportions, so that the determination of these metals can be effected with much greater accuracy. The method also allows of the determination of oxides such as silica and alumina, which occur in alloys and cause important variations in their properties. The aluminium chloride can eventually be obtained with less than 0.007% of manganese and 0.025% of magnesium. Details are given of the behaviour of the other metals present on heating in a current of dry hydrogen chloride gas. Any elementary silicon present sublimes as hydrides or silico-chloroform, and is subsequently separated from the aluminium chloride by evaporation with acids and filtration. The silicon in "Silumin" can be accurately determined by dissolving the alloy in dilute hydrochloric acid, filtering off the silicon, and weighing. Only 0.05% of silicon was found to escape in this process in the form of volatile compounds. Specimen analyses of various alloys are given. H. C. R.

**Titrimetric Determination of Aluminium in Aluminium Salts, in particular in "Liquor Aluminii Acetici."** A. WÖHLK (*Ber. Deut. pharm. Ges.*, 1923, **33**, 195—204).—Owing to various objections to the titrimetric method proposed by Valentin (*Apoth.-Ztg.*, 1912, 590), notably the uncertainty of the composition of the precipitated basic aluminium arsenate and of the accuracy of iodimetric titrations of arsenic acid in strongly acid solution, the following method, which gives accurate results, is preferred. To a known quantity (about 10 c.c.) of "Liquor aluminii acetici" is added 10 c.c. of a solution (12 g. of sulphuric acid and 6.5 g. of potassium sulphate made up to 100 c.c. with water), and the potassium alum formed is completely precipitated by addition of 90% ethyl alcohol (100 c.c.). The precipitate is collected, repeatedly washed with 20 c.c. of 70% alcohol, and finally dissolved in boiling water. The subsequent procedure depends on the reactions  $\text{Al}_2(\text{SO}_4)_3 + 3\text{BaCl}_2 = 3\text{BaSO}_4 + 2\text{AlCl}_3$  and  $\text{AlCl}_3 + 3\text{NaOH} = \text{Al}(\text{OH})_3 + 3\text{NaCl}$ . To the alum solution is added 20 c.c. of a barium chloride solution (containing 4 g.) and five drops of 1% phenolphthalein, and *N/1*-sodium hydroxide is run in, without removing the barium sulphate, until a red colour is obtained. The solution is diluted to 200 c.c., and the hydrolysis completed by heating to boiling. The titration with sodium hydroxide is then carried to the true end-point. The application of this method to aluminium salts in the presence of ammonium and iron salts is being investigated. W. T. K. B.



**The Simultaneous Electrometric Determination of Iron and Manganese.** E. MÜLLER and O. WAHLE (*Z. anorg. Chem.*, 1923, 130, 63—68).—When the titration of a ferrous salt with potassium permanganate is continued, after the normal end-point has been reached, in presence of hydrofluoric acid, a second reaction takes place, namely, the oxidation of the manganous salt, according to the equation  $\text{MnO}_4' + 4\text{Mn}'' + 8\text{H}' = 5\text{Mn}''' + 4\text{H}_2\text{O}$ . The second reaction requires one-quarter as much permanganate as the first. Both end-points are sharply marked on the electrometric titration curve, but if the first reaction takes place in presence of hydrofluoric acid, the first end-point is reached too soon, because ferrous salts in presence of fluoride-ions are very susceptible to atmospheric oxidation. Obviously the method of titration can be applied to the determination of manganese already present with the ferrous salt. It is recommended to carry out the first titration colorimetrically in presence of sulphuric acid in a platinum dish at 18°, then to add 7 g. of potassium fluoride and 5 c.c. of 2*N*-sulphuric acid per 100 c.c. of solution, and titrate the manganese electrometrically at 80°.

E. H. R.

**Interference of Cobalt in the Bismuthate Method for Manganese.** G. E. F. LUNDELL (*J. Amer. Chem. Soc.*, 1923, 45, 2600—2603).—The proper conditions for the determination of manganese by Blum's bismuthate method (*A.*, 1912, ii, 1214) have been investigated, and it is shown that, in addition to the conditions laid down by Blum, the following must also be observed. The solution should not contain more than 0.05 g. of manganese; moderate amounts of sulphuric acid are not harmful, as, for example, 5 c.c. of sulphuric acid and 10 c.c. of nitric acid in 50 c.c. of solution; chlorides must be absent; the temperature of the solution may be varied from 5° to 25°; half a minute is a sufficient time for agitating the solution, but a longer agitation will do no harm; the bismuthate should always be tested for its oxidising power before use; the asbestos used in the filtration must be very carefully purified, all hydrochloric acid and chlorides must be removed from it; the ferrous sulphate solution should not be kept more than ten minutes before titration, and the permanganate solution, which may be 0.03*N* or 0.10*N*, is best standardised against sodium oxalate as described by McBride (*A.*, 1912, ii, 494). When these precautions are taken, the accuracy of the method for amounts up to 0.05 g. is within 1 part in 500 parts. The process is singularly free from interference by other elements, the only elements which have been recognised as troublesome being chromium and cerium. The interference caused by these and other elements is discussed. Cobalt is oxidised by the bismuthate and the oxidised compound reacts with both ferrous sulphate and permanganate. The latter reaction does not commence until some permanganate has been decomposed and then proceeds so rapidly that it causes low results for manganese. In the presence of cobalt, Ford's method is to be preferred for accurate analyses and the persulphate arsenite method for routine work.

J. F. S.

**Determination of Small Quantities of Molybdenum. Application to Ammonium Phosphomolybdate for the Indirect Titration of Phosphorus.** A. VILA (*Compt. rend.*, 1923, 177, 1219—1221).—If ammonium molybdate or phosphomolybdate is reduced in hydrogen at 700° (silica tube), it is quantitatively reduced to molybdenum. A solution of molybdic acid (5 g.) in 60% phosphoric acid (10 c.c.) is decolorised with permanganate and diluted to 50 c.c. The molybdenum is dissolved in this solution. After diluting and boiling, molybdenum-blue,  $\text{MoO}_2 \cdot 4\text{MoO}_3$ , is formed quantitatively, and may be titrated against permanganate (cf. Fontès and Thivolle, A., 1923, ii, 264). The method is used for determining small quantities of phosphorus. E. E. T.

**Determination of Rare Metals, and their Separation from Other Metals. III. The Separation of Uranium from Titanium, Iron, and Aluminium.** L. MOSER (*Monatsh.*, 1923, 44, 91—96).—The separation by hydrogen sulphide from an ammoniacal sulphosalicylic acid solution occurs readily, but the uranium sulphide is precipitated in a colloidal condition, so that filtration is extremely difficult, and the precipitate carries down other salts from the solution. The separation by means of the soluble complex carbonate,  $(\text{NH}_4)_4\text{UO}_2(\text{CO}_3)_3$ , formed by addition of ammonium carbonate, which throws down the common metals, is quantitative only in presence of titanium if very small amounts of uranium compounds are present.

Titanium may be separated as the hydroxide,  $\text{Ti}(\text{OH})_4$ ; the two oxides are precipitated together by ammonia, and after ignition and weighing are dissolved by fusion with potassium sodium carbonate and treatment with hydrochloric acid. Addition of potassium bromate and sulphate precipitates the titanium hydroxide, which is filtered off, dried, and weighed; uranium may be separated from the bromate-free filtrate by precipitation with ammonia, but if aluminium is present, ammonium carbonate in excess is added to the neutralised solution to remove this as hydroxide; the precipitation must be repeated to get a good separation. Iron is also separated by the complex carbonate method, the precipitation being repeated for quantitative work. S. I. L.

**Determination of Uranyl Compounds.** G. JANDER and K. REEH (*Z. anorg. Chem.*, 1923, 129, 293—301).—Sexavalent uranium is reduced to the quadrivalent state in sulphuric acid solution, and may then be reoxidised by means of standard permanganate according to the equation:  $2\text{MnO}_4^- + 5\text{U}^{IV} + 2\text{H}_2\text{O} = 2\text{Mn}^{II} + 5\text{UO}_2^{++} + 4\text{H}^+$ . The end-point is quite sharp. In view of the fact that statements are to be found that acid reduction of  $\text{U}^{VI}$  proceeds to a point below  $\text{U}^{IV}$ , tests were carried out using zinc, zinc amalgam, and aluminium for the reduction of a standard uranyl solution. Both zinc and zinc amalgam were found to be most unsuitable, but aluminium in sulphuric acid reduces  $\text{U}^{VI}$  quantitatively to  $\text{U}^{IV}$ . A correction must be applied for any iron present in the aluminium used. H. H.

**Determination of Titanium by Reduction with Zinc and Titration with Permanganate.** G. E. F. LUNDELL and H. B. KNOWLES (*J. Amer. Chem. Soc.*, 1923, **45**, 2620—2623).—Titanium may be determined volumetrically as follows. A solution of titanic sulphate in 5 vol.% sulphuric acid is run through a Jones's reductor, 19 mm. bore containing a column of zinc 43 cm. in length, into a bottle containing three times as much ferric sulphate solution as is necessary to oxidise the tervalent titanium back to the titanic state of oxidation. The solution is then titrated with a 0.1*N* solution of permanganate. The results are extremely accurate in the absence of substances which interfere with the reaction. All substances with such interfering action except niobium can be readily removed by well-known methods. Substances which interfere are some organic compounds, tin, arsenic, antimony, molybdenum (ous), iron (ous), chromium (ous), vanadium (ous), tungsten, uranium, and niobium. The above method for the determination of titanium is superior to the method in which the reduced material is run into standard permanganate and to methods in which the titanous solution is collected and prepared in atmospheres of hydrogen or nitrogen. Titanous solutions required for standard solutions can be prepared by means of a Jones's reductor, which passes through the cork of a bottle through which a current of hydrogen is being circulated. J. F. S.

**Electrometric Determination of Vanadium, and Uranium, Separately, in the Presence of One Another, and in the Presence of Iron.** E. MÜLLER and A. FLATH (*Z. Elektrochem.*, 1923, **29**, 500—508).—The authors have repeated the electrometric titrations of Gustavson and Knudson (*A.*, 1923, ii, 185) of vanadium, uranium, and iron, separately and in the presence of one another. It is shown that vanadium when titrated electrometrically with potassium permanganate at 80° shows three sharply marked breaks in the titration curve. The volume of permanganate used between the first and second break corresponds with the oxidation from tervalent vanadium to quadrivalent vanadium, and that between the second and third break to the oxidation from quadrivalent vanadium to quinquivalent vanadium. These breaks are very sharp, very much sharper than those obtained in a titration at 18°. In the presence of iron at 80°, the three vanadium breaks are found in the curve, but the break for the oxidation  $\text{Fe}^{\text{II}} \rightarrow \text{Fe}^{\text{III}}$  is not clear; at the ordinary temperature, the iron break is sharp and the  $\text{V}^{\text{III}} \rightarrow \text{V}^{\text{IV}}$  disappears. Iron and vanadium can be estimated in mixtures by reducing in a Jones's reductor, then titrating at 80° to the second break, which leaves the vanadium in the  $\text{V}^{\text{IV}}$  stage, then in cold solution to the third break, where the iron is all oxidised, and finally at 80° to the fourth break, where the vanadium is in the stage  $\text{V}^{\text{V}}$ . The amount of iron can then be calculated from that of permanganate used for the cold titration between the second and third breaks and the vanadium from the amount used between the first and second, or the third and fourth, breaks. Uranium solutions reduced by zinc to the stage  $\text{U}^{\text{IV}}$  are oxidised

by permanganate in the presence of sulphuric acid to the stage  $U^{VI}$ , and at this point a definite break is shown in the titration curve for  $80^\circ$ . In the case of mixtures of uranium and iron, the titration with permanganate after reduction is carried to the first break in the titration curve at  $80^\circ$ , which indicates the completion of the oxidation  $U^{IV}$  to  $U^{VI}$ , and then to the second break at  $18^\circ$ , which indicates the completion of the oxidation  $Fe^{II} \rightarrow Fe^{III}$ . Mixtures of vanadium and uranium are titrated at  $80^\circ$  with permanganate, the permanganate used between the first and second breaks effects the oxidations  $V^{III} \rightarrow V^{IV}$  and  $U^{IV} \rightarrow U^{VI}$ , and that between the second and third breaks,  $V^{IV} \rightarrow V^V$ . Mixtures of uranium, vanadium, and iron are reduced with zinc and titrated at  $80^\circ$  to the second break in the titration curve with permanganate; at this point the oxidations  $V^{III} \rightarrow V^{IV}$  and  $U^{IV} \rightarrow U^{VI}$  are complete, then the titration is continued at  $18^\circ$  to the third break, where the oxidation  $Fe^{II} \rightarrow Fe^{III}$  is complete, and then at  $80^\circ$  to the fourth break, where the oxidation  $V^{IV} \rightarrow V^V$  is complete.

J. F. S.

**Volumetric Determination of Vanadium in Steel.** A. T. ETHERIDGE (*Analyst*, 1923, 48, 588—590).—Two g. of steel is dissolved in 5 c.c. of dilute sulphuric acid in a 500 c.c. flask. Two to three c.c. of nitric acid (*d.* 1.42) is added and any residual carbide dissipated if necessary by digestion with a little more nitric acid. The solution is evaporated until fumes of sulphur trioxide appear. Nitric acid destroys the diphenylcarbazine subsequently used as an indicator and must be removed. The sulphates are dissolved in 400 c.c. of water and the solution is boiled, porous plate being added to prevent bumping, after which a saturated solution of potassium permanganate is added, drop by drop, until a permanent precipitate is formed, and boiling is continued for fifteen minutes. A large excess of manganese dioxide must be avoided or chromium and vanadium may be associated with the precipitate. The solution is cooled, filtered through asbestos, and the precipitate washed with cold water, the filtrate being received in a large Erlenmeyer flask. Fifty c.c. of syrupy phosphoric acid is added and, after cooling, a slight excess of ferrous ammonium sulphate to reduce chromate and vanadate. This excess is titrated with 0.1N permanganate to a permanent pink. Fifty c.c. of concentrated sulphuric acid is now added and the solution cooled, after which sufficient standard ferrous ammonium sulphate solution is added to reduce all the vanadium and also to leave a small excess, the approximate amount of vanadium present being found by preliminary tests, either by this process or colorimetrically with hydrogen peroxide. After thorough shaking, standard 0.1N dichromate solution is added until within a few c.c. of the end, this end-point being approximately known from the preliminary test. The indicator is prepared as follows: 0.05 g. of diphenylcarbazine is dissolved in a few c.c. of glacial acetic acid and diluted to 500 c.c. Five c.c. of this solution is acidified with three drops of dilute sulphuric (1 : 3) and one drop of 0.1N dichromate solution added. About half of this solution is added to the liquid

in the flask and dichromate solution continually added until the purple colour has faded away. The remainder of the indicator is now added and the titration continued until the purple colour is discharged and the solution becomes apple-green. The ferrous ammonium sulphate is standardised under the same conditions of acidity and volume as in the test. The difference between the two titrations represents vanadium in terms of 0.1*N* dichromate solution. The process was tested on electrolytic iron to which known amounts of vanadium and chromium had been added. Up to 2% of vanadium, results correct to within 0.02% are obtained, but beyond 2% of chromium, the green chromic sulphate obscures the end-point, and for 4% chromium steel it is recommended that work be carried out on a 1 g. sample. The presence of cobalt interferes with the permanganate end-point. H. C. R.

**Colorimetric Determination of Small Quantities of Bismuth.** C. E. LAPORTE (*J. Pharm. Chim.*, 1923, [vii], 28, 304—305; cf. A., 1923, ii, 792).—The method is based on the precipitation of bismuth as quinine iodobismuthate followed by solution in acetone. The intensity of the coloration of the acetone solution varies from clear yellow to orange-yellow proportionally to its bismuth content; 0.0001 g. of bismuth can be determined with an error not exceeding 2—3%. To determine bismuth in urine, the ash is taken up in 10% nitric acid in sufficient excess to prevent the formation of the basic salt, and is treated with Leger's reagent as modified by Aubry (A., 1922, ii, 165), containing 1% quinine sulphate and 2% potassium iodide. It is better to make up the solutions of quinine sulphate and potassium iodide separately and mix the two as required. The precipitation of bismuth is quantitative, and the orange-yellow precipitate that is formed is dissolved in acetone and its intensity compared with a standard solution prepared similarly. D. R. N.

**An Improved Method for the Separation of Gas Mixtures.** M. SHEPHERD and F. PORTER (*Ind. Eng. Chem.*, 1923, 15, 1143—1146).—The apparatus described was designed for the separation of the hydrocarbons in natural gas by fractional distillation for the purpose of analysis and for the preparation of constituents in a state of purity with greater expedition than was possible with older types. The whole apparatus, including distillation bulbs, pump, reservoirs, and measuring burette, is constructed in one unit. Three distillation bulbs are provided permitting of a rapid distillation from one and condensation of the vapour in another (by varying the pressure on the liquid air jackets surrounding them). In the case of natural gas, the nitrogen and helium which remain uncondensed at  $-190^{\circ}$  are at once removed and measured. The methane fraction is twice distilled and condensed in successive distillation bulbs and is then removed and measured, and the higher homologues are similarly separated one by one, the temperatures of the bulbs being appropriately controlled throughout. Tests with an artificially prepared gas mixture have demonstrated the accuracy of this procedure. For the preparation of pure gases suitable for the determination of physical constants, repeated distillations are

necessary. Analyses performed by the above method differ from those obtained by the combustion method, but this is attributable to the impossibility of obtaining a correct percentage composition of a mixture of more than two hydrocarbons by the latter method and to the difficulty of obtaining complete combustion. C. I.

**Determination of Methyl Alcohol.** A. B. LYONS (*J. Amer. Pharm. Assoc.*, 1922, **11**, 682—686; cf. *ibid.*, 12).—Dried egg-albumin is used in preference to milk or peptone, and Chapin's method of oxidation, using permanganate, is employed. A very dilute solution of methyl alcohol containing about 1% of ethyl alcohol is oxidised, and 1 c.c. is mixed with 1 c.c. of water containing 0.005—0.010 g. of egg-albumin, and 2 c.c. of sulphuric acid containing a trace of ferric chloride. The purple colour, which reaches a maximum intensity in ten minutes, is compared with a standard.

CHEMICAL ABSTRACTS.

**Detection of Methyl Alcohol in Ethyl Alcohol.** C. H. LA WALL (*Amer. J. Pharm.*, 1923, **95**, 812—820).—The literature of the subject is reviewed. It is considered that the test depending on the oxidation of the alcohols with permanganate and the testing of the solution of aldehydes for formaldehyde with the magenta-sulphuric acid test solution described in the U.S. Pharmacopœia, tenth revision, is satisfactory. The cooling of the solution after the addition of the sulphuric acid can be obviated by adding acid previously diluted (1 : 3) and cooled. The test is sensitive to 1 part of methyl alcohol in 500 parts of ethyl alcohol, and if smaller proportions are present or suspected a preliminary fractionation may be carried out and the test applied to the 1 c.c. fraction coming over first from a 10 c.c. sample. In this way, positive reactions were obtained with 1 part of methyl alcohol in 10,000 parts of ethyl alcohol. H. C. R.

**Ether Anæsthesia. I. The Estimation of Ethyl Ether in Air and in Blood, and its Distribution Ratio between Blood and Air.** P. A. SHAFFER and E. RONZONI (*J. Biol. Chem.*, 1923, **57**, 741—760).—A modification of the Nicloux method for the estimation of ether in air, water, or blood is described. The solution is aerated and the air passed through a series of three tubes containing 50% sulphuric acid and dichromate in excess of that required for the oxidation. When absorption is complete, the solutions are heated to boiling to complete the oxidation. After cooling, the contents of the tubes are washed into a flask, diluted with water, potassium iodide is added, and the iodine liberated titrated with thiosulphate. The difference between this result and that obtained with a blank experiment gives the amount of dichromate used in oxidising the ether to acetic acid. No carbon dioxide is produced if the temperature and concentration of acid are properly controlled. If desired, the ether may be absorbed in one tube of concentrated acid. This is then diluted to 40 or 50% and a measured quantity of dichromate added; the remainder of the procedure is as above. Using this method, the distribution of ether between air and water and air

and blood has been determined for a series of temperatures. The ratios obtained below 35° are somewhat higher than those obtained by Haggard (A., 1923, ii, 343); between 35° and 40°, the results agree. E. S.

**Determination of  $\beta$ -Naphthol in  $\alpha$ -Naphthol and  $\alpha$ -Naphthol in  $\beta$ -Naphthol.** J. PROCHAZKA (*Ind. Eng. Chem.*, 1923, 15, 944—945).—To determine  $\beta$ -naphthol in  $\alpha$ -naphthol, use is made of the fact that the latter couples in acid solution with *p*-nitrodiazobenzene, whilst the former does not, or only very slowly.  $\alpha$ -Naphthol (0.36 g.) is dissolved in 30—40 c.c. of alcohol, cooled to 5°, and titrated with *p*-nitrodiazobenzene solution (100 c.c. = 1 g. of nitrite) containing about 30—50% excess of hydrochloric acid above the theoretical amount for diazotisation. Rather less than the calculated quantity of diazo-solution is run in fairly quickly, and the solution left for about thirty minutes. The *p*-nitrobenzene-azo- $\alpha$ -naphthol separates, and the disappearance of the diazo-compound is determined by spotting on filter-paper with dilute sodium hydroxide solution. Addition of diazo-solution is then continued. When all the  $\alpha$ -naphthol has combined, the spot test, after further addition of diazo-solution, shows the red colour of *p*-nitrobenzene-azo- $\beta$ -naphthol. The volume of diazo-solution used is a measure of the purity of the  $\alpha$ -naphthol; the  $\beta$ -naphthol is obtained by difference. The method of determining  $\alpha$ -naphthol in  $\beta$ -naphthol consists in adding to an alcoholic solution of the naphthol rather more than sufficient *p*-nitrodiazobenzene to combine with all the  $\alpha$ -naphthol present. After half an hour, the solution is diluted with boiling water, the precipitate of impure *p*-nitrobenzene-azo- $\alpha$ -naphthol collected on a filter, washed with hot water, and then boiled with 0.5% sodium hydroxide solution. The blue solution is filtered and compared colorimetrically with standard solutions of pure *p*-nitrobenzene-azo- $\alpha$ -naphthol or, since the colour is fugitive, with a secondary standard, for instance the colour from tetrazotised benzidine coupled with H-acid (Diamine Blue 2B). E. H. R.

**The Detection of Pentose, Formaldehyde, and Methyl Alcohol.** J. B. SUMNER (*J. Amer. Chem. Soc.*, 1923, 45, 2378—2380).—Bial's reagent for pentoses will keep if the six g. of orcinol and forty drops of 10% ferric chloride solution are dissolved together in 200 c.c. of ethyl alcohol, without the addition of hydrochloric acid. Fifteen drops of this solution, 5 c.c. of the sugar solution, and an equal volume of fuming hydrochloric acid are heated at 100°. A clear blue colour develops if 1 mg. of arabinose or xylose is present; with less pentose, the colour is green, with more, a precipitate is formed.

With formaldehyde, a white precipitate appears, but only on heating if the concentration is small. With a very small quantity of formaldehyde the precipitate is not formed, but a yellow coloration is developed. When the material is heated at 100° for fifteen minutes, the precipitate turns brown; it now dissolves in an excess of alkali to give a pink solution, or, with much precipitate, pink

flocks are produced. With such a small quantity of formaldehyde that there is no precipitate after heating for fifteen to twenty minutes, the addition of sodium hydroxide produces a pink or salmon-coloured solution, with a green fluorescence, which is so intense that this test will readily show one part of formaldehyde in ten million parts of water.

One part of formaldehyde in one million parts of water may be detected by the use of an alcoholic solution of orcinol and two drops of 20% sodium hydroxide solution. The solution becomes pink owing to oxidation by atmospheric oxygen. The test is only of use in the absence of certain interfering substances. Acetaldehyde gives a similar precipitate with orcinol, ferric chloride, and hydrochloric acid, but only in concentrated solution; this precipitate does not darken on heating, and dissolves in alkali to give a yellow solution, which, however, does not show any fluorescence.

The formation of the white precipitate may be used as a test for methyl alcohol, after its oxidation to formaldehyde. The most suitable oxidising agent is potassium dichromate and sulphuric acid, since this forms very little formaldehyde from ethyl alcohol. One c.c. of the suspected alcohol, *e.g.*, from the distillation of an alcoholic beverage, 2 c.c. of 6.7% potassium dichromate solution, and 2 c.c. of 62% sulphuric acid are allowed to remain. If the reduction to blue chromic sulphate takes much longer than forty seconds, too much water is present. Fifteen c.c. of water is added, and the mixture heated at 100° for ten minutes. Five mg. of orcinol in one c.c. of water is added, and the heating continued. If the alcohol contains 5% or more of methyl alcohol, a precipitate is formed after about five minutes. With only 1% fifteen minutes are required. The test will show methyl alcohol down to 0.5%, but it may then be necessary to heat for thirty minutes, and then cool. Even smaller quantities may be detected by removing the chromium by heating with sodium hydroxide. The filtered solution has a green fluorescence if traces of methyl alcohol are present. Formic acid, amyl alcohol, acetone, and furfuraldehyde do not interfere with the reaction. Glycerol is eliminated during the distillation of the alcohol, but gives a positive test if even as little as 5 mg. is added to the distillate.

W. S. N.

**Determination of Pentoses and Pentosans. II. Determination of Furfuraldehyde.** N. C. PERVIER and R. A. GORTNER (*Ind. Eng. Chem.*, 1923, **15**, 1255—1262).—Several new volumetric methods for determining furfuraldehyde in dilute aqueous solution were tested. Iodine in alkaline solution did not give dependable results and acid permanganate was unsuccessful owing to the catalytic reduction of the permanganate by furfuraldehyde. The use of potassium bromate in acidified furfuraldehyde solutions containing potassium bromide was eminently successful. Specific directions are given for obtaining theoretical yields of furfuraldehyde from pentose materials and for the volumetric determination of this substance in the resulting distillates. Representative results of determinations on pure pentoses and pure furfuraldehyde are



recorded and the factors to be used for the conversion of potassium bromate used to furfuraldehyde, pentose, pentosan, or the corresponding methyl derivatives are given. The acidity of the solution to be titrated should not exceed 4—5% as further oxidation of the primary product of the interaction of bromine and furfuraldehyde results in the presence of high concentrations of acid. The velocity of this secondary reaction appears to be so small as to be without appreciable effect on the titration if the conditions proposed are adhered to. Either hydrochloric or sulphuric acid may be used and a potassium bromide solution of approximately 1% concentration is satisfactory. The potassium bromate solution must be added slowly and the presence of any considerable excess at all times avoided. The amount of furfuraldehyde present does not influence the accuracy of the method. In titrating dilute solutions with potassium bromate, the end-point can be readily located by the use of a simplified electrometric apparatus consisting of two platinum wires, a galvanometer, and a key. The time factor of the reaction involved is made the basis of the foregoing method for finding the end-point. Hydroxymethylfurfuraldehyde, a product of the acid distillation of hexose materials, apparently interferes slightly with the use of the proposed method, but the effect is small enough to be disregarded. Lævulic acid, a further decomposition product of hexoses, is without any effect whatever. Methyl pentoses or pentosans will interfere in that methylfurfuraldehyde is formed, and this will react with the bromate solution. A bibliography of the subject is appended.

H. C. R.

**Dinitrosalicylic Acid as a Reagent for Blood-sugar.** J. B. SUMNER and V. A. GRAHAM (*Proc. Soc. Exp. Biol. Med.*, 1922, **20**, 96; cf. A., 1921, ii, 564).—Blood (1 c.c.) is laked with 2 c.c. of water, 4 c.c. of a 2.94% solution of neutral sodium dinitrosalicylate and 2 c.c. of 0.4*N*-sulphuric acid are added, and the mixture is filtered; 3 c.c. of the filtrate is heated for three minutes in a Folin sugar tube in a boiling water-bath, 1 c.c. of 3% sodium hydroxide solution is added, and the heating is continued for ten minutes. The solution is then cooled and diluted to a volume suitable for colorimetric comparison with a standard prepared by heating 2 c.c. of a 0.015% solution of dextrose with 1 c.c. of a 1.78% solution of neutral sodium dinitrosalicylate for three minutes, adding 1 c.c. of the alkali, and heating for ten minutes.

CHEMICAL ABSTRACTS.

**Determination of Lactose by the Polarimetric and the Gravimetric Methods.** A. L. BACHARACH (*Analyst*, 1923, **48**, 521—528).—Careful redetermination of the polarimetric constants of lactose gave the following results:  $[\alpha]_D^{20} = +52.40 + (t-20) \times 0.072$ ;  $[\alpha]_{\lambda=546}^{20} = +61.94 + (t-20) \times 0.085$ . The latter formula is applicable when the green band of the mercury vapour arc is the source of illumination. For the gravimetric determination of lactose, the modified Fehling method of Quisumbing and Thomas (A., 1922, ii, 92) was found satisfactory in the respects claimed by them. The copper was, however, determined after ignition by

weighing as cupric oxide. The ratio of cupric oxide to lactose was constant and equal to 1.565. H. C. R.

**A New Titrimetric Method for Determining Formic Acid.**

O. RIESSER (*Biochem. Z.*, 1923, **142**, 280—281).—The author points out that the method described by Utkin-Ljubovzov (*A.*, 1923, ii, 588) for the determination of formic acid had already been published by him (*Z. physiol. Chem.*, 1916, **97**, 355), and used by other workers. It is unnecessary to filter the precipitated mercurous chloride, and the determination may be carried out in neutral solutions. J. P.

**Application of the Method of Diffusion to the Detection and Separation of Fatty Acids.** A. HEIDUSCHKA and J. RIPPER (*Z. Elektrochem.*, 1923, **29**, 552—555).—Details are given of the application of the method of diffusion to the separation of the so-called heptadecoic acid into its constituent fatty acids, palmitic acid and stearic acid. An alcoholic solution of heptadecoic acid is allowed to diffuse through a collodion membrane, and it is shown that the respective rates of diffusion of the constituents decrease as the molecular weights increase. The rate of diffusion is not always proportional to the concentration. A mixture containing an excess of palmitic acid may yield a diffusate containing an excess of stearic acid. The results were found to be applicable to a mixture of lauric and stearic acids. J. S. G. T.

**Determination of Tartaric Acid by Oxidation with Potassium Iodate and Sulphuric Acid.** R. STREBINGER and J. WOLFRAM (*Oesterr. Chem. Ztg.*, 1923, **26**, 156—157).—The oxidation of the tartaric acid proceeds according to the equation  $C_4H_6O_6 + 2KIO_3 + H_2SO_4 = K_2SO_4 + I_2 + 4CO_2 + 4H_2O$ . A weighed quantity of about 0.3 g. of the tartaric acid is added to a flask containing 1 g. of potassium iodate, a few drops of water and 30 c.c. of concentrated sulphuric acid, and the mixture is heated on a sand-bath for thirty minutes until the greater part of the liberated iodine has been expelled. After cooling, the mixture is diluted with water, the solution boiled to expel remaining traces of iodine, again cooled, and diluted to a definite volume. The excess of iodate is then determined by treating an aliquot portion with potassium iodide and titrating the iodine with thiosulphate solution. If desired, the tartaric acid may be precipitated as lead tartrate by means of lead acetate in acetic acid solution; the lead tartrate is collected, washed with hot water, and then oxidised as described. W. P. S.

**Titration of Amino- and Carboxyl-groups in Amino-acids, etc. I—III. In Aqueous Solution.** L. J. HARRIS (*Proc. Roy. Soc.*, 1923, [B], **95**, 440—484).—From a consideration of the titration curves of amino-acids, it is deduced that the amino- and carboxyl-groups can be estimated by titration. At a  $p_H$  of 0.7—0.1, the mono-amino-mono-carboxylic acids are completely dissociated as acid salts of the amino-group, so that the amino-group can be estimated by titration with acid to this  $p_H$ . Similarly, their carboxyl groups are completely dissociated at a  $p_H$  of 11.75 and can be determined by titration with alkali to this degree of alkalinity.

In practice, the titration is carried to the mid-point, *i.e.*, the point at which 50% of the amino- (or carboxyl-) group is neutralised. This point is determined from the titration curve of the acid under investigation. Mixtures of amino-acids may be determined by means of a series of titrations to different  $p_H$  values. The original paper should be consulted for the theoretical basis of the work and the necessary corrections involved in the special cases of the various amino-acids. C. R. H.

**Action of Carbonyl Chloride on Ricinolein.** A. PIUTTO and A. CURZIO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1921, [iii], **27**, 40—47).—The action of carbonyl chloride on castor oil or on ricinolein results in the formation of a compound which contains the percentage of chlorine corresponding with *glyceryl*  $\lambda$ -chlorocarbonato-*ricinoleate*,  $(CH_3 \cdot [CH_2]_5 \cdot CH[O \cdot COCl] \cdot CH_2 \cdot CH \cdot CH \cdot [CH_2]_7 \cdot CO_2)_3 C_3H_5$ ; with ricinoleic acid, the chlorocarbonato-acid itself appears to be formed. On the other hand, olive, almond, arachis, and sesamé oils take up only 0.08—0.18% of chlorine when treated with carbonyl chloride. Adulteration of castor oil with other oils is, therefore, detectable in this way. The name *chlorine index* is proposed for the percentage of chlorine thus absorbed, the value for the samples of castor oil examined being 9.03. T. H. P.

**Melting Point and Iodine Value of Refined Natural  $\alpha$ -Camphor.** MAURICE S. SALAMON (*Analyst*, 1923, **48**, 536—539).—The camphor was purified by sublimation, only the middle fraction being used. No difficulty was experienced in obtaining samples by this means which had a melting point of 179°, the melting point remaining constant after repeated sublimation. Iodine value determination on such samples by Wijs's method gave values not exceeding 0.1. It is extremely difficult to remove the last traces of oil, and it is probable that this small residual iodine value is due to a minute trace of oil still present in the camphor. To determine the iodine value of camphor oil, samples of oil were expressed from both Chinese and Japanese crude camphor and the dissolved camphor was removed as completely as possible by repeated freezing. The iodine value of the oil finally obtained varied between 86.0 and 91.7. It is considered that this oil contained not more than 10% of camphor and in calculating the percentage of camphor in samples, from the iodine value it is recommended to take the iodine value of the oil as 100. H. C. R.

**Saponin from *Gypsophila paniculata*.** L. KOFLER and O. DAFERT (*Ber. Deut. pharm. Ges.*, 1923, **33**, 215—229).—Previous methods of determining the saponin content of the root (*e.g.*, with baryta, magnesia, lead acetate) are shown either to give too low results or to involve alteration of the substance. In order to extract the saponin quantitatively and unchanged, the powdered root is extracted exhaustively with boiling water, the extract evaporated to a syrup, and the saponin fractionally precipitated, first with alcohol and then with ether. Each of the two precipitates represents about 10% of the starting material, with an ash content

of 10—19% and 4—6% and a hæmolytic index of 1 : 100,000 and 1 : 200,000 for the alcohol and ether fractions, respectively. By means of Pauli's electrodialysis apparatus the ash in the saponin is reduced to 0.07%. Elementary analysis of the alcohol and ether fractions gives, respectively, C = 47.88%, H = 7.60%, and C = 48.40%, H = 7.21%. The saponin is considered to have a mol. wt. of 3000 or more. [Cf. *B.*, Jan.] W. T. K. B.

**Microchemical Detection of Hydrocyanic Acid.** F. VON NEUREITER (*Deut. Z. ges. gerichtl. Med.*, 1923, **2**, 313—317; from *Chem. Zentr.*, 1923, iv, 230—231).—The material in which the presence of cyanides is suspected is mixed with concentrated oxalic acid solution in a glass vessel which is covered by a slide carrying a hanging drop of 1% silver nitrate solution coloured blue with Methylene-blue. In the presence of hydrocyanic acid a turbidity is produced which is seen under the microscope to consist of fine blue needles of silver cyanide the identity of which can be established by ordinary reactions. G. W. R.

**The Colorimetric Determination of Hydrocyanic Acid as Thiocyanate.** I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, **63**, 188—190).—To 5—10 c.c. of a cyanide solution are added 1 c.c. of 1% sodium tetrathionate solution and 5 drops of 10% ammonia solution. The mixture is warmed on a water-bath for five minutes at 50—55°, cooled, and treated with 2 c.c. of 4*N*-nitric acid and 3 drops of *N*-ferric chloride solution. The colour is matched against a standard. Working with 10 c.c. of test solution, 1 mg. of hydrocyanic acid per litre is easily detected. The sensitiveness of the reaction is 0.3 mg. per litre. The above conditions must be closely adhered to. A. G. P.

**Determination of Uric Acid in Blood-serum and Tissue Extracts.** K. HARPUDE (*Z. ges. Exp. Med.*, 1923, **32**, 378—386; from *Chem. Zentr.*, 1923, iv, 443—444).—The method, for which detailed directions are given, consists, in the case of sera, of removal of proteins followed by precipitation of the uric acid as zinc urate. The precipitate after centrifuging is taken up with sodium chloride solution and the uric acid determined colorimetrically by means of phosphotungstic acid. In the case of tissues, a modified method is described in which the material is first extracted with 3% sulphuric acid in a reflux apparatus. G. W. R.

**Determination of Uric Acid and Purines in Blood-serum and Urine by the Copper Urate Method.** H. CHABANIER, M. LEBERT, and C. LOBO-ONELL (*Bull. Soc. Chim. biol.*, 1923, **5**, 731—738).—The purines are precipitated in the form of their insoluble copper compounds, and the nitrogen in the precipitate is determined by Kjeldahl's method. By this method uric acid added to urine or to serum can be determined to within about 6%. C. R. H.

**A Quantitative Colour Reaction given by Adrenaline and Urine.** H. FRIEND (*J. Biol. Chem.*, 1923, **57**, 497—505).—Adrenaline may be determined colorimetrically by means of the

red coloration which is produced when it is treated successively with sulphanilic acid, nitrous acid, and ammonia. For the determination of adrenaline in urine, the latter is precipitated with lead acetate and the excess of lead removed by means of ammonium sulphate. The determination is then carried out on two portions of the filtrate, one of which is first treated with ferric chloride at  $50^{\circ}$  to destroy the adrenaline. The difference between the results gives the adrenaline content of the urine. According to this method, normal urine contains 0.2—0.4 mg. of adrenaline per 100 c.c.; larger variations occur in pathological urines. E. S.

**Determination of Bilirubin in Urine.** K. HOESCH (*Münch. Med. Woch.*, 1923, 70, 534; from *Chem. Zentr.*, 1923, iv, 444).—The method depends on coupling with diazoacetophenone. After treating the urine with a solution of diazoacetophenone, potassium hydroxide and ethyl alcohol are added. The green precipitate is dissolved in hydrochloric acid and the solution extracted with chloroform. The blue chloroform solution is repeatedly extracted with water until the colour changes to a clear red. It is then evaporated. The residue consists of azobilirubin which can be determined colorimetrically by comparison with a standard solution of azobilirubin. G. W. R.

**The Refractometric Determination of Hæmoglobin.** J. L. STODDARD and G. S. ADAIR (*J. Biol. Chem.*, 1923, 57, 437—454).—When determined on hæmoglobin (from human blood) which has been dried at  $110^{\circ}$ , the refractive constant  $\alpha$  of hæmoglobin has a value of 0.001942. The difference between this value and that obtained by Howard (A., 1920, i, 451) is probably due to water of crystallisation in the latter's specimen. Two refractometric methods for the estimation of hæmoglobin in blood have been elaborated. In the first, the red corpuscles from a measured volume of blood are washed, hæmolyzed with water and saponin, treated with salt to precipitate the stromata, made up to volume, centrifuged, and the refractive index of the solution determined before and after coagulation of the hæmoglobin by heat. The hæmoglobin content of the blood can be calculated from these readings by means of the constant  $\alpha$ . The second method is shorter. Equal volumes of salt solution (0.8%) and salt solution containing sufficient saponin to hæmolyse the blood are added respectively to separate portions, of equal volume, of the blood. After centrifuging, the clear solutions are read in the refractometer and the hæmoglobin content is calculated as above. A correction must be made for the refraction due to the saponin. Determinations by these methods, combined with determinations of the oxygen capacity of the blood, indicate that the latter is determined more accurately by Van Slyke's than by Haldane's method. E. S.

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## General and Physical Chemistry.

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**The Quantum Theory of Line Spectra.** N. BOHR (*Danske Vid. Selsk. Skrifter, nat. mat. Afd.*, 1922, 4, [8], 101—118; from *Chem. Zentr.*, 1923, iii, 1337; cf. A., 1922, ii, 801).—The distinction between arc and spark spectra depending on the ratio of the number of electrons to the nuclear charge is discussed. A correlation exists between the arc and spark spectra of elements of different series of the periodic system. The probability of transition between different stationary states of an atomic system is also considered with reference to the author's theories. The series spectra of helium, lithium, beryllium, and the Stark and Zeeman effects are discussed. G. W. R.

**The Spectrum of Iodine, and the Band Spectrum of Mercury.** W. GERLACH (*Physikal. Z.*, 1923, 24, 467—469).—The nature of the spectrum of iodine is briefly referred to, and reasons are advanced for regarding the band 3460 Å. as the electron-affinity continuous band spectrum associated with the iodine atom, whilst the band 4800 Å. is attributable to the electro-negative iodine molecule. Brief reference is made to the resemblance between the spectra of iodine and mercury vapour. J. S. G. T.

**The Band Spectrum of Copper.** R. FRERICHs (*Z. Physik*, 1923, 20, 170—187).—Particulars are given of the determination of the respective wave-lengths and intensities of *R* and *P* series of lines in the bands  $\lambda\lambda$  4006, 4063, 4280, 4328, 4380, 4650, and 4690 Å. in the spectrum of copper excited by the introduction of finely powdered copper into an oxy-hydrogen blowpipe flame. The determination of combination relations amongst lines of the respective series indicates that the bands may be classified as follows: bands characterised by the same initial energy level of the emitting molecule: ( $n_1=0$ ), 4280, 4650; ( $n_1=1$ ), 4006, 4328, 4690; ( $n_1=2$ ), 4063, 4380; bands characterised by the same final energy level of the emitting molecules: ( $n_2=0$ ), 4280, 4006; ( $n_2=1$ ), 4650, 4328, and 4063; ( $n_2=2$ ), 4690 and 4380. The frequencies,  $\nu_0$ , of the respective zero lines associated with the various bands can be very accurately calculated by the formula  $\nu_0 = 23,311.15 + (1658.81n_1 - 44.71n_1^2) - (1903.48n_2 - 37.18n_2^2)$ , in which  $n_1$  and  $n_2$  are quantum numbers characterising the respective initial and final energy levels of the emitting molecules. An empirical formula of the Deslandres type, permitting the frequencies of the heads of the bands to be very accurately calculated, and involving half-quantum numbers and five constants is deduced. Two of the constants are shown to be related to the quantum level-numbers  $n_1$  and  $n_2$ . The origin of the bands is discussed briefly. The calculated value of the moment of inertia of the emitting molecule is  $0.35 \times 10^{-39}$  gr. cm.<sup>2</sup>. This result indicates the presence of hydrogen in the emitting system, a result which is partly confirmed experimentally. J. S. G. T.

**Combination Relations in the Band Spectra of the Copper Flame.** E. BENGTSSON (*Z. Physik*, 1923, 20, 229—236).—Particulars are given of the determination of the respective wave-numbers and intensities of lines in the bands  $\lambda\lambda$  4689, 4649, 4280, 4005, and 3777 Å. in the flame spectrum of copper. The lines in the various bands, except for seven lines in the band 4328 and five in the band 4062, can be arranged in two series, and the deduction of combination relations between the respective series in the manner employed by Hulthén (A., 1923, ii, 670) indicates that the bands 4280, 4005, and 3777 correspond with the same final condition of the molecule, whilst the bands 4280 and 4649 correspond with the same initial condition of the molecule, and similarly in regard to the pair 4005 and 4689. The frequencies,  $\nu_0$ , of the respective zero lines associated with the various bands can be calculated by the formula  $\nu_0 = 23552 \cdot 4 + 1743 \cdot 4n - 44 \cdot 15n^2 - [1977 \cdot 5n' - 37 \cdot 2n'^2]$ , in which  $n$  and  $n'$  are whole numbers ranging from 0 to 3, and represent quantum numbers associated respectively with the initial and final energy levels of the molecule.

J. S. G. T.

**Spark Spectra of Higher Order associated with Mercury.** L. BLOCH and E. BLOCH (*J. Phys. Radium*, 1923, 4, 333—348).—Particulars are given of measurements of the respective wave-lengths and intensities of about 600 classified lines in the spectra of  $\text{Hg}^{\text{II}}$ ,  $\text{Hg}^{\text{III}}$ , and  $\text{Hg}^{\text{IV}}$  between wave-lengths 6149·37 and 2224·87 Å. excited in an electrodeless discharge in mercury vapour by gradual increase of the exciting voltage. Classification of the lines into the respective orders is effected by reference to the variation of the lengths of the lines as the exciting voltage is increased.

J. S. G. T.

**The System of Quartets in the Scandium Spectrum and the Periodic System.** M. A. CATALÁN (*Anal. Fis. Quím.*, 1923, 21, 464—480; cf. A., 1923, ii, 104).—The author discusses the application of Kossel and Sommerfeld's alternation law ("Wechsel-satz") to the spectra of the neutral atoms of potassium, calcium, scandium, titanium, vanadium, chromium, manganese, and iron. It is concluded that every element gives various systems of series, but either all odd or all even; one element never gives both odd and even series. A table is given showing the relation to the periodic classification of the various systems of series obtained. Whilst potassium gives doublets only, calcium gives simplets and triplets, and scandium doublets and quartets. Larger numbers of systems are shown for elements in the later groups, for which, however, some systems still remain undiscovered. For example, in the iron spectrum, triplets and quintets are known, whilst simplets, septets, and nonets remain to be discovered. G. W. R.

**The K-Series of the Spectrum of Molybdenum.** S. TANAKA and J. TSUTSUMI (*Mem. Coll. Sci. Kyoto*, 1923, 7, 1—5).—In continuation of previous work (A., 1922, ii, 805), the authors have determined the wave-lengths of the four lines in the

*K*-series of the spectrum of molybdenum by observations of the second, third, fourth, and fifth order spectra produced by a reflector of mica. The results are in close agreement with the values determined by Leide and others.

J. S. G. T.

**The Optical Spectrum of Hafnium.** H. M. HANSEN and S. WERNER (*Nature*, 1923, **112**, 900—901).—A list is given of the strongest lines in the hafnium spectrum in the region between 7300 and 3500 Å., the intensity for both arc and spark spectra being also noted. The authors find in the region of the spectrum for which Exner and Haschek's zirconium measurements are sufficiently exhaustive, nearly all the strong hafnium lines here given among Exner and Haschek's zirconium spark lines as weak lines of intensity 1 or 2. The lines 6386, 4093, and 3505 are for the time being regarded as the most persistent hafnium lines in this part of the spectrum.

A. A. E.

**Ultra-red Natural Frequencies of Salts containing Sulphur.** V. J. SIHVONEN (*Z. Physik*, 1923, **20**, 272—279).—Employing the method used by Schaefer and Schubert (A., 1916, ii, 506), the authors have determined the natural frequencies of the anions of various salts containing sulphur, by observing the reflection of radiation included between  $\lambda\lambda$  5 $\mu$  and 20 $\mu$  from the polished face of compressed pastilles of the respective salts. Reflection maxima, indicating corresponding anionic natural frequencies, were observed at the following respective wave-lengths (measured in  $\mu$ ): sodium sulphite, 10.6, 19.5; barium sulphite, 10.9, 19.7; sodium ethyl sulphonate, 8.7, 9.7, 13.5, 19.2; potassium ethanesulphonate, 8.7, 9.7, 13.6, 19.2; sodium thiosulphate, 9.1, 10.2, 15.1, 18.5, 19.7; potassium thiosulphate, 9.1, 10.2, 15.2, 18.5, 19.5; barium thiosulphate, 9.3, 10.4, 15.0, 18.2; sodium dithionate, 8.2, 10.1, 17.3, 19.4; potassium dithionate, 8.2, 10.2, 17.6, 19.3; barium dithionate, 8.2, 10.2, 18.0; potassium trithionate, 8.3, 10.0, 15.1, 16.5, 19.3; potassium tetrathionate, 8.6, 10.1, 16.3, 19.4. Salts other than the sulphites and sulphates, included in these results, show two reflection maxima in the region 8 $\mu$  to 11 $\mu$ . The shorter of these wave-lengths is connected with the presence of the sulphate-ion, the longer with the presence of the sulphite-ion. The occurrence of a reflection maximum at 8.7 $\mu$  (the sulphate maximum) in the case of the ethanesulphonates investigated is interpreted as indicating the presence of a sulphuryl group. It is suggested that the sulphonic group is in a state of labile equilibrium, possessing alternately the frequencies associated respectively with the SO<sub>2</sub> and SO<sub>3</sub> configurations.

J. S. G. T.

**The Electrical Absorption and Dispersion Spectra of Methyl and Ethyl Alcohol in the Region  $\lambda\lambda$  30 to 90 Cm.** G. POTAPENKO (*Z. Physik*, 1923, **20**, 21—35).—The author has determined the respective values of the dielectric constants and absorption coefficients of methyl and ethyl alcohols for electric oscillations of wave-lengths ranging from 29.4 cm. to 89.7 cm. In the case of methyl alcohol, the value of the absorption coefficient increases



rapidly as the wave-length employed decreases below about 50 cm. For short wave-lengths, the value of the absorption coefficient of ethyl alcohol similarly increases rapidly and attains, in the case of the shortest wave-lengths employed, a very high value, 0.843, which approximates to that characterising a metallic reflector. Under similar conditions, the value of the dielectric constant of ethyl alcohol decreases rapidly, a result which is interpreted as affording evidence of anomalous dispersion. No evidence of the existence of maxima of absorption characterising certain definite wave-lengths, such as was deduced by Romanov from his observations (A., 1913, ii, 182), was obtained. Values of the respective refractive indices calculated from the results are in close agreement with those determined by Drude, von Bayer, Wildermuth, and Romanov.

J. S. G. T.

**Ultra-violet Absorption Spectra of Unsaturated Compounds. Spectra of Vapours of Acraldehyde, Crotonaldehyde, and Glyoxal.** A. LÜTHY (*Z. physikal. Chem.*, 1923, **107**, 285—304).

—The absorption spectra of solutions of  $\beta$ -methyl- $\Delta^2$ -butylene, allyl alcohol, acrylic acid, acraldehyde, crotonaldehyde, and glyoxal have been measured in hexane, and of the three last-named substances also in ethyl alcohol. The absorption spectra of the last three substances have also been obtained with the vapours of these substances.  $\beta$ -Methyl- $\Delta^2$ -butylene shows two bands, a flat one with a maximum at 2340—2350 Å. and a second, much stronger, band which has its maximum beyond 1935 Å. Allyl alcohol has a weak, flat band in the region of 2340 Å., possibly the maximum lies more towards the ultra-violet; the maximum of the second stronger band lies outside the region measured, namely, beyond 1935 Å. Acrylic acid has a flat band with maximum at 2409—2415 Å. and a second strong band with maximum at 2080 Å. Acraldehyde in hexane solution has a flat, broad band with a maximum at 3350 Å.; further towards the red two small bands at 3663 Å. and 3514 Å. are measured; it has a very strong band in the ultra-violet beyond 2080 Å. In alcohol and water solution, the maximum of the flat band is displaced toward the violet, whilst in ether solution the maximum is in the same position as in hexane solution. Crotonaldehyde has a flat band with maximum at 3290 Å. in hexane, which is displaced to 3205 Å. in ethyl alcohol solution, that is, slightly more than the displacement of the corresponding band of acraldehyde. A second very intense band of crotonaldehyde lies in the extreme ultra-violet. Glyoxal has no bands in the visible and long wave-length ultra-violet, but the author has measured seventeen bands in the ultra-violet at 4613, 4483, 4330, 4199, 4095, 4013, 3935, 3863, 3768, 3670, 3542, 3487, 3359, 3301, 3187, 3154, and 3119 Å. A very strong band occurs in the extreme ultra-violet at about 1960 Å., and between this band and the last small band there is a flat, broad band the maximum of which has not been measured. The bands obtained with acraldehyde vapour agree very well with the bands of the hexane solution, the bands of the vapour being slightly displaced towards

the red. The heads of the vapour bands have an analogous structure, the difference between the frequencies of the most intense lines being 1260. Crotonaldehyde has an entirely different spectrum from that of acetaldehyde in the vapour condition. In this case, the bands are weak and not sharp, but five regions which are much stronger than the remainder can be identified. The mean values are recorded. With glyoxal below 30 mm. pressure, a group of very sharp absorption bands occurs in the visible region. At higher pressures, a new absorption zone is found in the visible region. The second absorption region has the same position as that of acetaldehyde. Glyoxal, in the same way as acetaldehyde, shows strong absorption groups which coincide with the small bands in hexane solution.

J. F. S.

**Coloured Ions and the Colours of Salts.** J. PICCARD and E. THOMAS (*Helv. Chim. Acta*, 1923, 6, 1040—1043).—An attempt is made to correlate the colours of salts with the colour-producing properties of their constituent ions. Ions may be divided into three groups: (1) coloured ions; compounds containing them are always coloured; (2) ions possessing latent colour; molecules formed from these tend to be coloured; (3) ions which have no colour, latent or otherwise. Ions of the first group give a deeper colour with those of the second than with those of the third. The following classification is made. Group (1):  $\text{MnO}_4^{\text{I}}$ ,  $\text{MnO}_4^{\text{II}}$ ,  $\text{CrO}_4^{\text{II}}$ ,  $\text{Cr}_2\text{O}_7^{\text{II}}$ ,  $\text{PtCl}_6^{\text{II}}$ ,  $\text{AuCl}_4^{\text{I}}$ ,  $\text{Cr}^{\text{II}}$  and  $\text{Cr}^{\text{III}} + \text{aq}$ ,  $\text{Cu} + \text{aq}$ ,  $\text{Au}$ ,  $\text{Pt}$ ,  $\text{Fe}$ ,  $\text{Mn}$ ; Group (2):  $\text{S}^{\text{II}}$ ,  $\text{O}^{\text{II}}$ ,  $\text{I}^{\text{I}}$ ,  $\text{Br}^{\text{I}}$ ,  $\text{Cl}^{\text{I}}$ ,  $\text{OH}^{\text{I}}$  (phenols and derivatives, certain enols),  $\text{Fe}^{\text{III}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Cr}^{\text{II}}$ ,  $\text{Bi}^{\text{III}}$ ,  $\text{Sb}^{\text{III}}$ ,  $\text{As}^{\text{III}}$ ,  $\text{Hg}^{\text{I}}$ ,  $\text{Hg}^{\text{II}}$ ,  $\text{Pb}^{\text{II}}$ ,  $\text{C}^{\text{IV}}$ ,  $\text{Ag}^{\text{I}}$ ,  $\text{Ti}^{\text{IV}}$ ,  $\text{Cd}^{\text{II}}$ ; Group (3):  $\text{F}^{\text{I}}$ ,  $\text{SO}_4^{\text{II}}$ ,  $\text{ClO}_4^{\text{II}}$ ,  $\text{CH}_3\text{-CO}_2^{\text{I}}$ ,  $\text{Zn}^{\text{I}}$ ,  $\text{Cs}^{\text{I}}$ ,  $\text{Rb}^{\text{I}}$ ,  $\text{K}^{\text{I}}$ ,  $\text{Na}^{\text{I}}$ ,  $\text{Li}^{\text{I}}$ ,  $\text{Ca}^{\text{II}}$ ,  $\text{Al}^{\text{III}}$ ,  $\text{H}^{\text{I}}$ . Cadmium iodide is described as colourless, but as both its ions have latent colour, it might be expected to be coloured. Examination shows that a layer of the concentrated solution 10 cm. thick is distinctly yellow. Mercuric bromide and mercurous chloride also form distinctly yellow solutions.

E. H. R.

**The Luminescence of Titanium Oxide.** E. L. NICHOLS (*Physical Rev.*, 1923, [ii], 22, 420—424; cf. Nichols and Wilber, A., 1922, ii, 105).—Cathode rays, but not ultra-violet light from an iron spark, excite a very faint, orange-red fluorescence in titanium oxide, or, after fusion of the surface layer, a fine blue fluorescence, with rapid fatigue. A thin layer of the oxide, when heated, gave a very feeble, greyish-blue fluorescence up to  $425^\circ$ , strong red from  $425^\circ$  to  $677^\circ$ , and strong yellow from  $677^\circ$  to  $1,000^\circ$ . When the oxide is heated directly with an oxygen-hydrogen flame, two distinct phases are observed, according as the oxygen or the hydrogen is in excess.

A. A. E.

**Velocity of Photochemical Reactions under the Action of Light the Intensity of which is Periodic.** P. LASAREV (*Compt. rend.*, 1923, 177, 1436—1438).—Talbot's Law is shown to be readily deducible from a consideration of photochemical kinetics [cf. J. Russ. Phys. Chem. Soc. (physical sect.), 1915, 47, 958].

E. E. T.

**The Photolysis of Carbonic Acid.** E. BAUR and P. BÜCHI (*Helv. Chim. Acta*, 1923, 6, 959—965).—Attempts were made to repeat the experiments of Baly, Heilbron, and Barker (T., 1921, 119, 1025—1035), who observed the reduction of carbon dioxide to formaldehyde through the action of light in presence of a sensitising dye such as Malachite-green. Formaldehyde was indeed found in the solutions after illumination, but just as much or more when carbon dioxide was absent as when it was present. The production of formaldehyde was increased in presence of barium hydroxide, which precluded the possibility of the presence of carbon dioxide in solution. It is concluded that the formaldehyde is formed from the dye, especially when this is present as a colloidal solution of the leuco-base [? colour base], as it is in the barium hydroxide solutions. Solutions of dyes (Rhodamine and Phosphine) in xylene containing lecithin or spermaceti were exposed to light; also dyeings of Eosin, Rhodamine, Phosphine, and Malachite-green on cotton and silk, and resinsates of the same dyes were illuminated under water both pure and saturated with carbon dioxide. In no case could formation of formaldehyde, oxalic acid, or formic acid be detected. E. H. R.

**Validity of the Photochemical Law of Equivalence in the Case of Emulsions of Silver Halides.** J. EGGERT (*Physikal. Z.*, 1923, 24, 488—490).—The experimental method described in a previous paper (*ibid.*, 1921, 22, 673) has been considerably improved, and the result definitely established, that, provided the time of exposure of the emulsion to the radiation is not excessive, photochemical absorption of radiation by emulsions of silver chloride or silver bromide obeys the photochemical law of equivalence, viz., one silver atom is affected per quantum of energy absorbed. For longer exposures, the ratio of the number of silver atoms affected to the number deduced from quantum considerations diminishes as the time of exposure increases. The author considers that the latent image is constituted of metallic silver. J. S. G. T.

**The Photo-electric Effect of Cæsium Vapour.** J. KUNZ and E. H. WILLIAMS (*Physical Rev.*, 1923, [ii], 22, 456—460).—Previous work (A., 1922, ii, 809) has been repeated with greater precision by the use of a quartz tube with plane parallel end plates. The critical wave-length for photo-electric emission from cæsium vapour was found to be 3180 Å. (average), in agreement with the convergence wave-length 3184.28 Å., which is related to the ionisation potential,  $V_i$ , according to the equation  $V_i = hc/e\lambda_i$ . It follows that the separation of an electron from a cæsium atom requires the same amount of work whether produced by an impinging electron or by absorption of light. A. A. E.

**Spectro-photo-electrical Effects in Argentite.** P. H. GEIGER (*Physical Rev.*, 1923, [ii], 22, 461—469).—When argentite is connected in a closed circuit with a galvanometer, and one surface of contact is illuminated, an *E.M.F.* is produced which increases with the intensity up to about 0.013 volt for 600 candle-metres and over.

Continued exposure results in marked fatigue. The effect, which is not thermo-electric, is shown also with proustite ( $\text{Ag}_3\text{AsS}_3$ ), pyrrargyrite ( $\text{Ag}_3\text{SbS}_3$ ), bournonite [ $3(\text{Cu}_2\text{PbS})\text{Sb}_2\text{S}_3$ ], molybdenite ( $\text{MoS}_2$ ), stephanite ( $\text{Ag}_3\text{SbS}_4$ ), and acanthite ( $\text{Ag}_2\text{S}$ ), although to a less extent than with argentite ( $\text{Ag}_2\text{S}$ ); cuprite gave indefinite results, whilst the effect was not observed in the case of galenite, stibnite, and polybasite. The electrical resistance of argentite was found to be only half as great for 20 as for 4 volts, and is about 0.8 as great in the light as in the dark. Slow recovery followed a condition of insensitiveness to light attained after some time.

A. A. E.

**Röntgenographic Chemical Investigations. I. Röntgen Spectra and the Periodic System.** H. STINTZING (*Z. physikal. Chem.*, 1923, **107**, 154—162).—A theoretical paper in which it is shown that up to the present the study of Röntgen spectra has only led indirectly to the possibility of determining structure according to Bohr's theory. The author puts forward a number of numerical relationships in the periodic system which may serve as an indication of the lines on which the direct investigation of the structure of atoms and atomic nuclei may be pursued. It is suggested that such an investigation could be carried out by means of  $\gamma$ -rays. It is also pointed out that positive ray analysis may explain atomic structure and other chemical problems, particularly the definite fixing of whole number atomic weights.

J. F. S.

**Röntgenographic Chemical Investigations. II. Technique of Röntgenology.** H. STINTZING (*Z. physikal. Chem.*, 1923, **107**, 163—180; cf. preceding abstract).—A description of the most suitable forms of apparatus and the most favourable conditions for the investigation of Röntgen spectra. A new arrangement of the electrodes is described for Röntgen analytical purposes. It is shown that if the discharge is divided between the discharge tube and a spark gap in parallel, then the maintenance of a definite tube voltage as measured by the spark potential has little influence on the production and the intensity of a suitable Röntgen radiation.

J. F. S.

**Constitution of the X-Ray Spectra belonging to the *L*-Series of the Elements.** H. HIRATA (*Proc. Roy. Soc.*, 1924, [A], **105**, 40—60).—Experimental data due to Siegbahn (*A.*, 1919, ii, 488), and to Siegbahn and Friman (*A.*, 1916, ii, 167, 277, 361) are used to calculate the respective values of the ratio of the wave number,  $\nu$ , to Rydberg's constant,  $N$ , in the *L*-series of the X-ray spectra of forty-eight elements included between zinc (atomic number 30) and uranium (atomic number 92). Values so determined are shown to confirm approximately certain deductions made by Sommerfeld from the extension of the theory of "wasserstoffähnlich" spectra to the *K* and *L* series of X-ray spectra (*Ann. Physik*, 1916, [iv], **51**, 133). The slight discrepancy is attributable to the number of electrons in the *K*- and *L*-orbits being so large that their effects on the motion of an electron in the same or an inner orbit

are appreciable. Moreover, the radius of the innermost ( $K$ ) orbit cannot be considered negligible compared with the radii of the outer orbits. Sommerfeld's theory is extended by taking account of these correcting factors. A mathematical discussion, involving quantum considerations, of the initial and final stationary orbits corresponding with  $X$ -ray radiation, the planes of the stationary orbits, and the intensities of  $X$ -ray radiation leads to the conclusion that an electron moves from a certain outer orbit to the neighbouring inner one without changing its spatial quantum number, but if there are intermediate orbits between the initial and final orbits, the spatial quantum number changes every time the electron passes through one of the intermediate orbits. J. S. G. T.

**Reflection of the Characteristic Röntgen Radiation associated with the Chemical Elements composing a Crystal by the Elements.** B. WALTER (*Z. Physik*, 1923, 20, 257—271).—Employing an ionisation chamber for the measurement of the respective intensities of radiation of various wave-lengths reflected by crystals of bromides, iodides, or containing caesium, on which Röntgen radiation excited by means of a tungsten anticathode was incident, Clark and Duane found that the intensity of reflected radiation characteristic of bromine, iodine, etc., was of the same order of magnitude as, and even greater than, the intensity of reflection of the incident radiation characteristic of the material of the anticathode (A., 1923, ii, 468). Employing a photographic method of comparing the intensities of the reflected radiation of different wave-lengths, and using Röntgen radiation excited by means of a molybdenum anticathode, the author has been unable to confirm this result. The intensity of the reflected radiation characteristic of the crystal element was in all cases immeasurably small. No satisfactory explanation of the apparent discrepancy shown by the results obtained by the respective methods is at present available. It is pointed out that the results obtained by Clark and Duane indicate a very rapid decrease of intensity of the reflected radiation on the long wave-length side of the head of the absorption band characterising the crystal elements in question. This result is contrary to what would be anticipated from a knowledge of the distribution of intensity throughout the continuous spectrum afforded by a Röntgen tube. J. S. G. T.

**Particles of Long Range Emitted by the Active Deposits of Radium, Thorium, and Actinium.** L. F. BATES and J. S. ROGERS (*Proc. Roy. Soc.*, 1924, [A], 105, 97—116).—The emission of long-range particles by the active deposits of radium, thorium, and actinium has been investigated by means of the scintillation method (A., 1921, ii, 671). In the case of radium active deposit, in addition to particles of range 9.3 cm. previously found by Rutherford, particles of respective ranges 11.2 and 13.3 cm. were found. For every  $10^7$   $\alpha$ -rays emitted by radium- $C'$ , the respective numbers of these particles present are 380, 125, and 65. Thorium active deposit emits particles of ranges 15.0 and 18.4 cm., in addition to particles of ranges 8.6 and 11.5 cm. (A., 1916, ii, 282). The

relative numbers of these particles emitted were found to be 47, 55,  $10^6$ , and 220, respectively. Actinium active deposit was found to emit particles of range 6.49 cm. previously recorded by Marsden and Perkins (A., 1914, ii, 410) to the extent of 0.322% of the total number of  $\alpha$ -rays emitted by actinium-*C*. Indications of the presence of particles of range greater than 6.5 cm. were obtained. Evidence as to whether these long-range particles were  $\alpha$ -rays or H-particles is inconclusive. Schemes hitherto proposed for the modes of transformation of the *C* products of the radioactive substances must be considered incomplete. More especially, for the atoms of radium-*C* and thorium-*C* explanation must be found for the presence of four particles of different ranges.

J. S. G. T.

**The Absolute Energies of the Groups in Magnetic  $\beta$ -Ray Spectra.** C. D. ELLIS and H. W. B. SKINNER (*Proc. Roy. Soc.*, 1924, [A], 105, 60—69).—Absolute determinations, correct to 1 part in 500, have been made of the respective energies of the electrons associated with six of the principal homogeneous groups of  $\beta$ -rays emitted from radium-*B*. The values, expressed in  $10^{-5}$  volt, deduced from determinations of the curvature of the respective rays in a magnetic field, are: 0.3725, 0.4983, 1.529, 2.067, 2.638, and 3.379.

J. S. G. T.

**Discoloration and Luminescence due to Becquerel Rays.** K. PRZIBRAM (*Z. Physik*, 1923, 20, 196—208).—Literature dealing with the discoloration and luminescence accompanying the incidence of Becquerel rays on substances, *e.g.*, rock salt, is reviewed, more especially with reference to conclusions concerning the phenomena reached by Meyer and the author in a previous paper (A., 1922, ii, 339). The mechanism of the phenomena is discussed from the point of view of the quantum theory.

J. S. G. T.

**Ionisation: Hydrogen and Oxygen.** H. D. SMYTH (*Proc. Roy. Soc.*, 1923, [A], 105, 116—128).—In continuation of previous work (A., 1923, ii, 602), the author has investigated the ionisation of hydrogen and oxygen by electron impact. The results obtained show that ionisation in hydrogen at about 16.5 volts is not accompanied by dissociation, as has been generally supposed. Atomic hydrogen-ions are first produced at a potential  $4.25 \pm 0.06$  volts above that at which molecular ions first appear, and the proportion of atomic ions remains very small up to 720 volts. In hydrogen at sufficiently high pressure, atomic ions predominate over molecular ions, and appear at approximately the same voltage. They originate owing to dissociation due to collisions of ionised molecules with other molecules. In oxygen, molecular ions are produced at about 15.5 volts, whilst doubly and singly charged atomic ions appear at about 7 and  $7.5 \pm 0.2$  volts higher. Results in the case of oxygen can be interpreted by thermochemical equations similar to those previously employed in the case of nitrogen.

J. S. G. T.

**Ionisation of Salt Vapours.** W. M. LATIMER (*J. Amer. Chem. Soc.*, 1923, 45, 2803—2808).—The heats of ionisation of the

hydrogen and alkali metal chlorides, bromides, and iodides have been tabulated for the gaseous condition. The ionisation constant of sodium chloride at its boiling point has been found to be  $4 \times 10^{-13}$ . From a consideration of the fields of force about the ions and the molecular diameters, it seems that the heats of ionisation cannot be calculated by any method which treats the ions as rigid structures of electrons about a positive nucleus. J. F. S.

**Radioactivity of the Alkalis.** G. HOFFMANN (*Physikal. Z.*, 1923, 24, 475—476).—The radioactive character of salts of sodium, potassium, rubidium, and caesium and the relative magnitudes of the small activities associated with these elements have been determined in two different ways. The results are in satisfactory agreement with values of the activities given by Hahn and Rothenbach (A., 1919, ii, 312). J. S. G. T.

**Thermionic and Photo-electrical Properties of the Electro-positive Metals.** A. F. A. YOUNG (*Proc. Roy. Soc.*, 1923, [A], 104, 611—639).—The thermionic and photo-electrical properties of sodium and potassium have been investigated. It is found that sodium does not give a measurable thermionic emission, that is, greater than  $10^{-10}$  amperes, for temperatures up to  $390^\circ$ . Potassium is found to give currents measurable in some cases by an electroscope at temperatures down to the ordinary. The currents are held to be thermionic in origin and not due to chemical action. The values of  $b$  for potassium in the emission formula  $i = A_1 e^{T^{1/2} - b/T}$  are found to be lower than those obtained with other metals, and the values of  $A_1$  are also low. The change of the potassium from solid to liquid makes no difference in the magnitude of the thermionic current or in the value of  $b$ . Determinations of the photo-electric work function  $\phi_0$  from photo-electric measurements, made at the same time as the thermionic measurements and at nearly the same temperature, show that  $\phi_0$  is always greater than the thermionic work function  $\phi$  calculated from the value of  $b$ . J. F. S.

**Dielectric Constants of Organic Liquids at the Boiling Point.** F. V. GRIMM and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1923, 45, 2794—2802).—The dielectric constant of thirty-five organic liquids has been determined at the boiling point. The following values are recorded: benzene, 2.17; toluene, 2.17; *m*-xylene, 2.15; chloroform, 4.23; carbon tetrachloride, 2.10; carbon disulphide, 2.58; ethyl ether, 4.11; these values are accurate to 0.01 unit; *p*-cymene, 2.27; ethyl bromide, 8.81; ethylene bromide, 4.09; isoamyl bromide, 4.70; *n*-butyl iodide, 4.52; methyl iodide, 6.48; ethyl acetate, 5.30; chlorobenzene, 4.20; aniline, 4.54; *o*-toluidine, 4.00; butaldehyde, 10.78; paracetaldehyde, 6.29; anisaldehyde, 10.38; acetone, 17.68; methyl ethyl ketone, 14.46; acetophenone, 8.64; ethyl alcohol, 17.30; *n*-propyl alcohol, 11.83; *n*-butyl alcohol, 8.19; isoamyl alcohol, 5.82; *o*-nitrotoluene, 11.82; pyridine, 9.38; quinoline, 5.05; these values are accurate to 0.02 unit; acetonitrile, 26.2; phenylacetonitrile, 8.5; ethylene chlorohydrin, 13.2; and

nitromethane, 27.75; these values are accurate to 0.1 unit. A method has been suggested for evaluating the volume occupied by the molecules in the liquid state. The above idea has been applied to Bakker's equation for the latent heat of vaporisation. J. F. S.

**[Relation between] Cathode Drop of Potential, Ionisation Potential, and Atomic Weight.** A. GÜNTHER-SCHULZE (*Z. Physik*, 1923, 20, 153—158).—The author shows that the average normal cathode drop of potential  $V_n$ , in the case of a discharge through any elementary gas of atomic weight  $M$ , is approximately related to the ionisation potential,  $V_i$ , of the gas, by the equation  $V_n = (0.245M + 4)V_i\alpha$ , in which  $\alpha$  is a constant, having the value unity for all monatomic gases, whilst the appropriate value of  $\alpha$  in the case of diatomic gases is to be determined from consideration of the loss of energy due to electronic impacts, and the efficiency of such impacts. It follows that the efficiency of the process of ionisation of the gas due to kations is, to a first approximation, inversely proportional to the square of the atomic weight of the gas. J. S. G. T.

**Influence of Neutral Salts on the Potential of the Hydrogen Electrode.** J. PRZEBOROWSKI [with M. FLEISSNER and A. SABRODINA] (*Z. physikal. Chem.*, 1923, 107, 270—278).—The action of 0.1N and 0.01N solutions of potassium nitrate, chloride, and bromide, sodium nitrate, chloride, and bromide, and lithium chloride and bromide in hydrobromic acid solution on the potential of the hydrogen electrode has been investigated. It is found that the potential of the hydrogen electrode in 0.1N and 0.01N hydrobromic acid solutions increases in all cases. A slight increase of the potential is found for solutions containing the potassium salts at concentrations less than 1N. The influence of the neutral salts increases with increase in their concentrations. The influence of these salts increases with their solubility, hygroscopic properties, and power of forming crystal hydrates. The influence of the salts is in the following order:  $\text{KNO}_3$ ,  $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{NaCl}$ ,  $\text{NaBr}$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ , lithium bromide having the greatest influence. Bromides have a greater influence than chlorides, the kation being the same in both cases. With a constant concentration of neutral salt and a variable concentration of hydrobromic acid, the fall in the *E.M.F.* is almost independent of the hydrobromic acid concentration for salts which form crystal hydrates. The corresponding difference of *E.M.F.* for salts which do not form crystal hydrates varies very much with the different salts, and still more the greater the concentration of hydrobromic acid. The action of neutral salts can be explained by the assumption that only non-hydrated hydrogen-ions have an influence on the potential; the ions formed from neutral salts dehydrate the hydrogen-ions and so increase the concentration of non-hydrated ions, and in consequence the potential. The electrolytic solution tension of the hydrogen changes with the concentration of the neutral salt. In addition to the ions of neutral salts, the undissociated molecules also exercise a dehydrating action on the hydrogen-ions. J. F. S.



**Hydrogen Electrode in Alkaline Solutions.** A. H. W. ATEN (*Trans. Amer. Electrochem. Soc.*, 1923, **43**, 89—98).—The potential of the hydrogen electrode has been determined in solutions of sodium hydroxide and in solutions of sodium hydroxide containing sodium chloride. It is shown that when a hydrogen electrode, saturated with hydrogen, is in equilibrium with 0.1*N* hydrochloric acid, it is in the same state of equilibrium with 1.0*N* hydrochloric acid, and *vice versa*. This, however, is not the case when a solution of an alkali hydroxide is used. When a hydrogen electrode in equilibrium with 1.0*N* sodium hydroxide is placed in 0.1*N* sodium hydroxide, a very considerable time elapses before it reaches a new equilibrium. The same phenomenon is observed in a more marked degree when the electrode is changed from 0.1*N* sodium hydroxide to 0.1*N* hydrochloric acid, or the reverse. The explanation given is that the electrode must absorb sodium-ions or give them out, as the case may be, in order to reach an equilibrium with the final solution. J. F. S.

**Effect of Current Density on Overvoltage.** M. KNOBEL, P. CAPLAN, and M. EISEMAN (*Trans. Amer. Electrochem. Soc.*, 1923, **43**, 55—74).—The value of the hydrogen overvoltage has been determined with cathodes composed of twenty-two different materials, that of chlorine, bromine, and iodine at three different anodes, and that of oxygen at nine different anodes. The determinations have been carried out at various current densities from 1.0 milliamperes to 1.5 amperes per sq. cm. All measurements were made at  $25.0^{\circ} \pm 0.2^{\circ}$ . An investigation of the method of measuring overvoltage has led to the conclusion that the use of a small glass tip less than 1 mm. diam., pressed against the active electrode surface while the current is passing, will give correct results. J. F. S.

**Effect of Pressure on Overvoltage.** S. J. BIRCHER and W. D. HARKINS (*J. Amer. Chem. Soc.*, 1923, **45**, 2890—2898).—The effect of pressure on the potential of the hydrogen electrode and on the potential and overvoltage of a mercury cathode has been ascertained at  $0^{\circ}$  for pressures from 757 mm. to 9 mm. The results show that the effect of pressure on the potential of a cathode at which hydrogen is being liberated is in general very small at pressures between 760 mm. and 11 mm. The slight changes which occur are due to bubble expansion and consequent shielding of the cathode, and to increased stirring caused by more rapid bubble liberation at low pressure. Overvoltage, defined with reference to a reversible hydrogen electrode, increases as the pressure is decreased. This increase is paralleled entirely by a decrease in potential of the hydrogen electrode. Between 760 mm. and 11 mm., the range of variation of the overvoltage is about 50 millivolts. The present data are of importance in connexion with the theory of overvoltage due to MacInnes and Adler (*A.*, 1919, ii, 131). Here the overvoltage,  $E$ , is given by  $E = (3RT/2pr) \cdot \gamma$ , where  $p$  is the pressure in the bubbles,  $r$  their radius, and  $\gamma$  the surface tension of the liquid. Since the bubble radius is practically constant with variation of

pressure, the overvoltage should vary inversely as the pressure, and thus increase very rapidly as low pressures are approached. The present work indicates that the overvoltage increases with decrease of pressure only to the extent that the hydrogen electrode potential decreases, that is, as the logarithm of the pressure. On the other hand, the overvoltage of a number of inactive metals is found to have the same temperature coefficient, and to decrease 2 millivolts per degree in 0.1*N* sulphuric acid. This seems to point to the surface tension of the liquid as an important factor in overvoltage. This fact indicates that MacInnes and Adler's hypothesis is a partial rather than a complete hypothesis of overvoltage. In the experiments, care was taken to avoid stirring the liquid round the cathode, so the smallness of the increase of overvoltage with decrease of pressure cannot be due to the effect of stirring. The overvoltage at a mercury meniscus in dilute sulphuric acid is found to increase as the large bubble at the top of the meniscus becomes larger, and to decrease suddenly when the bubble escapes.

J. F. S.

**Free Energy of Dilution and the Activity of the Ions of Hydrogen Iodide in Aqueous Solution.** J. N. PEARCE and A. R. FORTSCH (*J. Amer. Chem. Soc.*, 1923, **45**, 2852—2857).—The *E.M.F.* of cells of the type  $H_2|H(c), AgI|Ag$  has been measured at 25°, 30°, and 35° for concentrations of hydriodic acid between 0.246*M* and 0.005*M*. The decrease of free energy and heat content attending the cell reaction has been calculated for 25°. The decrease of free energy accompanying the transfer of one gram-molecule of hydrogen iodide from the various concentrations to a concentration exactly 0.005*M* has been calculated. From these values, the geometric mean activity coefficients of the ions of hydrogen iodide have been calculated, and it is found that for concentrations up to 0.005*M* these coefficients are practically equal to the corresponding coefficients for hydrogen chloride at the same concentrations. Obviously, therefore, the activities of the iodide- and chloride-ions are equal when in equivalent concentrations of their salts. J. F. S.

**Activities of Zinc, Cadmium, Tin, Lead, and Bismuth in their Binary Liquid Mixtures.** N. W. TAYLOR (*J. Amer. Chem. Soc.*, 1923, **45**, 2865—2890).—Accurate determinations of the activities of liquid zinc, cadmium, tin, lead, and bismuth in the binary alloy systems zinc-tin, zinc-cadmium, cadmium-bismuth, cadmium-lead, and cadmium-tin have been made at temperatures from 400° to 600° from *E.M.F.* measurements of cells of the type  $M|electrolyte|Alloy$ . The electrolyte was the eutectic mixture of lithium and potassium chloride with a small amount of zinc or cadmium chloride and potassium hydroxide. With the single exception of the system cadmium-bismuth, which gave a very complicated type of activity curve, all the alloy systems investigated showed escaping tendencies or activities greater than that required by Raoult's law. In regard to divergencies from this ideal solution law, and also in regard to the heats of mixing, the results of the

present work furnish strong evidence for the validity of the internal-pressure theory as applied to liquid metal systems. J. F. S.

**Velocity of Hydrogen-ions in Gels under the Influence of a Current.** N. ISGARISCHEV and A. POMERANZEV (*Z. Elektrochem.*, 1923, **29**, 581—586).—The migration velocity of the hydrogen-ion in gelatin gels has been measured in the presence of different electrolytes, including the chlorides of ammonium, potassium, sodium, barium, calcium, magnesium, lithium, manganese, and cadmium, and the sulphates of most of the above-named metals and also of zinc and rubidium, under various experimental conditions. A characteristic slowness of the hydrogen-ion is observed on passing from one potential to another, which is explained by the fact that the gel has a semi-rigid structure in which the ions are included and have thereby lost to some extent their free condition and power of progressive movement. The influence of the various kations in the gel on the movement of the hydrogen-ions is in direct relationship with the atomic volumes of the kations. J. F. S.

**Magnetic Properties of some Paramagnetic Double Sulphates at Low Temperatures.** L. C. JACKSON and H. KAMERLINGH ONNES (*Proc. Roy. Soc.*, 1923, [A], **104**, 671—676; cf. A., 1923, ii, 609).—In continuation of previous work on the magnetic properties of compounds of iron, nickel, and cobalt, the magnetic susceptibility of cobalt potassium sulphate, cobalt rubidium sulphate, and manganese ammonium sulphate has been determined at temperatures from  $14\cdot54^{\circ}$  Abs. to  $291\cdot0^{\circ}$  Abs. The results show together with those given in the previous paper (*loc. cit.*) that all the cobalt compounds obey Weiss's law  $\chi'm(T+\Delta)=C$  down to about  $70^{\circ}$  Abs., where  $\chi'm$  is the molecular susceptibility, but deviate from the law below  $70^{\circ}$  Abs. in such a manner that the susceptibility at the lowest temperature is greater than the value calculated by Weiss's law. The magneton numbers of the cobalt compounds are not equal, but increase as the molecular weight of the compound increases. Manganese ammonium sulphate follows the simple Curie law  $\chi T=C$  over the whole range of temperature investigated. Comparing this result with those obtained for hydrated and anhydrous manganese sulphate, it is found that the manganese compounds show a simple behaviour as regards the dependence of the susceptibility on temperature the greater the magnetic dilution of the substance. The complications found with cobalt, nickel, and iron compounds do not occur. J. F. S.

**The Crystallisation of certain Salts in the Magnetic Field.** G. ROASIO (*Rev. géol.*, 1923, **4**, 297).—Experiments with salts of iron, nickel, and cobalt show that the magnetic field exercises an influence on (1) the orientation of the crystals, the angles between axes and lines of force varying with the substance, but being constant for a given compound; and (2) the growth of the crystals, which become elongated in a definite direction, the angles remaining constant but again varying with the substance.

**Specific Heat and Heat of Mixing in the Neighbourhood of the State of Critical Miscibility.** N. PERRAKIS (*Compt. rend.*, 1924, **178**, 83—86; cf. A., 1923, ii, 836).—The specific heats and heats of mixing of the following pairs have been measured: (1) diphenyl ether and ethyl alcohol; (2) benzene and ethyl alcohol; (3) benzene and *n*-butyl alcohol; and (4) *o*-cresol and ethyl alcohol. It is shown that the found specific heat of a mixture is greater than that calculated from the simple law of mixtures, this fact necessitating a correction in the calculation of the heats of mixing. Curves representing the above constants are approximately rectilinear for a longer or shorter portion of their course, according as the mixture under examination is near to, or remote from, a state of non-miscibility. Thus, the length of the rectilinear portions of the curves decreases in the order (1), (2), (3), (4), this being also the order of increasing miscibility. E. E. T.

**Thermodynamics of the Ionisation of Monatomic Gases.** R. BECKER (*Physikal. Z.*, 1923, **24**, 485—486).— $C_\sigma$  and  $C_e$ , the respective concentrations of the atoms and electrons in a thermally-ionised monatomic gas at temperature  $T^\circ$ , are related by the equation  $C_e^2/C_\sigma = e^{-Q_\sigma/kT} (KT)^{3/2} \cdot (2\pi\mu)^{3/2} / p_\sigma h^3$ , in which  $Q_\sigma$  denotes the heat of ionisation,  $\mu$  the mass of the electron,  $p_\sigma$  is a statistical factor, and the other symbols have the customary significance. It follows, on the basis of the quantum theory, that if  $\alpha_\sigma(\nu)$  denote the power of absorption of the gas for radiation of frequency  $\nu = (Q_\sigma + \epsilon)/h$ , where  $\epsilon$  is the kinetic energy associated with an electron in a  $\sigma$ -orbit, then  $q_\sigma(\epsilon)/\alpha_\sigma(\nu) = (\epsilon + Q_\sigma)^2 p_\sigma / \epsilon \mu c^2$ ,  $q_\sigma(\epsilon)$  denoting the statistically calculated electron-absorbing cross sectional area of the ion available for trapping an electron  $\epsilon$  in a  $\sigma$ -orbit. This equation, applied to absorption measurements relating to the principal series of absorption bands, should afford quantitative information relating to the trapping of free electrons by an ion. J. S. G. T.

**Calorimetric Determinations. V. The History of the Thermochemical Standard Substances.** P. E. VERKADE (*Chem. Weekblad*, 1924, **21**, 13—20).—The considerations leading up to the adoption of benzoic acid as a standard by the International Union at its third conference at Lyons in 1922 are described in some detail, and the desirability of deciding on some other material as a second standard is pointed out. S. I. L.

**The Heat of Formation of Bleaching Powder and the Thermochemical Explanation of its Decomposition and Formation.** SHUICHIRO OCHI (*J. Chem. Ind. Japan*, 1923, **26**, 961—978; cf. *ibid.*, 1923, **26**, 1; A., 1923, ii, 564, 573).—Assuming that the formula of bleaching powder is  $\text{OCl}\cdot\text{CaCl}_2\cdot\text{H}_2\text{O}$ , the author has made a determination of the heat of formation and then tried to solve thermochemically the problem of the decomposition and the formation of the compound by applying the value obtained. As the reaction  $\text{OCl}\cdot\text{CaCl}_2 + \text{H}_2\text{O}_2 = \text{CaCl}_2 + \text{O}_2 + \text{H}_2\text{O}$ , proceeds

quantitatively and is not affected by the impurities contained in bleaching powder, the heat of formation was measured with a simple calorimeter using hydrogen peroxide,  $\text{OCl}\cdot\text{CaCl}=\text{CaCl}_2+\text{O}+13,040$  cal. and  $[\text{Ca},\text{O},\text{Cl}_2]=177,260$  cal. The method employing the bomb calorimeter and that of decomposing with hydrochloric acid did not give accurate results. The averages were 176.1 Cal. from the former and 179.7 Cal. from the latter. The heat of decomposition of  $\text{OCl}\cdot\text{CaCl}$  was calculated as follows:  $\text{OCl}\cdot\text{CaCl}=\text{CaCl}_2+\text{O}+13,040$  cal.  $\text{OCl}\cdot\text{CaCl},\text{H}_2\text{O}=\text{CaCl}_2,\text{H}_2\text{O}+\text{O}+14,440$  cal.  $=\text{CaCl}_2+\text{H}_2\text{O}(\text{liquid})+\text{O}+10,740$  cal.  $=\text{CaCl}_2+\text{H}_2\text{O}(\text{vapour})+\text{O}+150$  cal.  $\text{OCl}\cdot\text{CaCl},\text{aq.}=\text{CaCl}_2,\text{aq.}+\text{O}+20,620$  cal.  $\text{OCl}\cdot\text{CaCl}=\text{CaO}+\text{Cl}_2-25,360$  cal.  $\text{OCl}\cdot\text{CaCl},\text{H}_2\text{O}=\text{Ca}(\text{OH})_2+\text{Cl}_2-12,120$  cal. and  $\text{OCl}\cdot\text{CaCl},\text{aq.}=\text{Ca}(\text{OH})_2+\text{aq.}+\text{Cl}_2-20,650$  cal. All oxygen-forming decompositions are exothermic reactions, whilst the chlorine-forming ones are endothermic. At the ordinary temperature, chlorine may not therefore be evolved as indicated above, but is produced by the decomposition of  $\text{Cl}_2\text{O}$ , which may be easily formed from moist bleaching powder. The chlorate, which occurs without exception, is considered to be the product of the oxidation of the other molecule of  $\text{OCl}\cdot\text{CaCl}$  or  $\text{Ca}(\text{OCl})_2$  caused by the eliminated oxygen in the presence of water. The partial pressure of decomposing oxygen from  $\text{OCl}\cdot\text{CaCl}$  is calculated to be  $2.86 \times 10^{13}$  atm., by Nernst's heat theorem. The heat of reaction between calcium hydroxide and chlorine is represented as follows:  $\text{Ca}(\text{OH})_2+\text{Cl}_2=\text{OCl}\cdot\text{CaCl},\text{H}_2\text{O}+12,120$  cal. and  $\text{Ca}(\text{OH})_2+\text{aq.}+\text{Cl}_2=\text{OCl}\cdot\text{CaCl},\text{aq.}+20,650$  cal. The partial pressure of chlorine, reacting on calcium hydroxide, is calculated by Nernst's heat theorem: 0.004 atm. at  $0^\circ$ , 0.016 at  $15^\circ$ , 0.49 at  $30^\circ$ , 0.138 at  $45^\circ$ , 0.355 at  $60^\circ$ , 1.000 at  $78^\circ$ , 3.1 at  $100^\circ$ , and 26.7 at  $150^\circ$ . The author has explained the preparation of bleaching powder from the thermochemical point of view.

K. K.

**General Theory of the Phenomenon of Sorption.** B. ILJIN (*Z. physikal. Chem.*, 1923, **107**, 145—153).—A theoretical paper in which an equation in the form of that of a unimolecular reaction is derived for the kinetics of sorption; this equation is given the form  $dc/dt=kc_\alpha \cdot e^{-kt}$ , where  $c_\alpha$  is the sorption capacity and in general is a function of the concentration,  $p$ , or the temperature,  $T$ , and  $k$  is a constant which is a function of the temperature. An equation for the sorption isothermal in the form  $c_\alpha=c_{\max}(1-e^{-\omega p})$  is deduced in which  $\omega$  is a constant. It is shown that under certain conditions the sorption capacity, as placed in the above equation, is not always constant, and the correction in the kinetic equation introduced on this account increases the agreement between theory and experiment. In consequence, the number of sorption processes expressed by the equation  $c=c_\alpha(1-e^{-kt})$  is increased. The dependence of the sorption capacity on the temperature is given by the equation  $c_\alpha=c_0e^{-\delta/\sqrt{T}}$ , where  $\delta$  is a constant. This equation agrees well with the experimental data. The influence of temperature on the initial sorption velocity  $w_i$  has been determined, and it is shown that  $w_i$  can increase with the temperature, whereas  $c_\alpha$  always decreases

with increase in temperature. This explains the crossing of the isotherms of the sorption kinetics for different temperatures.

J. F. S.

**Investigations on the Adsorption of Iodine by Various Substances.** A. LOTTERMOSER (*Kolloid Z.*, 1923, **33**, 271—274).

—The adsorption of iodine from solutions in potassium iodide and carbon tetrachloride by starch, basic lanthanum acetate, lecithin-albumin, calcium hydroxide, cholic acid, and calcium oxide has been investigated. It is shown in the case of basic lanthanum acetate that when the basic acetate is prepared at 18° iodine is adsorbed to form a brown precipitate, but when the precipitate is kept for twelve hours, or warmed at 40—50°, it then adsorbs iodine to form a blue precipitate. Heating at 70° gives a precipitate which adsorbs iodine with the formation of a dirty green precipitate, whilst if the precipitate is boiled it then adsorbs iodine to form a yellow adsorption compound. The adsorption curves in the various cases are entirely different. The longer the basic acetate is kept the less iodine is adsorbed. This is due to the fact that the structure of the basic acetate changes on keeping, and in four weeks it becomes crystalline, and then ceases to adsorb iodine. Calcium hydroxide adsorbs iodine from a solution in carbon tetrachloride with the formation of a brown colour; in this case it is held that the iodine is chemically combined with the calcium hydroxide. Calcium oxide adsorbs iodine from solutions in carbon tetrachloride according to an adsorption isotherm, and calcium carbonate does not adsorb iodine at all. Cholic acid adsorbs iodine from solutions in potassium iodide when it crystallises from such solutions, but crystalline cholic acid when placed in a solution of iodine in potassium iodide does not adsorb iodine.

J. F. S.

**Adsorption Compounds. IV.** R. HALLER (*Kolloid Z.*, 1923, **33**, 306—309; cf. A., 1919, ii, 198; 1921, ii, 21).—The dyeing of cotton and wool by indigotin, Alizarin VI, Indanthren-blue-*RS* and Para-red sol, both alone and in the presence of sodium hydrogen sulphate, has been investigated and both the dye solution and the dyed fibres have been examined microscopically. In the case of indigotin with cotton, a greyish-blue colour is produced which is not changed much by sodium hydrogen sulphate and practically the whole of the dye can be removed by washing with water. The indigotin particles are very loosely held by the fibres. With wool, the case is different; here the fibres become dyed more rapidly and more intensely, and very little of the colour is lost on prolonged washing. The presence of sodium hydrogen sulphate gives a deeper colour, and the dye is homogeneously disseminated through the fibre. With Alizarin VI suspensions, cotton, on boiling with the solution, forms a weak adsorption compound, which breaks down on washing repeatedly with water. In the presence of sodium hydrogen sulphate, there is a strong adsorption and the cotton is dyed brownish-yellow; the adsorption compound thus formed is more stable towards water and on repeated washing the cotton remains pale yellow. With wool, the adsorption is much stronger than with cotton, the

fibres becoming violet coloured, but in the presence of sodium hydrogen sulphate, chrome-yellow. Both withstand washing with water, and microscopic examination shows that the fibres are homogeneously coloured. The results obtained with Indanthren-blue-*RS* are similar to those obtained with alizarin. The experiments show that wool is a more powerful adsorbent than cotton. Wool forms stable derivatives with chemically inactive substances which can only be termed adsorption compounds. The results raise a doubt as to the correctness of the generally held view that the dyeing of wool is a chemical process. J. F. S.

**Diffusion of Hydrogen through Metals.** H. G. DEMING and B. C. HENDRICKS (*J. Amer. Chem. Soc.*, 1923, **45**, 2857—2864).—An apparatus is described which enables the diffusion of gases through metals to be measured at temperatures up to 1,000° under perfectly definite conditions. The specific rate of diffusion of hydrogen through several common metals has been measured, and the following values, expressed in mg. per hour per sq. cm. area per mm. thickness, have been obtained: aluminium, no diffusion detectable at 555°; zinc, 0.0012 at 375°; lead, 0.001 at 265°; copper, 0.011 at 500°; copper, 0.028 at 770°; nickel, 0.012 at 500°, and 0.100 at 750°. In addition, the specific rate of diffusion of hydrogen has been measured for copper and nickel over a considerable range of temperature. The following results are recorded: copper, 500°, 0.027; 550°, 0.032; 645°, 0.042; 687°, 0.056; 770°, 0.072. These values are c.c. of hydrogen per hour diffusing through 1 cm.<sup>2</sup> of copper 0.391 mm. thick. Nickel, 403°, 0.004; 450°, 0.007; 527°, 0.020; 580°, 0.029; 625°, 0.056; 695°, 0.114; 745°, 0.153. In this case, the nickel plate was 0.653 mm. thick. J. F. S.

**Solubility. IX. Metallic Solutions.** J. H. HILDEBRAND, T. H. HOGNESS, and N. W. TAYLOR (*J. Amer. Chem. Soc.*, 1923, **45**, 2828—2836; cf. A., 1923, ii, 315).—A theoretical paper in which the authors discuss the various methods of estimating the relative internal pressures of metals. Tables are given of the values of this quantity deduced from expansion and compressibility, surface tension, and heat of vaporisation. Data are given showing the correlation between these tables and the behaviour of binary metallic solutions. J. F. S.

**Individual Thermodynamic Properties of Ions.** J. N. BRÖNSTED (*J. Amer. Chem. Soc.*, 1923, **45**, 2898—2910).—The principle of the specific interaction of ions is presented in the form of a simple equation and a diagram. The individualities of the thermodynamic properties of salts vary linearly with their concentration when the total concentration is kept constant. On the basis of this law, several of the results obtained by means of the principle of the specific interaction may be derived. Thermodynamic and experimental evidence to prove the invalidity of the principle of the independent activity coefficients has been adduced. Solubility measurements embracing a series of cobaltic ammine salts in solutions of sodium sulphate and chloride have been carried out at 20°, and

the results are found to be in full agreement with the principle of specific interaction.  
J. F. S.

**Dependence of the Mobility of Univalent Ions on the Temperature.** P. WALDEN and HERM. ULICH (*Z. physikal. Chem.*, 1923, **107**, 219—234).—A theoretical paper in which it is shown that the mobility of some ions changes proportionally with the fluidity of the solution and also follows Stokes's law. The deviations of the other ions from Stokes's law are represented by simple empirical relationships. The regularities found are in opposition to the deductions from Born's hydration hypothesis. It is shown to be probable that the meaning of the regularities found may be obtained from Cunningham's formula (*Proc. Roy. Soc.*, 1910, [A], **83**, 357). Many facts are shown to be best explained by the existence of a firmly held water sheath on the ions.  
J. F. S.

**The Crystal Structure of Metals, Mixed Crystals, and Metallic Compounds.** K. BECKER (*Z. Metallk.*, 1923, **15**, 303—305).—A review of the present knowledge of the crystal structure of metals is given, together with a table showing the systems in which thirty-nine metals crystallise as shown by the Debye-Scherrer method of X-ray analysis. Fifteen of these metals crystallise in a face-centred cubic lattice, nine in a space-centred cubic lattice, nine in the hexagonal, two in the tetragonal, two in the rhombohedral, and two in a diamond lattice. In addition, five elements have a second crystalline modification. Values for the density of the elements calculated from the dimensions and arrangement of the lattice are always about 2% higher than those actually found by experiment. Metallic mixed crystals with a static arrangement of the atoms give X-ray photographs in which the lattice constants, if both metals crystallise in the same system, are an approximate linear function of those of the constituents. If the lattices are dissimilar the atoms of the metal present in the smaller amount arrange themselves in the lattice of the other metal. No relation appears to exist between the symmetry of crystals of intermetallic compounds and that of their components; thus,  $\text{Cu}_2\text{Zn}_3$  and  $\text{Al}_3\text{Mg}_4$  have a regular face-centred lattice, whereas zinc and magnesium crystallise in the hexagonal system;  $\text{Cu}_2\text{Al}$  and  $\text{CuAl}$  are tetragonal or hexagonal and  $\text{NiAl}$  has a simple cubic lattice, whilst copper, nickel, and aluminium all have a cubic face-centred lattice (cf. A., 1923, ii, 519).  
A. R. P.

**Rhythmic Crystallisation.** H. KÄGI (*Kolloid Z.*, 1923, **33**, 284—286).—In an earlier paper, a description of the production of rhythmic crystals of the racemic form of the menthyl ester of benzyl-acetoacetic acid was given (A., 1920, i, 748); further details for the production of rhythmic crystal figures are now given. It is shown that the ester employed must melt at 48—52°, and that it is best purified by distillation in steam, since crystallisation from acetic acid and alcohol produces a separation of the isomerides. Further, a freshly prepared benzene solution should be used, for when kept a mutarotation occurs, as shown by the following values of the rotation



measured at intervals of eight days,  $-9.1^{\circ}$ ,  $-9.9^{\circ}$ ,  $-10.1^{\circ}$ . The solution having the last-named value gives no ring-formed crystal structure.

J. F. S.

### Explanation of the Colloidal Appearance of the Proteins.

J. LOEB (*Rev. Gen. Colloïdes*, 1923, 1, 3—17).—Portion of a lecture delivered at the Institute of Medicine in Chicago, November 24th, 1922, in honour of Pasteur. The lecture deals with the properties of the proteins and shows that the chemistry of these substances is not different from that of crystalloid substances, and that they can combine stoichiometrically with acids and bases to form protein salts which in solution dissociate electrolytically. The very large ions and molecules of the proteins are unable to diffuse freely across gels and membranes which are easily permeable to the smaller crystalloid ions. These facts lead to an unequal partition of diffusible crystalloid ions between a solution of a protein and an external aqueous solution, or between a protein gel and an aqueous solution. In this partition, the total concentration of crystalloid ions is always greater in the protein solution or gel than in the surrounding aqueous solution. This is the cause of the colloidal appearance of solutions and gels of proteins. Measurement of the membrane potential shows that the excess concentration of crystalloid ions in the solution of protein over that outside this solution can be determined by means of Donnan's theory of membrane equilibria, and that all the effects of electrolytes on osmotic pressure, swelling, and viscosity of proteins can be calculated with satisfactory exactitude by Donnan's equilibrium equation. Colloidal chemistry, therefore, appears to be only an imperfectly observed condition of equilibrium of the classical chemistry, at least so far as it deals with the proteins. The mistake is due to two causes, first, the omission of colloid chemists to measure the hydrogen-ion concentration of their solutions, which is the chief variable factor in these cases, and second the failure to measure and take into consideration the membrane potential of the solutions and protein gels, which furnishes the proof that the theory of membrane equilibria must be used to explain the colloidal appearance of proteins.

J. F. S.

### Variable and Invariable Properties of Dispersion.

W. OSTWALD (*Kolloid Z.*, 1923, 33, 300—306).—A theoretical paper, in which it is shown that the independence of, for example, the osmotic pressure and the mean kinetic energy of a particle on its degree of dispersion is rather an intuitively derived fact than a rigidly derived consequence of the molecular kinetic theory. On the other hand, the thermodynamic or the capillary physical theory of disperse systems gives a strict explanation of this remarkable independence. The osmotic pressure, mean kinetic energy, density, refractive power, and cataphoretic velocity belong to the group of properties which are proportional to the absolute surface of the particles and also to the square of the specific surface. If the measure of these properties is given by  $W$ , then  $W = K n o (o/v)^2$  or  $o/n \cdot (o/v)^2 = K$ , where  $o$  is the surface,  $v$  the volume,  $n$  the number of monodisperse particles, and  $K$  a very general topographical con-

stant, which depends entirely on the shape of the particles; for cubes  $K = 216$  and for spheres  $K = 113$ . This constant, in particular, is independent of the degree of dispersion. The experimentally observed independence of the above-named properties of the degree of dispersion is due therefore to the fact that these properties depend in a double sense on the degree of dispersion. These two functions are opposed to one another and in the final result eliminate each other. When one or other of the two functions varies so that the above-named condition is not fulfilled, exceptions to the secondary independence appear. The properties which are most strongly dependent on the degree of dispersion are those which are governed by only one of the functions. J. F. S.

**Determination of Size and Distribution of Size of Particles by Centrifugal Methods.** T. SVEDBERG and J. B. NICHOLS (*J. Amer. Chem. Soc.*, 1923, **45**, 2910—2917).—Stokes's law has been modified to give an exact formula for determining the radius of a particle sedimenting under centrifugal force. This formula has the form  $r = \sqrt{9\eta \log_e(x+a)/a} / \sqrt{2(d_p - d_l)w^2t}$ , where  $r$  is the radius,  $a$  the distance from the axis of rotation to the meniscus of the sol in a centrifuge tube,  $x$  the distance which the boundary has moved in time  $t$ ,  $\eta$  the viscosity of the liquid, and  $d_p$  and  $d_l$  are respectively the densities of the particle and the dispersion medium. A special type of centrifuge is described which permits a sol to be observed or photographed while it is being precipitated. This method depends on the projection of a uniform beam of light up through a tube containing the material each time the tube passes over a certain point. The rate of movement of the particles in the tube may then be observed. To illustrate the method for a fairly uniformly sized colloid, results for two different gold sols, clay, barium sulphate, and arsenious sulphide are given. Another method is discussed for determining the distribution of size of particles, depending on the variation of concentration with distance from the axis of rotation in a disperse system subjected to centrifugal force. J. F. S.

**Theory of Emulsification.** P. FINKLE, H. D. DRAPER, and J. H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1923, **45**, 2780—2788).—A paper in which the present position of the theory of emulsification is outlined. The types and relative stabilities of emulsions formed by the aid of various soaps have been explained by the aid of the theory of orientation of the soap molecules in the interface. The curvature of the film of soap adsorbed at the interface is more convex towards water, yielding more stable emulsions of the oil-enclosed type the larger the metal atom in the soap. As the number of hydrocarbon chains attached to a single metallic atom increases, the curvature is reversed, becoming strongly convex towards the oil phase with soaps of the tervalent metals, aluminium and iron, which yield the most stable emulsions of water in oil. Experimental data on the type and relative stabilities of emulsions of various liquids with water show that the transition from the most stable oil-enclosed to the most stable water-

enclosed emulsion for both stearates and oleates follows the order: caesium, potassium, sodium, calcium, silver, magnesium, zinc, aluminium, iron. This order is in accordance with the valencies and atomic diameters of the metals as interpreted by the orientation hypothesis. It is suggested that the type of emulsion produced by a solid powder is determined by the angle of contact of the interface with the solid. In order for the powder to remain in the interface the angle must be finite, and unless the angle is  $90^\circ$ , the interface will be on one side or the other of the points of contact of the particles, and its tension will cause the film to be concave on that side.

J. F. S.

**Preliminary Attempt to Measure Gravimetrically the Distance Effect of Chemical Affinity.** T. W. RICHARDS and W. T. RICHARDS (*Proc. Nat. Acad. Sci.*, 1923, 9, 379—383).—After a brief discussion of attempts which have been made to ascertain the law connecting the force of cohesion and distance, a number of experiments, designed to measure the force of chemical affinity at short distances, are described. The experiments consisted in suspending horizontally a plate of aluminium, 6 cm. sq., to one arm of a delicate balance and after counterpoising it, bringing materials which have considerable affinity for it underneath it and measuring the pull by the change of apparent weight. The materials used were oxides of silver, copper, iron, zinc, and magnesium, sulphur, iodine, and bromine, the two last-named substances being covered with mica. In the case of the oxides and sulphur, the distance between the aluminium and the oxide was about 0.001 m., with iodine 0.01 mm., and with bromine 0.02 mm. The experiments show that in no case is there an attractive force amounting to 0.1 mg. Hence it is concluded that the force of chemical affinity must decrease very rapidly as the distance between the attracting atoms increases.

J. F. S.

**Extremely Dry Liquids.** G. N. LEWIS (*J. Amer. Chem. Soc.*, 1923, 45, 2836—2840).—A theoretical paper in which it is shown that the only plausible explanation of the effects produced by exhaustive desiccation of liquids which seems to be consistent with thermodynamics rests on the assumption that water is a catalyst for processes between various molecular states, and that its removal merely inhibits such processes. If this explanation is correct, the process of drying only “freezes” an existing equilibrium and (at constant temperature) cannot alter the static properties of a liquid. This leads, among other things, to the prediction that liquids will be found which exhibit abnormally low, as well as abnormally high, boiling points.

J. F. S.

**Theory of Chemical Reactivity.** F. O. RICE (*J. Amer. Chem. Soc.*, 1923, 45, 2808—2820).—A theoretical paper in which an explanation for the high temperature coefficient of chemical reactions is offered; it is assumed that the law of mass action in its classical form is true, and that its apparent failure is due to using

stoicheiometric equations which do not represent, even approximately, the reactions taking place in solutions. When the ordinary stoicheiometric equations are replaced by equations representing more nearly what occurs, it has been shown that certain molecules are connected with an equilibrium constant in such a way that their concentrations vary with the temperature. These are referred to as active molecules, and it is due to these that "slow" reactions have a high temperature coefficient. The hypothesis predicts that chemical reactions will fall into comparatively few classes, each class having a characteristic temperature coefficient. In this hypothesis, the assumption is made that the non-hydrated hydrogen- and hydroxyl-ions are the catalytically active particles, and this leads to the conclusion that stoicheiometrically neutral water is distinctly alkaline catalytically, and it is not until the hydrogen-ion concentration has a  $p_H$  value about 5 that the concentrations of the non-hydrated ions become equal, and the catalytic activity is at a minimum.

J. F. S.

**An Extension of the Equation for the Velocity Constant of a Unimolecular Reaction.** H. J. PRINS (*Chem. Weekblad*, 1923, 20, 686—689).—Starting from the assumption that in the ideal gas the relation between the atomic energy and the combining energy is the same for the greater proportion of the individual molecules, but in a few individuals may vary from the average value, and combining the mathematical probability of any given configuration so deduced with the relation between the stability and entropy of the system, it is possible to arrive at Boltzmann's equation,  $S = k \log_e W + A$  where  $S$  is the entropy and  $W$  the probability of the given configuration at a given instant; then from the assumption that the small proportion of activated molecules take up radiant energy from the medium, as expressed in the photochemical law of Einstein, it is possible to form a conception to account for the relation  $v = \nu N_a$  for the velocity of dissociation of simple molecules in the gaseous phase.

S. I. L.

**The Rate of Hydrolysis of Methyl Acetoacetate.** G. LJUNGGREN (*Ber.*, 1923, 56, [B], 2469—2471).—The hydrolysis of methyl acetoacetate by sodium hydroxide has been re-examined, since the velocity constants observed by Goldschmidt and Oslan (A., 1900, i, 132, 373) and Goldschmidt and Scholz (A., 1907, ii, 244) diminish rapidly for a reason which these authors have not been able to explain. A source of error in Goldschmidt's experiments is caused by the ketonic hydrolysis of methyl acetoacetate which proceeds fairly rapidly in acid solution and hence commences rapidly when the alkaline solution is introduced into an excess of acid in order to stop alkaline hydrolysis. The main cause of error, however, lies in the unsuitability of phenolphthalein for the titration in the presence of the markedly acidic methyl acetoacetate. The previously observed irregularities disappear when phenolphthalein is replaced by Bromothymol-blue. The velocity constant is 0.01211, this value being lower than that observed by Goldschmidt. H. W.

**The Formation of Aniline Black, a Bimolecular Reaction.** J. PICCARD and F. DE MONTMOLLIN (*Helv. Chim. Acta*, 1923, 6, 1021—1029).—The oxidation of aniline by potassium dichromate and sulphuric acid to Aniline-black has been found to be a reaction of the second order (bimolecular). The experimental method used was the comparison of the rates of reaction at different concentrations of aniline, these being measured by the time taken for the solution to attain a given degree of opacity. It might be supposed that there may be a rapid unimolecular reaction at first, as suggested by Goldschmidt (A., 1920, i, 226) followed by a measurable bimolecular reaction, but this suggestion is disproved by the recovery of unchanged aniline from solutions in which oxidation has been cut short. The reaction velocity increases with increasing acidity, but the order of the reaction is not affected. The question is complicated by the discovery that the oxidation of aniline to Aniline-black is autocatalytic. If the velocity at any moment is proportional to the concentration of aniline present and to the amount already oxidised, which is also proportional to the initial amount of aniline, then the observed reaction velocity is at least proportional to the square of the aniline concentration. The reaction is then unimolecular in Goldschmidt's sense, but bimolecular from the point of view of reaction velocity. It is impossible to draw conclusions regarding the intermediate products from the reaction velocity.  
E. H. R.

**Second Report of the Committee on Contact Catalysis.** W. D. BANCROFT (*J. Physical Chem.*, 1923, 27, 801).—A review of the experimental work done during the last two years.

**Catalytic Metals.** J. PICCARD and E. THOMAS (*Helv. Chim. Acta*, 1923, 6, 1044—1045).—The precipitate obtained by reducing copper sulphate with a chromous salt contains, when freshly prepared, 98.9% of copper. It is therefore essentially metallic copper, not cuprous oxide, as stated in Abegg's handbook. A very active form of silver is obtained by reducing a solution of silver perchlorate with a solution of chromous acetate in perchloric acid. It forms a white powder,  $d$  1.7, containing 99.6% Ag, and is twice as active as "molecular" silver, prepared by the action of zinc on silver chloride. The activities were compared in the catalysis of the decomposition of chromous chloride by the reaction  $2\text{CrCl}_2 + 2\text{HCl} = 2\text{CrCl}_3 + \text{H}_2$ . A catalytically active colloidal palladium solution is obtained by dissolving palladium hydroxide in glacial acetic acid and reducing with hydrogen. It is valuable for promoting reductions with hydrogen.  
E. H. R.

**Hydrogenation of Fats. I. Influence of Various Substances on the Nickel Catalyst.** G. KITA and T. MAZUME (*Mem. Coll. Sci. Kyoto*, 1923, 3, 81—94).—The influence of the addition of aluminium oxide, magnesium phosphate, magnesium oxide, calcium borate, calcium phosphate, sodium carbonate, stearic and palmitic acids, and moisture, respectively, to the nickel catalyst was studied as regards the volume of hydrogen absorbed and the

rate at which this absorption took place. The effect of these additions was found to depend on the conditions under which the mixing was carried out. In most cases, optimal proportions of the mixture exist which give the maximum rate of absorption of hydrogen, this optimum mixture depending on the conditions under which the mixing was effected. In most cases, a much greater improvement in the activity of the catalyst was obtained if the exciting substance was added to the nickel oxide before its reduction, this being especially the case with aluminium and magnesium oxides and calcium borate. In the case of calcium phosphate, an exceedingly active catalyst was obtained by adding 12% of calcium phosphate to nickel carbonate and reducing the mixture. The addition of stearic and palmitic acids to the oil to be hydrogenated was found to have a beneficial effect on the rate of hydrogenation, especially the former acid in quantities up to 10% of the oil. Sodium carbonate was found to have a retarding effect on the catalyst in all the proportions studied. The oil used in all the above experiments was soja-bean oil refined with sodium hydroxide, and hydrogenation was carried out at atmospheric pressure and at 170°. The presence of moisture in the catalyst, whilst not specially affecting the activity of a powerful catalyst, was found to have a serious disturbing influence on a weak catalyst. This feature and the existence of optimum quantities of exciting substances suggests an analogy with the action of enzymes.

H. C. R.

**Heterogeneous Catalysis.** L. GURWITSCH (*Z. physikal. Chem.*, 1923, 107, 235—248).—The author describes a number of cases of heterogeneous catalysis from which he draws the conclusion that such catalysis is best explained by adsorption and the formation of adsorption compounds. There is no need to assume the formation of definite intermediate compounds. Among the examples quoted are the polymerisation of pinene in the presence of partly dehydrated floridin (Florida earth). In this reaction a considerable amount of heat is evolved and the products consist of camphenes and polyterpenes. The amount of polyterpenes produced is less the lower the temperature at which the reaction takes place. The amount of pinene changed is greater the smaller the water content of the floridin down to 6.19% of water, at which point 99% of the pinene is changed, and of this 4.9% is converted into polyterpenes. The greater the water content of the floridin up to 30% the greater is the percentage of the changed pinene converted into polyterpenes. The mechanism of the reaction is therefore the formation of polyterpenes as primary product, due to the adsorption of pinene by the floridin; the polyterpenes are then broken down by the heat of the primary reaction, with the formation of isomeric monoterpenes. The water of hydration of the floridin takes a part in the reaction, and the active force which brings about the polymerisation is the force of attraction between the pinene and the strongly dehydrated floridin. Partly dehydrated "grown" alumina prepared according to Wislicenus's method catalyses the reaction between carbon disulphide and water, giving hydrogen sulphide and carbon dioxide,

and in the same way ethyl chloride and water give ethyl alcohol and aluminium chloride. Precipitated alumina, whether moist or partly dehydrated, or moist "grown" alumina, have no such action. The reaction is explained by the adsorption of the carbon disulphide or ethyl chloride by the alumina which is thereby brought into intimate contact with the water and so into reaction. The practice of coating glass vessels with paraffin wax to reduce the decomposition of hydrogen peroxide is quoted, and in this connexion it is deduced theoretically that since high molecular paraffins have a greater power of adsorption than lower molecular paraffins, the former will catalyse the decomposition of hydrogen peroxide more than the latter, and also organic compounds containing oxygen having a greater physico-chemical energy have a greater adsorptive power than the paraffins, consequently they catalyse the decomposition of hydrogen peroxide more than the paraffins. It follows therefore that adsorptive power and catalytic power run parallel. These conclusions are confirmed experimentally, for it is shown that the catalytic power with respect to the decomposition of hydrogen peroxide increases in the order paraffin m. p. 52°, palmitic acid, paraffin m. p. 88°, cerotic acid. Other cases which also show the importance of adsorption in heterogeneous catalysis are quoted.

J. F. S.

**Possible Reconciliation of the Octet and Positive-Negative Theories of Chemical Combination.** W. A. NOYES (*J. Amer. Chem. Soc.*, 1923, **45**, 2959—2961).—A discussion of what happens to the electrons on the separation of two atoms from one another. The two alternative views, namely, that one electron remains attached to each atom, in which case both atoms would be electro-neutral, and that both electrons remain with one atom making it electro-negative whilst the other is electro-positive, are considered. It is shown that an atom does not always separate from a compound in the same electrical condition as it enters it.

J. F. S.

**Chemical Valency from the Point of View of Energy.** H. G. GRIMM and K. F. HERZFELD (*Physikal. Z.*, 1923, **24**, 486—488).—The authors discuss the question of how loosely a valency electron must be associated with the nucleus in order that it may become detached in a chemical reaction. The heat of formation of a metallic compound is regarded as numerically equivalent to the algebraic sum of the heat of sublimation of the metal, the heat of ionisation of the vapour, and the heat of dissociation of the kation, together with the energy due to electronic affinities and that associated with the ionic lattice. The respective heats of formation of the fluorides of the elements in the third period of the periodic classification are deduced in this manner, and attention is directed to an analogy between the values so calculated and the respective heats of ionisation of the corresponding elements. Deductions are then made as to the possibility or otherwise of the production of the respective fluorides in which one, two, three, or four fluorine atoms are associated with a single positive atom as the result of chemical reaction.

J. S. G. T.

**The Construction of Simple Micro-balances.** H. J. DENHAM (*J. Text. Inst.*, 1924, **15**, T., 10—13).—A short-beam, quartz fibre, micro-balance is described; it is intended for use with a graticuled reading telescope and a graduated scale, or by a mirror galvanometer method, and has a sensitivity of  $2 \times 10^{-4}$  mg. with maximum load about 1 mg. A short review is given of the subject of micro-balances generally.

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J. C. W.



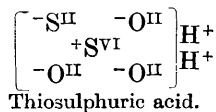
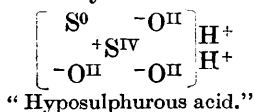
## Inorganic Chemistry.

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**Composition of Chlorine Hydrate.** A. BOUZAT and L. AZINIÈRES (*Compt. rend.*, 1923, **177**, 1444—1446).—Chlorine hydrate, prepared in presence of liquid chlorine, not water, as the liquid phase, has the formula  $\text{Cl}_2, 6\text{H}_2\text{O}$ . E. E. T.

**Mechanism of the Hydrogen Chlorine Combination.** A. L. MARSHALL and H. S. TAYLOR (*Nature*, 1923, **112**, 937—938).—In an attempt to test the validity of Nernst's theory (A., 1919, ii, 208) of the wide deviation of the hydrogen-chlorine combination from Einstein's photochemical equivalence law, atomic hydrogen has been led into a mixture of hydrogen with chlorine and bromine, respectively. The amount of hydrogen chloride formed appeared greatly to exceed that due to the atomic hydrogen present, a result which would be anticipated from the theory. A. A. E.

**Electroisomerism : The Constitutional Formula of "Hypo-sulphurous" [Thiosulphuric] Acid and the True Thiosulphuric Acid.** J. PICCARD and E. THOMAS (*Helv. Chim. Acta*, 1923, **6**, 1032—1036).—The conception of the acid  $\text{H}_2\text{S}_2\text{O}_3$  as thiosulphuric acid,  $\text{OH}\cdot\text{SO}_2\cdot\text{SH}$ , implies that it is a mixed anhydride of sulphuric acid and hydrogen sulphide, just as chlorosulphonic acid is a mixed anhydride of sulphuric and hydrochloric acids. Its properties do not agree with this conception, for it decomposes, not into sulphuric acid and hydrogen sulphide, but into sulphurous acid and sulphur in aqueous solution. It is shown that at the temperature of liquid air, in carbon dioxide solution, sulphur trioxide and hydrogen sulphide combine to give what is presumed to be the true thiosulphuric acid. In this compound, the sulphur takes the place of negative, bivalent oxygen in sulphuric acid. Ordinary "hyposulphurous acid" (thio-sulphuric acid) must be an electronic isomeride of the true thio-sulphuric acid, the additional sulphur atom being neutral. In the true thiosulphuric acid, the central sulphur atom is sexavalent; in the isomeride it is quadrivalent. The difference can only be expressed by co-ordinative formulæ thus :



E. H. R.

**The Existence of Free Thiosulphuric Acid in the Presence of Fuming Hydrochloric Acid and the Preparation of Alcoholic Solutions of Thiosulphuric Acid.** J. CASARES GIL and J. BEATO (*Ber.*, 1923, **56**, [B], 2451—2453).—If a concentrated solution of sodium thiosulphate (3—4 drops) is added to fuming hydrochloric acid (3—4 c.c.), sodium chloride is precipitated, after which the clear solution can be preserved without change for about an hour at 15°; it gives the reactions typical of thiosulphuric acid.

An alcoholic solution of thiosulphuric acid is obtained by the action of dry hydrogen sulphide on lead thiosulphate (dried at 105°) suspended in alcohol. The precipitated lead sulphide is filtered and excess of hydrogen sulphide removed from the filtrate by a current of air. The acid decomposes in the course of a few days at about 28° into sulphur and, apparently, pentathionic acid.  
H. W.

**Colloidal Selenium.** A. GUTBIER [with A. FIECHTL] (*Kolloid. Z.*, 1923, **33**, 334—337).—Relatively stable sols of selenium may be prepared by evaporating on the water-bath, to a syrupy consistency, an aqueous solution containing equimolecular quantities of selenium dioxide and dextrose and then adding one drop at a time of concentrated ammonia, taking care that the solution remains syrupy. After cooling and mixing with water, reddish-brown sols are obtained which after a short time are stable, and contain about 0.016 g. of selenium per 100 c.c. The stability of the sol is increased by the presence of a slight excess of dextrose. The sols are stable on boiling, but on freezing they are completely and irreversibly coagulated if there is no excess of dextrose. The sols are sensitive to electrolytes. Glycerol sols can be prepared in the same way as the hydrosol and have similar properties.  
J. F. S.

**Ammonia Equilibrium.** A. T. LARSON and R. L. DODGE (*J. Amer. Chem. Soc.*, 1923, **45**, 2918—2930).—The equilibrium values for the reaction  $N_2 + 3H_2 \rightleftharpoons 2NH_3$  have been determined at 10, 30, 50, and 100 atmospheres pressure for the temperature range 325° to 500°. The following values observed for the percentage of ammonia at equilibrium are recorded: at 10 atms. pressure, 350°, 7.35; 400°, 3.85; 450°, 2.04; 500°, 1.20; 30 atms. pressure, 350°, 17.80; 400°, 10.09; 450°, 5.80; 500°, 3.48; 50 atms. pressure, 350°, 25.11; 400°, 15.11; 450°, 9.17; 500°, 5.58; 100 atms. pressure, 400°, 24.91; 450°, 16.35; 500°, 10.40. Equilibrium constants have been calculated for each of the pressure-temperature conditions investigated. These constants are found to increase with increase of pressure. By means of empirical formulæ the percentage of ammonia at equilibrium has been calculated for a temperature range 200—1,000° and a pressure range 10—100 atms.  
J. F. S.

**The Reduction of Azoimide.** J. PICCARD and E. THOMAS (*Helv. Chim. Acta*, 1923, **6**, 1039—1040).—The reduction of azoimide by chromous chloride in acid solution takes place according to the equation  $HN_3 + H_2 = NH_3 + N_2$  (cf. Briner and Winkler, *A.*, 1923, ii, 485).  
E. H. R.

**Vapour Pressure of Nitric Oxide.** H. GOLDSCHMIDT (*Z. Physik*, 1923, 20, 159—165).—Particulars are given of the determination of the vapour pressure of nitric oxide at temperatures between  $-148^{\circ}$  and  $-181^{\circ}$ . The results indicate that at  $T^{\circ}$  (Abs.), the vapour pressure of the liquid phase (measured in mm. of mercury) is given by the equation  $\log p = 6.92669 - 0.010801T + 1.75 \log T - 778.13/T$ . The corresponding equation for the solid phase is  $\log p = 6.92669 - 0.005895T + 1.75 \log T - 837.42/T$ . The occurrence of considerable association amongst the molecules of liquid nitric oxide is established. From the results the following values of physical constants relating to nitric oxide are calculated: b. p.  $-151.13^{\circ}$ ; triple point,  $-163.21^{\circ}$ ; vapour pressure at the triple point, 170.2 mm.; latent heat of evaporation at respective temperatures:  $-151.13^{\circ}$ , 3199 cal.;  $-155^{\circ}$ , 3230;  $-160^{\circ}$ , 3289;  $-163.21^{\circ}$  (liquid), 3324;  $-163.21^{\circ}$  (solid), 3863;  $-165^{\circ}$ , 3872;  $-168^{\circ}$ , 3885;  $-173^{\circ}$ , 3902;  $-177^{\circ}$ , 3912;  $-183^{\circ}$ , 3923; latent heat of fusion at the triple point, 539 cal.  $\pm 1\%$ . J. S. G. T.

**Hydrofluosilicic Acid.** II. C. A. JACOBSON (*J. Physical Chem.*, 1923, 27, 761—770; cf. A., 1923, ii, 561).—Experiments are described which show that silicon tetrafluoride and water vapour do not react at temperatures between  $30^{\circ}$  and  $125^{\circ}$ . Four types of experiment have been carried out with the object of ascertaining the condition of hydrofluosilicic acid in the vapour phase. In the first case, air was passed through dilute solutions of the acid at various temperatures and the resulting products passed through water for absorption. In the second and third cases, strong solutions of the acid were distilled, first at the ordinary temperature and then by boiling with various desiccating agents introduced in the stream of vapour. In every experiment where the water was removed from the vapour mixture, no trace of hydrofluosilicic acid was obtained in the receivers. In the fourth case, an attempt was made to liberate the acid from its sodium salt by means of concentrated sulphuric acid and to condense the acid in a receiver cooled by ice and salt. No liquid condensed, because the sulphuric acid removed the water from the gas mixture, leaving the apparatus filled with silicon tetrafluoride. The vapour density measurements made by Baur and Glaessner (A., 1904, ii, 119) on the gas obtained by treating barium silicofluoride with sulphuric acid indicate the complete decomposition of hydrofluosilicic acid into hydrogen fluoride and silicon tetrafluoride. All the above results indicate that hydrofluosilicic acid is a non-volatile acid like carbonic acid and sulphurous acid and cannot exist under ordinary conditions in the vapour state. J. F. S.

**Diffusibility of Helium through Thuringian Glass.** A. PIUTTI and E. BOGGIO-LERA (*Mem. Accad. Lincei*, 1923, [v], 14, 125—132).—The explanation advanced by Lo Surdo (A., 1921, ii, 331) of the divergence of the results of Ramsay, Collie, Patterson, and Masson (A., 1914, ii, 727, 847) from those of Merton (A., 1914, ii, 726), Strutt (A., 1914, ii, 201), and Piutti and Cardoso (A., 1920, ii, 311) is not valid (cf. Baly, *Ann. Reports*, 1913, 37; 1914, 41),

since the amount of helium able to penetrate from the air into a discharge tube, even one of large surface, kept for many hours at  $260^{\circ}$  is about 1% of the quantity recognisable spectroscopically by the methods used by the above investigators. The velocity of diffusion of helium through Thuringian glass is proportional to the pressure, and increases very rapidly with rise of temperature, being apparently an exponential function of the latter. T. H. P.

**The Free Electron Characteristics of Sodium-Potassium Alloys.** C. V. KENT (*Physical Rev.*, 1923, [ii], **22**, 479—485).—The free electron parameters of the sodium-potassium alloys have been calculated from optical data obtained by Morgan (*ibid.*, 1922, **20**, 204). The number of free electrons per atom is about 1.5 for all the alloys, but with an indication of a minimal value of 1.2 for the one-third sodium alloy. The frequency of impact of a free electron with molecules (1 to  $3 \times 10^{14}$ ) increases linearly with increase of either constituent to a maximum for the compound NaK supposed to exist in the liquid alloys. Calculated resistivities agree with those experimentally determined. A. A. E.

**Displacement of Metals from Solutions of their Salts by Less Electropositive Elements. I. Replacement of Sodium and Potassium by Magnesium and Aluminium.** F. W. BERGSTROM (*J. Amer. Chem. Soc.*, 1923, **45**, 2788—2794).—Amalgamated aluminium reacts with sodamide in liquid ammonia solution to form a definite crystalline compound, sodium ammono-aluminate, to which any of the following formulæ may be given:  $\text{Al}(\text{NH}_2)_2 \cdot \text{NHNa} \cdot \text{NH}_3$ ;  $\text{Al}(\text{NH}_2)_3 \cdot \text{NaNH}_2$ ;  $\text{Na}[\text{Al}(\text{NH}_2)_4]$ . This compound loses one molecule of ammonia when heated in a vacuum above  $90^{\circ}$ . The equations for the reaction are shown to be  $\text{Al} + 3\text{Na}(\text{NH}_2) \rightleftharpoons \text{Al}(\text{NH}_2)_3 + 3\text{Na}$ ;  $\text{Al}(\text{NH}_2)_3 + \text{NaNH}_2 = \text{Al}(\text{NH}_2)_2 \cdot \text{NHNa} \cdot \text{NH}_3$ ;  $3\text{Na} + 3\text{NH}_3 = 3/2\text{H}_2 + 3\text{NaNH}_2$ . The actions of potassamide on amalgamated aluminium and on magnesium are analogous in character. An explanation is given which depends on the fact that dilute solutions of the alkali metals in ammonia are salt-like in character. The initial stages may be regarded as metatheses, although actually involving equilibria which suffer continual displacement because of secondary reactions. A solution of sodium in liquid ammonia reacts with amalgamated aluminium to form the same sodium ammono-aluminate mentioned above. Sodamide is probably first formed, and this then reacts in accordance with the equations above. The mercury of the amalgam does not play an essential part in the reaction. J. F. S.

**Equilibria in Solutions containing Mixtures of Salts. III. System, Water and the Chlorides and Carbonates of Sodium and Potassium at  $25^{\circ}$ . IV. System, Water and the Sulphates and Carbonates of Sodium and Potassium at  $25^{\circ}$ .** W. C. BLASDALE (*J. Amer. Chem. Soc.*, 1923, **45**, 2935—2946; cf. A., 1918, ii, 231; 1920, ii, 237).—Certain optical and crystallographic properties of the hydrates of sodium carbonate and of the hydrate of the double sodium potassium carbonate have been determined, which

can be used in identifying these compounds by means of the microscope. The solubility data necessary for the preparation of complete phase rule diagrams for the systems  $\text{H}_2\text{O}-\text{Na}_2\text{CO}_3-\text{KCl}$  and  $\text{H}_2\text{O}-\text{Na}_2\text{CO}_3-\text{K}_2\text{SO}_4$  at  $25^\circ$  have been determined. J. F. S.

**Triple Salts.** F. EPHRAIM (*Helv. Chim. Acta*, 1923, 6, 920—930).—The important part played by space considerations in determining the possibility of formation of complex compounds is well illustrated by the series of triple nitrites, of which the best known member is the salt  $\text{K}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$ . The extent to which each of the constituent metals can be replaced by related metals is determined by the atomic volumes of the metals. The copper (at. volume 7.1) can be replaced by nickel (6.6), cobalt (6.8), and iron (7.1), but not by any metal with greater atomic volume, such as manganese (7.4) or zinc (9.2). The potassium (45.3) can only be replaced by rubidium (56.2), caesium (70.4), and ammonium, not by sodium (22.9), or thallium (17.2). The lead (18.2) can be replaced only by calcium (25.2), strontium (32.6), and barium (36.3), save under exceptional conditions. When nickel, with the small atomic volume 6.6, replaces copper, it is possible to introduce cadmium (13.0) and mercury (14.1) in place of the bigger lead atom.

Most of the known triple salts are derived from weak acids, but one triple chloride,  $6\text{KCl}, \text{CuCl}_2, 3\text{HgCl}_2, 2\text{H}_2\text{O}$ , has been described (von Bonsdorff, *Ann. Phys. Chem.*, 1834, 33, 81). The existence of this salt could not be confirmed, but a new triple *potassium copper mercuric chloride*,  $8\text{KCl}, \text{CuCl}_2, 4\text{HgCl}_2$ , was discovered. It separates from a hot, aqueous solution of its components in yellowish-brown needles. It is not stable in the cold in contact with the mother-liquor. Attempts to prepare similar salts containing nickel or magnesium instead of copper, or bromine instead of chlorine, were unsuccessful. A triple chloride of another type,  $\text{KCuCl}_3, 2\text{KPbCl}_3$ , was discovered, however. It can only be obtained from a solution of its constituents in concentrated hydrochloric acid, and forms microscopic, brownish-yellow prisms. Another type of salt which was prepared containing three different metals has the composition  $\text{K}_2[\text{Cu}(\text{NO}_2)_4, \text{H}_2\text{O}] + 2\text{K}_2[\text{HgCl}_4, \text{H}_2\text{O}]$ . It crystallises in thick, black prisms, and is probably to be regarded as a mixture of its constituents, possibly as a solid solution. The known potassium copper nitrite is found to have the formula  $\text{K}_3[\text{Cu}(\text{NO}_2)_5, \text{H}_2\text{O}]$  instead of  $\text{K}_3[\text{Cu}(\text{NO}_2)_5]$ . The following new triple nitrites are described: *caesium barium nickel nitrite*,  $\text{Cs}_2\text{Ba}[\text{Ni}(\text{NO}_2)_6]$  forms an orange-brown powder, very sparingly soluble in water; *caesium lead copper nitrite*,  $\text{Cs}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$ , sparingly soluble, black, microscopic crystals. A new *ammonium manganese carbonate*,  $(\text{NH}_4)_2\text{CO}_3, \text{MnCO}_3, 4\text{H}_2\text{O}$ , microscopic prisms, was also obtained. E. H. R.

**The Fusibility of the Ternary System Sodium Fluoride-Calcium Fluoride-Aluminium Fluoride.** P. P. FEDOTÉEV and W. P. ILJINSKY (*Z. anorg. Chem.*, 1923, 129, 93—107).—The examination of the system  $\text{AlF}_3-\text{NaF}$  (A., 1913, ii, 324) has been completed and the investigation extended to the ternary system with calcium

fluoride, the concentration triangle being fully worked out. The system  $\text{NaF-CaF}_2$  shows a simple eutectic at  $810^\circ$ , 67.5 mol. %  $\text{NaF}$ . Fusions of calcium fluoride with aluminium fluoride are only realisable between the limits 30 mol. % and 60 mol. %  $\text{AlF}_3$ ; the eutectic is at  $820^\circ$ , 37.5 mol. %  $\text{AlF}_3$ , and there is a marked tendency to supercooling, with formation of solid solutions of the components. The system  $\text{NaF-AlF}_3$  has two maxima, one corresponding with cryolite, 25 mol. %  $\text{NaF}$ , m. p.  $1,000^\circ$ , which melts without decomposition, the other with a compound with 40 mol. %  $\text{NaF}$ , which melts with decomposition at  $725^\circ$ ; the minima are at  $885^\circ$ , 86 mol. %  $\text{NaF}$ , and  $685^\circ$ , 53.4 mol. %  $\text{NaF}$ .

The temperatures of invariant equilibrium for the ternary system are  $780^\circ$ ,  $705^\circ$ , and  $675^\circ$ , the minimum point for the space pyramid lying between the compositions  $\text{NaF : CaF}_2 : \text{AlF}_3 = 58.7 : 5.9 : 35.4$  and  $:: 56.5 : 8.3 : 35.2$  mol. %, respectively; the diagram shows thirteen regions.

S. I. L.

**Crystal Structure of Sodium Chlorate.** N. H. KOLKMEIJER, J. M. BIJVOET, and A. KARSSSEN (*Z. Physik*, 1923, **20**, 82).—Referring to the work of Kiby on the crystal structure of sodium chlorate (A., 1923, ii, 687), the authors point out that the calculation of the parameters relating to light atoms from the observed intensities of the higher orders of  $X$ -ray reflections, making the approximate assumption that the reflecting power is proportional to the electronic number and independent of the angle of deviation of the rays, is unjustifiable.

J. S. G. T.

**Vapour Pressures of Lithium Chloride Solutions at  $20^\circ$ .**

B. F. LOVELACE, W. H. BAHLKE, and J. C. W. FRAZER (*J. Amer. Chem. Soc.*, 1923, **45**, 2930—2934).—The lowering of the vapour pressure of water due to dissolved lithium chloride has been measured at  $20^\circ$  and in the concentration range of 0.1N to 1.0N. An improved method for removing air from the solutions before measuring is described. This consists in introducing the solution as nearly air-free as possible into the bulb which had previously been pumped air-free, and rapidly distilling a small portion of the solvent at the pressure of its vapour into a bulb containing phosphoric oxide. The observed lowering of the vapour pressure has been compared with the values calculated from freezing-point measurements and a difference of  $-0.015$  to  $+0.014$  mm. between the two sets of values found.

J. F. S.

**An Explanation of the Explosive Decomposition of Bleaching Powder and the Mode of its Decomposition at Higher Temperatures.**

S. OCHI (*J. Chem. Ind. Japan*, 1923, **26**, 978—983).—When bleaching powder is heated above  $100^\circ$ , the chlorine-forming, oxygen-forming, and chlorate-forming decompositions occur together. If it contains a comparatively large amount (e.g., 18.01 %) of water, it is very rapidly decomposed at temperatures above  $100^\circ$  and the chlorine-forming and the chlorate-forming decompositions predominate. In this case, explosive decomposition may not occur, but such a powder is unsuitable for storage. By decreasing the

water content of the powder, the mode of decomposition is changed to the oxygen-forming one, which proceeds mildly at first but advances suddenly when the temperature is raised a little higher than  $150^{\circ}$ ; explosion then occurs. The decomposition may be expressed as follows:  $\text{OCl}\cdot\text{CaCl}_2\cdot\text{H}_2\text{O}=\text{CaCl}_2\cdot\text{H}_2\text{O}+\text{O}+14,440 \text{ cal.}$  The explosive decomposition may be brought about by external heating or by the accumulation of heat produced by auto-decomposition.

K. K.

### The Reaction of Carbon Dioxide with Bleaching Powder.

S. OCHI (*J. Chem. Ind. Japan*, 1923, **26**, 1154—1161).—The action of carbon dioxide on bleaching powder is accelerated not only by the rise of the reacting temperature and the increase of the water content of the powder, but also by the imperfection of crystallisation of the powder. The gas produced by the decomposition of bleaching powder is composed of chlorine only. On passing moist carbon dioxide or air containing carbon dioxide into bleaching powder at about  $60^{\circ}$ , chlorine is produced; it is free from carbon dioxide when the velocity of the gas is well regulated. Chlorine containing a certain amount of carbon dioxide is purified in the same way. In making the powder with chlorine containing carbon dioxide, it is concluded that the water content of the raw materials must be increased and the temperature of the bleaching chamber must be raised.

K. K.

**The Structure of Aragonite.** W. L. BRAGG (*Proc. Roy. Soc.*, 1924, [A], **105**, 16—39).—By X-ray analysis, it is shown that the crystal structure of aragonite is based on the simple orthorhombic lattice. The cell, the sides of which are of lengths  $4.94 \text{ \AA.}$ ,  $7.94 \text{ \AA.}$ , and  $5.72 \text{ \AA.}$ , contains four molecules of  $\text{CaCO}_3$ , and the symmetry is that characterising the space group  $Q^{16}_h$ . The structure is built of calcium atoms and  $\text{CO}_3$  groups having a form almost identical with the  $\text{CO}_3$  groups in calcite. Calcium atoms are arranged on a distorted hexagonal close-packed point system, intimately related in its dimensions to the distorted cubic close-packed point system associated with the calcium atoms in calcite. In aragonite, the  $\text{CO}_3$  groups are arranged differently from the corresponding groups in calcite, each oxygen atom being surrounded by three calcium atoms in the former crystal, and by two only in the latter. Considered as a whole, the  $\text{CO}_3$  group lies between two groups of three calcium atoms in both crystals. A comparison of the observed intensities of reflection of the rays and calculated amplitude factors for aragonite shows that, in accordance with the empirical law discovered by Sir W. H. Bragg in the case of calcite, the intensity is proportional to the amplitude-factor and not to the square of the latter, as suggested by theory. Twinning of aragonite crystals about the plane (110) is simply explained by the suggested structure.

J. S. G. T.

**Hydration of Anhydrite. II.** G. WEISSENBERGER and B. SOINI (*Kolloid Z.*, 1923, **33**, 290—296; cf. A., 1923, ii, 241).—The hydration of anhydrite has been investigated by measuring the

viscosity of suspensions of anhydrite in water at 18°, 30°, 40°, 50°, and 62°. It is shown that the addition of water to anhydrite proceeds to a definite end value. The quantity of added water is dependent on the concentration and on the temperature, but is independent of the size of the particles. The greater the concentration and the lower the temperature, the smaller is the amount of water added. The intensity of the combination with water achieved technically is approximately parallel with the internal friction of dilute suspensions measured viscosimetrically, but not with the amount of water taken up. J. F. S.

**The Constitutional Formula of Barium Peroxide.** J. PICCARD (*Helv. Chim. Acta*, 1923, 6, 1036—1038).—The strain theory renders it improbable that barium peroxide has the formula

$\text{Ba} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$ , whereas the double formula, containing a six-membered

ring,  $\text{Ba} \begin{smallmatrix} \text{O} & \text{O} \\ \diagdown & \diagup \\ \text{O} & \text{O} \end{smallmatrix} \text{Ba}$ , should represent a stable system. The

ready formation of barium peroxide from barium oxide and molecular oxygen can be simply represented, without rupture of the oxygen molecule, if the double formula be assumed, thus:

$\text{Ba} \begin{smallmatrix} \text{O} & \cdots & \text{O} \\ \diagdown & & \diagup \\ \text{O} & = & \text{O} \end{smallmatrix} \text{Ba} \rightarrow \text{Ba} \begin{smallmatrix} \text{O} & \text{O} \\ \diagdown & \diagup \\ \text{O} & \text{O} \end{smallmatrix} \text{Ba}$ . The fact that sodium per-

oxide cannot be formed from sodium oxide and oxygen, but only from sodium and oxygen, points to a similar oxidation mechanism in this case:  $\text{Na} + \text{O} = \text{O} + \text{Na} \rightarrow \text{Na} - \text{O} - \text{O} - \text{Na}$ . The mode of formation of many organic peroxides gives additional support to the theory. E. H. R.

**Crystal Structure of Magnesium Stannide.** L. PAULING (*J. Amer. Chem. Soc.*, 1923, 45, 2777—2780).—Crystals of the intermetallic compound, magnesium stannide,  $\text{Mg}_2\text{Sn}$ , have been prepared and investigated by means of Laue and X-ray spectrum photographs with the aid of the theory of space groups. This compound is found to have the calcium fluoride structure with  $d_{100} = 6.78 \pm 0.02 \text{ \AA}$ . The structure places eight magnesium atoms round each tin atom at the corners of a cube and four tin atoms round each magnesium atom at the corners of a tetrahedron. The closest approach of tin and magnesium atoms is  $2.94 \pm 0.01 \text{ \AA}$ . J. F. S.

**X-Ray Analysis of Zinc-Copper Alloys.** E. A. OWEN and G. D. PRESTON (*Proc. Physical Soc.*, 1923, 36, 49—65).—Particulars are given of an investigation by means of X-ray analysis of the respective structures of alloys constituting the  $\alpha$ ,  $\beta$ ,  $\beta'$ ,  $\gamma$ , and  $\epsilon$  phases of the zinc-copper alloys. J. S. G. T.

**The Solubility of Cadmium Sulphide.** J. PICCARD and E. THOMAS (*Helv. Chim. Acta*, 1923, 6, 1046).—The solubility of cadmium sulphide in dilute sulphuric acid is apparently greatly increased at the boiling point, that is, the equilibrium in the equation  $\text{CdSO}_4 + \text{H}_2\text{S} \rightleftharpoons \text{CdS} + \text{H}_2\text{SO}_4$  moves to the left. It is now shown, however, that complete solution of the sulphide can be accomplished



by passing a current of carbon dioxide through a suspension of the sulphide in cold dilute acid. The reaction is therefore subject to the usual mass-action laws.

E. H. R.

**Atomic Weight of Lead from the Belgian Congo.** T. W. RICHARDS and P. PUTZEYS (*J. Amer. Chem. Soc.*, 1923, **45**, 2954—2958).—The atomic weight of a sample of radioactive lead obtained from a mixture of minerals found in radium ore from the Belgian Congo was determined as 206·20, as compared with a control sample of ordinary lead which gave a value of 207·18. Evidently, therefore, the lead in these minerals consists chiefly of uranium lead; and the minerals must have been formed long after the original deposit of the uraninite.

J. F. S.

**Hardness of Lead-Thallium and Cadmium-Thallium Alloys.** C. DI CAPUA (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 343—346).—The thermal diagram obtained by the author for the miscibility gap of the system lead-thallium confirms that given by Lewkonja (A., 1907, ii, 261) and by Kurnakov and Pushin (A., 1907, ii, 262), the gap extending over the region 6—23% of lead. The hardness diagram resembles the pressure of flow curve for these alloys (cf. Kurnakov and Schemtschuschny, A., 1909, ii, 855). Thallium increases the hardness of lead to a maximum at 50—60% Tl, a minimum being reached at about 80%, which is the saturation point; from 80 to 94%, the course of the hardness curve does not correspond with the diagram of state. The hardness of thallium is increased by addition of lead to a maximum corresponding with the formation of saturated mixed crystals of lead in thallium. The hardness diagram for cadmium-thallium alloys agrees well with the fusion diagram and indicates a slight solubility of cadmium in thallium in the solid state.

T. H. P.

**X-Ray Analysis of Solid Solutions.** E. A. OWEN and G. D. PRESTON (*Proc. Physical Soc.*, 1923, **36**, 14—30).—By X-ray analysis it is established that a distortion of the respective lattices characterising the atomic structures of solid solutions of copper-aluminium, aluminium-magnesium, and copper-nickel is produced when a solute atom replaces an atom in the lattice of the solvent. The eutectic alloy of aluminium and copper is shown to consist of  $\text{CuAl}_2$  and another substance.  $\text{CuAl}_2$  possesses a simple tetragonal lattice of side 4·28 Å. and axial ratio 0·562, whilst the atomic structure of  $\text{CuAl}$  resembles that of a solid solution of aluminium in copper, but the distortion is considerably greater.

J. S. G. T.

**Instability of Cupric Hydroxide.** G. FOWLES (*Chem. News*, 1924, **128**, 2—5).—The hypothesis of Weiser (A., 1923, ii, 566) to account for the stabilising effect of dilute solutions of certain salts such as manganous sulphate on suspensions of gelatinous cupric hydroxide is held to be untenable, because other solvents which exert a slight solvent action on cupric hydroxide, such as sodium hydroxide, accelerate its decomposition. The amounts of added salts were not trifling when their action is considered, and varying molecular quantities were required to produce the same effect.

The author adduces experimental evidence to prove that no such continuous solvent action as Weiser imagines can possibly take place. Crystalline varieties of cupric hydroxide on being kept at the ordinary temperature gradually become discoloured, the change being first noticeable after about two years. One sample at least twelve years old eventually went quite black. The crystalline hydroxide appears to pass very slowly through those changes, which are so rapid in the gelatinous variety that the intermediate stages are not seen. In each case, the changes are accelerated by soluble hydroxides. The crystalline variety must therefore be regarded as a highly stable intermediate form in a state of suspended transformation. It is considered that the gelatinous copper hydroxide used by Weiser contained adsorbed or combined sodium hydroxide which was effectively removed by the hot salt solutions added as insoluble basic salts. The stabilisation described therefore consisted in removing a catalyst and in allowing the unstable gelatinous substance safely to pass into the more stable crystalline form. In every case in which stabilisation was successful, a substance was added which would very thoroughly remove a soluble base. Sodium sulphate and suspensions of colloidal metallic oxides, however, showed no stabilising power. H. C. R.

**Chemical Constant of Mercury.** F. SIMON (*Z. physikal. Chem.*, 1923, **107**, 279—284).—The atomic heat of mercury has been measured at temperatures between  $9^{\circ}$  and  $14^{\circ}$  Abs. and the following values have been obtained:  $9.78^{\circ}$ , 1.107;  $10.17^{\circ}$ , 1.151;  $10.89^{\circ}$ , 1.244;  $11.09^{\circ}$ , 1.284;  $12.35^{\circ}$ , 1.443;  $12.55^{\circ}$ , 1.482, and  $13.35^{\circ}$ , 1.570. These values are expressed by the equation  $C_p = \frac{3}{2}$  Debye function (120) +  $\frac{1}{4}$  Einstein function (25) +  $21 \cdot 10^{-5} T^{3/2}$ . The chemical constant of mercury has been calculated to +1.950 with a maximum error of 0.06%. This value is 0.084 larger than the theoretical value. J. F. S.

**Ebullioscopy of Double Salts of Mercuric Chloride with Alkali Chlorides.** F. BOURION and E. ROUYER (*Compt. rend.*, 1924, **178**, 86—88).—The proof (A., 1923, ii, 568) that mercuric chloride exists in solution, partly as treble molecules, is taken into account in connexion with the ebullioscopic determination of the molecular weights of sodium, potassium, and ammonium mercurichlorides (cf. A., 1923, ii, 534), which are shown to be of the type  $MCl, HgCl_2$ , or  $M[HgCl_3]$ . If the association of mercuric chloride is ignored, the results lead to the formula  $2MCl, HgCl_2$ . E. E. T.

**Complex Sulphates of Quadrivalent Cerium and the Position of this Element in the Periodic Classification.** V. CUTTICA (*Gazzetta*, 1923, **53**, 761—768).—The formulæ of the two cerous-ceric sulphates show that these compounds may be regarded as derivatives of a hypothetical ceri-sulphuric acid,  $H_4Ce(SO_4)_4$ , originating from ceric hydroxide by replacement of the four oxygen atoms by four  $SO_4$  radicals. The assumption that this complex acid is present in sulphuric acid solutions of ceric sulphate finds support in the compositions of the double compounds formed by ceric sulphate with sodium and thallos sulphates. No tendency

to unite with ceric sulphate is, however, observed with lithium sulphate, and the double silver compound,  $10\text{Ce}(\text{SO}_4)_2 \cdot 6\text{Ag}_2\text{SO}_4$ , is totally different from those given by sodium and thallium.

A solution containing bismuth sulphate, which is isomorphous with the sulphates of the rare earths, deposits, according to the conditions, one of the three compounds: (1)  $\text{Ce}^{\text{IV}}(\text{SO}_4)_4 \cdot \text{Ce}^{\text{III}}(\text{Bi})\text{H} \cdot 12\text{H}_2\text{O}$ , (2)  $\text{Ce}(\text{SO}_4)_2 \cdot \text{Bi}(\text{OH})\text{SO}_4 \cdot 5\text{H}_2\text{O}$ , and (3)  $\text{Ce}(\text{SO}_4)_2 \cdot 2\text{Bi}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ . Compound (1) contains always little bismuth, the presence of which is due to the solubility in the solid state of bismuth sulphate in cerous sulphate; it forms orange, bipyramidal prisms belonging to the hexagonal system and similar in every way to those of the acid sulphate,  $\text{Ce}^{\text{IV}}(\text{SO}_4)_4 \cdot \text{Ce}^{\text{III}}\text{H} \cdot 12\text{H}_2\text{O}$ . Compound (2) crystallises in long, cedar-yellow needles, and compound (3) in long, yolk-yellow prisms.

The question of the position to be assigned to cerium in the periodic system is discussed, and it is considered that the weight of the evidence favours the view that this metal belongs to the first sub-group of group IV. That cerium should be placed in the same column as thorium is indicated by the fact that cerium and thorium sulphates form mixed crystals. As a general rule it is, indeed, found that isomorphism exists between the salts of the lowest oxide of the heavy metal occupying the lowest position in each group and those of the element of the first sub-group of the preceding group.

With organic bases, as with silver and bismuth, the hypothetical acid,  $\text{H}_4\text{Ce}(\text{SO}_4)_4$ , forms double or complex salts with constitutions varying according to the nature of the base. Only with strong bases does normal salification occur.

[With L. BONAMICI.]—In addition to those described above, the following salts have been prepared:  $\text{Ce}(\text{SO}_4)_2 \cdot 2\text{Na}_2\text{SO}_4$ , orange-yellow, prismatic crystals;  $\text{Ce}(\text{SO}_4)_2 \cdot 2\text{Tl}_2\text{SO}_4$ , deep orange-red, prismatic crystals; with guanidine sulphate,

$2\text{Ce}(\text{SO}_4)_2 \cdot \text{NH} \cdot \text{C}(\text{NH}_2)_2 \cdot 0.5\text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  
elongated, yellow prisms;  $\text{Ce}_2(\text{SO}_4)_2 \cdot 5\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$ , amber-yellow crystals.  
T. H. P.

**Double Sulphites of Cerium, Lanthanum, and Didymium with the Alkali Elements.** V. CUTTICA (*Gazzetta*, 1923, 53, 769—772).—According to Grossmann (A., 1905, ii, 326), the sulphites of cerium, lanthanum, and didymium exhibit no tendency to form molecular compounds with sulphites of the alkali metals, but the author finds that such double sulphites are readily obtainable under suitable conditions. If excess of an alkali metal sulphite is added to a solution of the hydrogen sulphite of the rare earth metal and the liquid subsequently heated, on a water-bath, in a flask connected with a water pump so that air is largely excluded, the double sulphite separates as a microscopic powder, which is highly stable in the air but undergoes gradual oxidation to sulphate if suspended in water.

In this way were prepared: *cerium potassium sulphite*,  $\text{Ce}_2(\text{SO}_3)_3 \cdot \text{K}_2\text{SO}_3 \cdot 4\text{H}_2\text{O}$ ; *cerium ammonium sulphite*,  
 $2\text{Ce}_2(\text{SO}_3)_3 \cdot 3(\text{NH}_4)_2\text{SO}_3$ ;

*cerium sodium sulphite*,  $\text{Ce}(\text{SO}_3)_3 \cdot \text{Na}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$ ; *lanthanum potassium sulphite*,  $2\text{La}_2(\text{SO}_3)_3 \cdot 3\text{K}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$ ; *lanthanum ammonium sulphite*,  $\text{La}_2(\text{SO}_3)_3 \cdot (\text{NH}_4)_2\text{SO}_3$ ; *didymium potassium sulphite*,  $\text{Dy}_2(\text{SO}_3)_3 \cdot \text{K}_2\text{SO}_3 \cdot 4\text{H}_2\text{O}$ .

If in the above method of preparation, a deficit of sodium sulphite is employed, the *cerium sodium sulphite*,  $3\text{Ce}_2(\text{SO}_3)_3 \cdot 2\text{Na}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$ , is obtained.

T. H. P.

### **Ternary Alloys of Aluminium, Copper, and Magnesium.**

BUNTARO OHTANI (*J. Chem. Ind. Japan*, 1923, 26, 427—448).—The author has studied that part of the ternary system containing alloys of which the copper content extends up to 13% and magnesium content to 14%. The liquidus of these alloys is depressed with increasing copper and magnesium content and the liquidus surface of the system slopes downwards from the aluminium corner. The solubility of magnesium and of copper in aluminium decreases according to the increasing content of copper and magnesium respectively. For example, in the presence of 8% of magnesium, the maximum solubility of copper is reduced from 6% to 3%. The alloys of composition within the limit above described form a homogeneous solid solution ( $\alpha$ ), but the alloys of a composition beyond this limit have two arrest-points on these cooling curves and show a duplex structure consisting of  $\alpha$  and an eutectic ( $\alpha + \beta$ ) on the cooling curve ingot. This eutectic surface slopes downwards from the Al-Cu binary eutectic line to the Al-Mg alloy side. Tensile tests and measurements of Brinell's hardness and specific gravities on chill and sand castings were applied. The hardness increases slowly with copper content and rapidly with magnesium content within the limit of 1% magnesium, then slowly increases. The specific gravity increases linearly with copper content and decreases linearly with magnesium content. If the ratio of magnesium and copper is 5 : 6, the specific gravity remains constant.

K. K.

### **Manganese Dioxide in the Catalytic Oxidation of Carbon Monoxide.**

W. A. WHITESSELL and J. C. W. FRAZER (*J. Amer. Chem. Soc.*, 1923, 45, 2841—2851).—Manganese dioxide, which has a great catalytic activity in the oxidation of carbon monoxide at temperatures as low as  $-20^\circ$ , may be prepared (a) by the decomposition of potassium permanganate with concentrated nitric acid, (b) by treating Frémy's oxide with concentrated nitric acid, diluting, and washing, (c) by the oxidation of manganous sulphate with potassium permanganate in nitric acid solution, and (d) by the oxidation of precipitated manganous hydroxide. Analytical results show that the amount of impurities such as adsorbed alkali plays an important part in the activity of these catalysts. Experiments show a considerable temperature interval between the points required to oxidise hydrogen and carbon monoxide by these samples of active manganese dioxide. Carbon monoxide adsorbed by manganese dioxide is desorbed as carbon dioxide. It is suggested that the mechanism of the oxidation of carbon monoxide consists in the adsorption and simultaneous oxidation by the manganese

dioxide, followed by desorption of the carbon dioxide and re-oxidation of the catalyst. J. F. S.

**Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. VII. The Reduction of Manganate by Formaldehyde.** J. HOLLUTA (*Z. physikal. Chem.*, 1923, 107, 249—269; cf. A., 1923, ii, 864).—A continuation of previous work, in which it is shown that the reduction of manganate by formaldehyde takes place with the intermediate formation of formate-ions and consequently is a reaction which takes place in two stages. The order of the reaction has been determined by two methods and the influence of the concentration of the participating species on the velocity of the reaction has been investigated. In keeping with the theory of successive reactions, it is found that the velocity coefficient of the second order calculated on the basis of the equation  $2\text{MnO}_4'' + \text{H}\cdot\text{CHO} = 2\text{MnO}_2 + \text{CO}_3'' + 2\text{OH}'$  exhibits a tendency to decrease, whilst that calculated on the basis of the equation  $\text{MnO}_4'' + \text{H}\cdot\text{CHO} = \text{MnO}_2 + \text{HCO}_2' + \text{OH}'$  shows a tendency to increase. In consequence of the great difference of velocity of the reduction by formaldehyde and by formates, the velocity coefficient, calculated on the second equation given above, comes very close to the true coefficient. The connexion between the alkalinity of the solution and the velocity coefficient has also been studied, and it is found that the latter as a first approximation is inversely proportional to the square root of the hydroxyl-ion concentration and also directly proportional to the eighth root of the partial pressure of the oxygen liberated by the manganate. Small divergences from these relationships are explained. The influence of the hydroxyl-ion on the molecular condition of the formaldehyde in its connexion with the reduction of the manganate is discussed. The mechanism of the reduction is represented by the scheme  $2[\text{MnO}_4'' + 3\text{H}_2\text{O} = \text{Mn}(\text{OH})_4 + 2\text{OH}' + \text{O}], \text{O} + \text{H}\cdot\text{CHO} + \text{OH}' = \text{HCO}_2' + \text{H}_2\text{O}$  (rapid reaction measured);  $\text{O} + \text{HCO}_2' + \text{OH}' = \text{CO}_3'' + \text{H}_2\text{O}$ . J. F. S.

**Slow Coagulation of Concentrated Ferric Oxide Sols to Reversible Jellies.** E. SCHALEK and A. SZEGVARI (*Kolloid Z.*, 1923, 33, 326—334).—Concentrated ferric oxide sols set, on the addition of definite concentrations of electrolytes, to coherent jellies, which on shaking become again liquid and then again set; this process may be repeated indefinitely. On changing the concentration of electrolyte, the sol and gel undergo the usual flocculation. The time necessary for the re-solidification of the jelly is a reproducible quantity. The velocity of solidification increases rapidly with the temperature, and its logarithm is proportional to the temperature; it also increases rapidly with the concentration of the added electrolyte; the logarithm of the velocity is also proportional to the concentration. Consequently, the process is to be regarded as a slow coagulation. The solidification process is sensitised by alcohol. In comparison with the sol, the liquefied gel shows an increased displacement elasticity. Ultramicroscopic examination of the resolidification shows that the particles do not come closer together and there is no formation of secondary particles. Similar

results have been obtained with zirconium, scandium, and aluminium hydroxide sols and with stannic oxide sols. J. F. S.

**Pharmacological Investigations on Iron. I. Colloidal Ferrous Sulphide prepared in Presence of Gelatin.** L. SABBATANI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 326—330).—Colloidal ferrous sulphide solutions, prepared from ferrous sulphate and sodium sulphide in presence of gelatin, are highly stable and serve well for pharmacological experiments, the gelatin and sodium sulphate they contain being without disturbing effect. The most stable and most highly disperse solutions are those containing 0.05 g.-mol. of ferrous sulphide per litre and 5% of gelatin. Such solutions set hard and must be liquefied in warm water and used when tepid; they readily undergo oxidation, which may be prevented by covering the surface with a layer of vaselin oil or, better, paraffin wax. If great care is taken, they withstand sterilisation in steam and they may be diluted with water which has been thoroughly boiled and then cooled. Oxidation, which is facilitated by heating or diluting the solutions, proceeds in accordance with the equation:  $2\text{FeS} + 3\text{O} = \text{Fe}_2\text{O}_3 + \text{S}_2$ . T. H. P.

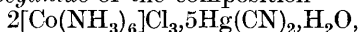
**Double Halides of Cobalt Bases.** F. EPHRAIM and P. MOSIMANN (*Helv. Chim. Acta*, 1923, **6**, 1112—1132).—The halides of cobaltamine bases do not form double salts with other halides with such readiness as was expected. As far as could be ascertained, double salts were only formed with salts of zinc, cadmium, mercury, and lead and, in the case of luteo-salts, with antimony and bismuth trichlorides. In the case of both luteo- and roseo-salts, zinc forms a double chloride, cadmium a chloride, and bromide, and mercury a chloride, bromide, and iodide; there is thus a diminishing tendency to form double salts as the atomic weight of the halogen increases. Flavo-salts and croceo-salts do not form double salts with zinc, but both do so with mercury and the flavo-salts form a double chloride and bromide, but not an iodide with cadmium salts. The complexity of the salts increases with the atomic weight of the heavy metal; thus the luteo-chloride combines with  $1\text{ZnCl}_2$ ,  $2\text{CdCl}_2$ ,  $3\text{HgCl}_2$ , or  $4\text{PbCl}_2$ .

The following new compounds are described.

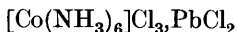
**Luteo-salts.**—Two *hexamminecobalti-cadmium chlorides* were obtained, both microcrystalline powders,

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot 2\text{CdCl}_2 \cdot 3\text{H}_2\text{O}$  and  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot \text{CdCl}_2 \cdot \text{H}_2\text{O}$ ; the double *bromide*,  $[\text{Co}(\text{NH}_3)_6]\text{Br}_3 \cdot 3\text{CdBr}_2 \cdot 3\text{H}_2\text{O}$ , forms very thin, flat, rectangular tablets. Hexamminecobalti-zinc chloride,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot \text{ZnCl}_2 \cdot \text{H}_2\text{O}$ , forms lustrous, apparently hexagonal prisms. Two *hexamminecobalti-mercuric bromides* were obtained,  $[\text{Co}(\text{NH}_3)_6]\text{Br}_3 \cdot 3\text{HgBr}_2$ , microscopic needles, and

$[\text{Co}(\text{NH}_3)_6]\text{Br}_3 \cdot \text{HgBr}_2$ , glistening, rectangular leaflets. The iodide corresponding with the second bromide has been previously described; there was also obtained  $[\text{Co}(\text{NH}_3)_6]\text{I}_3 \cdot 3\text{HgI}_2 \cdot 6\text{H}_2\text{O}$  in well-formed microscopic crystals. A *chlorocyanide* of the composition

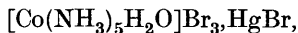


forming glistening, six-sided leaflets, was also obtained. Two *hexamminecobalti-lead chlorides* were obtained;



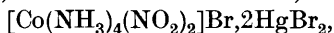
forms long, hairy needles, and  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3, 4\text{PbCl}_2$ , extremely thin, six-sided leaflets showing all colours. Three *bromides* are described:  $[\text{Co}(\text{NH}_3)_6]\text{Br}_3, 4\text{PbBr}_2, 2\text{H}_2\text{O}$ , forms glistening, four-sided leaflets;  $3[\text{Co}(\text{NH}_3)_6]\text{Br}_3, 2\text{PbBr}_2$  forms long, glistening, orange-brown needles, and  $[\text{Co}(\text{NH}_3)_6]\text{Br}_3, \text{PbBr}_2$ , needles. *Hexamminecobalti-antimony chloride*,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3, \text{SbCl}_3, \text{H}_2\text{O}$ , forms a pale yellow precipitate; the *bismuth* compound is similar, but anhydrous.

*Roseo-salts*.—The composition of *aquopentamminecobalti-zinc chloride* is doubtful, but approximates to  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3, \text{ZnCl}_2$ . The *cadmium* salt, aggregates of red, microscopic prisms, has the composition  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3, 2\text{CdCl}_2, 3\text{H}_2\text{O}$ . The double *bromide* forms dark red, glistening plates,  $2[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Br}_3, 3\text{CdBr}_3$ . Two *aquopentamminecobalti-mercuric bromides* were obtained,



bright red, microscopic, star-shaped aggregates of needles, and  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Br}_3, 3\text{HgBr}_2$ , fine needles, or a dull rose, crystalline powder. The corresponding *iodide* appears to contain  $\text{Co} : \text{Hg} = 1 : 1$ .

*Flavo- and croceo-salts*.—*trans-Dinitrotetrammine(croceo)cobalti-mercuric chloride* forms yellow, microscopic four-sided plates or needles,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}, 2\text{HgCl}_2, 2\text{H}_2\text{O}$ . Two mercuric chlorides of the flavo-*cis*-series were obtained,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}, 2\text{HgCl}_2$ , long, yellowish-brown needles, and  $2[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}, \text{HgCl}_2$ , similar crystals. Similarly, one double bromide of the *trans*-series was obtained,  $2[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Br}, 3\text{HgBr}_2$ , microscopic, rectangular leaflets, and two of the *cis*-series,

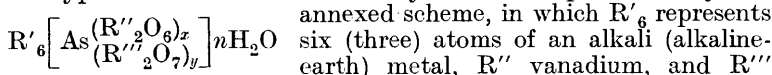


felted, microscopic yellow needles, and the second, containing potassium bromide,  $2[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Br}, \text{HgBr}_2, \text{KBr}$ , needles. The double *iodide* of the croceo-series forms dark yellow, six-sided tablets,  $\text{Co} : \text{Hg} = 3 : 2$ , and of the flavo-series, bright yellow needles of the same composition. *cis-Dinitrotetrammine(flavo)cobalti-cadmium chloride*,  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}, \text{CdCl}_2$ , forms fine bundles of needles, and the corresponding *bromide*,  $\text{Co} : \text{Cd} = 2 : 1$ , long, brown needles. Corresponding croceo-cadmium salts were not obtained.

E. H. R.

**Molybdovanado-arsenates and Tungstovanado-arsenates (Hetero-tri-arsenates).** G. CANNERY (*Gazzetta*, 1923, 53, 773—778).—The compounds here described have been prepared by the following methods, the solutions in all cases being kept acid: (1) By means of solutions containing a small proportion of an arsenate together with vanadic and molybdic (or tungstic) acids; (2) by addition of vanadic anhydride to solutions of molybdo-arsenates or tungsto-arsenates; (3) by addition of arsenic acid to solutions containing molybdates (or tungstates) and vanadates. The composition of the complex compound varies with the concentration and acidity of the solution.

The variety of the ratios in which combination occurs between the constituent oxides in these compounds would appear to indicate that many of the compounds are mere isomorphous mixtures of far simpler true compounds. On the other hand, however, from the very small and but slightly variable proportions of arsenic present it may be assumed that the miscibility is effected between groupings of which the arsenic constitutes the central nucleus. The typical heterotri-arsenates may thus be represented by the



annexed scheme, in which  $R'_6$  represents six (three) atoms of an alkali (alkaline-earth) metal,  $R''$  vanadium, and  $R'''$  molybdenum or tungsten. Only in certain cases do the salts now described approximate to this hypothetical scheme.

Analysis of these compounds presents difficulties, means for overcoming which are described (cf. Friedheim, Decker, and Diem, A., 1905, ii, 764).

Three *ammonium arsenomolybdovanadates* have been prepared:  $6(NH_4)_2O, As_2O_5, 11MoO_3, 5V_2O_5, 50H_2O$ , an orange-yellow, microcrystalline precipitate;  $5(NH_4)_2O, As_2O_5, 20MoO_3, 3V_2O_5, 50H_2O$ , a yellow, microcrystalline precipitate;

$11(NH_4)_2O, As_2O_5, 25MoO_3, 4V_2O_5, 96H_2O$ , a red powder. Two *barium arsenomolybdovanadates*:

$15BaO, As_2O_5, 26MoO_3, 3V_2O_5, 62H_2O$ , and  $7BaO, As_2O_5, 33MoO_3, 4V_2O_5, 34H_2O$ , a yellow precipitate. *Thallium arsenomolybdovanadate*,  $3Tl_2O, As_2O_5, 32MoO_3, 5V_2O_5, 45H_2O$ , forms a yellow precipitate; *ammonium arsenotungstovanadate*,  $18(NH_4)_2O, As_2O_5, 21WO_3, 4V_2O_5, 13H_2O$ , red, prismatic crystals; *thallium arsenotungstovanadate*,  $6Tl_2O, As_2O_5, 21WO_3, 5V_2O_5, 13H_2O$ , a red powder; and *barium arsenotungstovanadate*,

$6BaO, As_2O_5, 17WO_3, 5\frac{1}{2}V_2O_5, 40H_2O$ , small, blood-red octahedra.

T. H. P.

**Molybdovanadates.** G. CANNERI (*Gazzetta*, 1923, 53, 779—794).—The composition of the molybdovanadates varies with the conditions under which they are formed, particularly with the acidity of the medium and with the temperature of crystallisation. The author finds that the electrical conductivity at  $30^\circ$  of solutions of sodium metavanadate acidified with increasing proportions of acetic acid varies continuously, the condensation of the molecules of vanadic acid being thus a continuous function of the concentration of the acetic acid; at the same time, the colour changes gradually from yellow to orange-red.

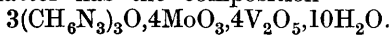
In view of the fact that dissolution of molybdic anhydride in solutions of metavanadates constitutes a method of preparing the molybdovanadates, the author has commenced an investigation into the systems  $NH_4VO_3 : MoO_3$ ,  $KVO_3 : MoO_3$  and  $NaVO_3 : MoO_3$  at different temperatures. The results at present available show that, within the limits imposed by the value of the solubility of molybdic anhydride in solutions of the metavanadates, compounds of two types, differing sharply in their physical properties, are formed. These crystallise respectively in large, orange-red prisms,



and in yellow, silky needles or, sometimes, in pulverulent form. One and the same solution may give both red and yellow crystals, either together or successively in either order. The value of the ratio  $V_2O_5:MoO_3$  varies gradually in the red crystals from 3:1 to values corresponding with the maximum percentage of vanadium, this approaching the proportion occurring in polyvanadates. The ratio changes suddenly in value for the yellow crystals, which are poorer in vanadium.

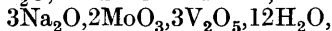
The various red crystals appear to consist of isomorphous mixtures, but the isomorphogenous terms cannot yet be defined neither can their chemical natures be established; it is, however, possible that they consist of polyvanadates and polymolybdates. Along with these isomorphous mixtures there exist certain well-defined compounds which are obtained under definite conditions. With these compounds difficulty is encountered in distinguishing between combined water and water of crystallisation, but the author regards them as heteropolyaquates and ascribes to them formulæ based on the hypothesis of Rosenheim (A., 1911, i, 109, 265; ii, 116, 612; 1913, ii, 59) and of Miolati and Pizzighelli (A., 1908, ii, 595) to which preference is to be accorded over Prandtl's views (A., 1913, ii, 61). According to the latter, the molybdovanadates are double salts, and should hence be completely dissociated in solution; in sufficiently dilute solution, therefore, fractional precipitation of the different constituents should be possible, but this is not found to be the case.

[With R. RAGIONIERI.]—The red crystals formed by the system  $NH_4VO_3:MoO_3$  have the same colour and crystalline habit in all cases. The pale yellow, silky crystals consist of the compound,  $4(NH_4)_2O, 5MoO_3, 3V_2O_5, 10H_2O$ . The *guanidine* compound prepared from the latter has the composition



[With G. WINSPEARE.]—The pale yellow crystals formed by the system  $KVO_3:MoO_3$  at  $30^\circ$  vary in composition according to the concentration of the solution; compounds of the formulæ  $4K_2O, 4MoO_3, 3V_2O_5, 7H_2O$  and  $3K_2O, 6MoO_3, 2V_2O_5, 7H_2O$  were separated.

[With C. DELLA PERGOLA.]—In the system  $NaVO_3:MoO_3$ , the compound  $4Na_2O, 8MoO_3, 3V_2O_5, 10H_2O$  occurs in equilibrium with the red, mixed crystals until the molybdenum is increased to make the ratio  $V_2O_5:MoO_3=1:2$ , and separates as a single pure phase when the molybdenum is still further increased in amount. The red salt,  $2Na_2O, MoO_3, 3V_2O_5, 9H_2O$ , yields the barium compound,  $3BaO, MoO_3, 4V_2O_5, 12H_2O$ , and the red salt,



the *guanidine* compound,  $3(CH_6N_3)_2O, MoO_3, V_2O_5$ .

T. H. P.

**Electrolytic Preparation of Antimony-Copper and Antimony-Bismuth Alloys.** A. MAZZUCCHELLI and L. TONINI (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 290—292).—Electrolysis of a hydrochloric acid solution of a mixture of antimony and copper, the latter constituting 20—50% of the total dissolved

metal, results in a homogeneous, brittle, violet deposit containing a small proportion of antimony trichloride (cf. Mazzucchelli, A., 1915, ii, 19) and copper and antimony approximately in the proportions corresponding with the compound  $\text{Cu}_3\text{Sb}$ . When the dissolved metal contains about 90% of copper, the deposit formed is graphite-grey and highly brittle and contains a little antimony trichloride, together with rather more copper and rather less antimony than the formula  $\text{Cu}_3\text{Sb}$  requires. Similar experiments with hydrochloric acid solutions of antimony and bismuth yield extremely brittle deposits containing the two metals in proportions varying in the same sense as the compositions of the original solutions. T. H. P.

**Some Properties of Osmium Dioxide Sol.** H. FREUNDLICH and H. BAERWIND (*Kolloid Z.*, 1923, **33**, 275—279).—The properties of the sol produced by shaking hydrated osmium dioxide with water have been investigated. It is shown that the colloidal particles are negatively charged and migrate to the anode. The sol, in its behaviour to electrolytes, shows the behaviour typical of negatively charged sols, that is, the kation of the precipitating electrolyte is determinative of the action of the electrolyte. The precipitation values are in keeping with the valency rule. Observation of the sol by means of an ultramicroscope shows that the particles are not spherical. The addition of gelatin to osmium dioxide sols at first brings about coagulation which is followed by a protective action. In keeping with this, it is found that on the addition of electrolytes gelatin exercises both a sensitising and a protective action. The sol is not coagulated at any concentrations by tannin and saponin. The migration velocity of osmium dioxide sols on the addition of gelatin increases almost up to the coagulating concentration; it then falls and finally increases, but there is no reversal of the charge of the sol. The osmium dioxide sol, as such, has no decomposing action on formic acid at  $100^\circ$ , but it is reduced to the metal sol and this brings about a rapid decomposition of the acid. J. F. S.

### Mineralogical Chemistry.

**Chalcophyllite from Chile.** E. V. SHANNON (*Amer. J. Sci.*, 1924, [v], **7**, 31—36).—Emerald-green crusts of minute, platy crystals from the Teniente copper mine near Rancagua gave:

$\text{CuO}$ .	$\text{Al}_2\text{O}_3$ .	$\text{As}_2\text{O}_5$ .	$\text{P}_2\text{O}_5$ .	$\text{SO}_3$ .	$\text{SiO}_2$ .	$\text{H}_2\text{O (at } 110^\circ)$ .	$\text{H}_2\text{O (over } 110^\circ)$ .	Total.
46.54	3.49	13.23	0.67	6.67	1.33	14.40	14.04	100.37

corresponding with  $4\text{CuO} \cdot \frac{1}{3}\text{Al}_2\text{O}_3 \cdot \frac{2}{3}\text{As}_2\text{O}_5 \cdot \frac{3}{3}\text{SO}_3 \cdot 10\text{H}_2\text{O}$ . The refractive indices of fresh material are  $\epsilon=1.552$ ,  $\omega=1.618$ ; these change when the material is exposed to air, owing to loss of water; and for material dried at  $110^\circ$  they are  $\epsilon=1.618$ ,  $\omega=1.680$ . L. J. S.

## Analytical Chemistry.

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### Application of X-Rays to Quantitative Chemical Analysis.

R. GLOCKER (*Fortschr. Geb. Röntgenstr.*, 1923, **31**, 90—92; from *Chem. Zentr.*, 1923, iv, 763).—The author proposes as a measure of the amount of an element present in a substance the intensity ratio of the discontinuity of the *K*-absorption (Absorptionssprung) when the substance is submitted to a continuous X-ray pencil. For the *K*-discontinuity, *f*, photometrically measured, the relationship  $f = e^{pc}$  is given, where *p* is the amount of the element present and *c* is a constant which is characteristic for the element and apparently an exponential function of the atomic number. The method has hitherto only been used for the *K*-absorption.

G. W. R.

### Benzidine as a Reagent, and as an Indicator for Specific Oxidation-potential.

I. M. KOLTHOFF (*Chem. Weekblad*, 1924, **21**, 2—4).—The work of Feigl and others (*A.*, 1920, ii, 709; 1921, ii, 278; 1922, ii, 865; *Z. anal. Chem.*, 1923, **62**, 369) and of Olszewski (*Chem. Ztg.*, 1923, **47**, 273) on the detection of metals and phosphates has been examined and confirmed, but the sensitiveness in most cases is not found so high as has been stated. An examination of the behaviour of oxidising agents towards benzidine shows that the colour reaction is not dependent on the concentration of the former, but on the oxidation-potential. Thus ferric salts give a coloration after one hour in a concentration as low as 1 mg. per litre, ferrous salts not at all; mixtures of ferrous and ferric salts give the same result independently of concentration, the effect depending on the proportion of ferrous to ferric compound; no coloration is obtained with a mixture of 1 part of ferric and 9 parts of ferrous salt even in concentration of 10 g. per litre. Similarly, iodates give a definite coloration, but the result is negative in presence of iodides. If the potential is above the specific point, the benzidine is oxidised; if below, it remains unaltered, but at the specific point the appropriate coloration is developed. S. I. L.

### Qualitative Reaction of Halogens in Organic Compounds.

J. PICCARD and F. DE MONTMOLLIN (*Helv. Chim. Acta*, 1923, **6**, 1020).—The usual copper wire test for halogen in organic compounds sometimes fails because the substance volatilises before it decomposes. It is recommended to hold a copper gauze in the flame about 1 cm. above the heated substance; the copper gauze is then attacked by the halogen in the flame giving the green colour. If the substance gives a luminous flame, two flames may be used, a small one to heat the substance and a larger one above, in which the copper gauze is held. To detect halogen in a volatile liquid, a piece of filter-paper saturated with the liquid is placed at the top of a vertical glass tube. The vapours fall down the tube, at the lower end of which is attached a bent tube. A flame containing copper gauze

is applied to the end of the latter tube, and an intense green coloration is obtained.

E. H. R.

**Determination of Chloride in Bleaching Powder.** MATSUWO NAKAMURA (*J. Chem. Ind. Japan*, 1923, **26**, 984—985).—The sodium arsenite-silver nitrate method for the determination of chloride gives no distinct end-point and the manipulation is too complex. In the method proposed, the hypochlorite is converted into chloride with hydrogen peroxide solution and titrated with silver nitrate. Fifty c.c. of bleaching powder solution (4.0—6.0 g. per litre) is treated with 3—5 c.c. of 3% hydrogen peroxide and then boiled for several minutes for decomposition of the excess of the peroxide. The solution is neutralised with dilute nitric acid and titrated with an 0.1N silver nitrate solution, using potassium chromate solution as indicator. The percentage of the chloride is obtained by subtracting that of the available chlorine from the total. A small amount of hydrogen peroxide remaining in the solution is not objectionable in the titration.

K. K.

**Determination of Water in Bleaching Powder.** S. OCHI (*J. Chem. Ind. Japan*, 1923, **26**, 1152—1154).—The water in bleaching powder is determined by the combustion method by heating the tube quickly at 200—250° (cf. *ibid.*, 1923, **26**, 349), but the amorphous form of bleaching powder produces much chlorine according to the equation:  $\text{Ca}(\text{OCl})\text{Cl} \cdot \text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + \text{Cl}_2$ . By absorption of the chlorine thus produced in a washing bottle containing potassium iodide solution next to the absorption tube, the amount of water fixed in the residue can be determined, and thus the total water content.

K. K.

**Determination of Bromine in Organic Compounds.** TETSUO MAZUME and KIICHIRO KINO (*J. Chem. Ind. Japan*, 1923, **26**, 1133—1139).—The authors have experimentally compared the method of Baubigny and Chavanne (A., 1904, ii, 203) and that of Stepanow (A., 1905, i, 335; 1907, ii, 50) and Bacon (A., 1909, ii, 179) for the determination of bromine in organic compounds, finding that the former gives lower results than the theoretical, whilst the latter is accurate and simple in manipulation. In the former case, nitrous acid is formed and part of the alkali bromide is decomposed, the bromine being lost. In the latter method, the titration with ammonium thiocyanate is conducted safely after coagulating the silver bromide without filtering it.

K. K.

**Determination of Fluorine in Organic Compounds.** J. PICCARD and C. BUFFAT (*Helv. Chim. Acta*, 1923, **6**, 1047—1048).—The method consists in converting the fluorine into potassium fluoride by heating the compound with potassium at 400°. The compound (fluorobenzene, 0.1—0.2 g.), is weighed in a thin-walled sealed glass tube, which is introduced into a bomb-tube containing 20 c.c. of absolute ether. About 0.5 g. of potassium is added and the tube is drawn out, exhausted, and sealed. The ampoule is broken and the tube heated at first gently, then at 400°. The

tube is then opened and the potassium fluoride determined by conductometric titration with calcium chloride. E. H. R.

**Volumetric Determination of [Sulphur in] Sodium Sulphide.** V. HASSREIDTER (*Chem. Ztg.*, 1923, **47**, 891—892).—The iodometric method of determining sodium sulphide in solution (A., 1923, ii, 790) suffers from the disadvantage that sulphites and thiosulphates, which may be present in commercial sodium sulphide, will also decolorise the iodine solution. These salts do not affect the determination of sodium sulphide if the latter is carried out by allowing the solution to run into a standard ammoniacal zinc solution until a drop of the latter just stains lead acetate paper. Alternatively, the standard zinc solution may be run into a known volume of sodium sulphide solution until the latter just fails to stain the test-paper. Somewhat more accurate results are obtained by allowing a known volume of the sulphide solution to flow into excess of alkaline copper sulphate solution, separating and washing the copper sulphide, dissolving it in nitric acid and depositing the copper electrolytically. One mg. Cu = 1.227 mg. Na<sub>2</sub>S. The copper solution is prepared in a similar way to Fehling's solution and should contain about 50 g. of copper sulphate crystals per l. H. C. R.

**Microchemical Detection of Sulphuric Acid as Silver Sulphate.** L. ROSENTHALER (*Mikrochemie*, 1923, **1**, 47).—Characteristic crystals (rhombic pyramids) are obtained when a sulphate solution is treated with silver nitrate in nitric acid solution; the crystals of silver sulphate may be obtained from a drop of 1% sodium sulphate solution; oxalates and chromates do not interfere with the reaction, but chlorides must be removed previously by adding the requisite amount of silver nitrate.

W. P. S.

**Micro-volumetric Determination of Arsenic, Antimony, and Iron.** A. BRUKL (*Mikrochemie*, 1923, **1**, 54—57).—The iodometric method is recommended for the determination of small quantities (less than 1 mg.) of arsenic or antimony: *N*/500 iodine solution is used for the titration with starch solution as the indicator. In the case of ferrous salts, the titration is made with titanium trichloride solution; a small combined container and burette for the latter is described, means being provided for filling the apparatus with an atmosphere of dry carbon dioxide. W. P. S.

**New Light Filter. [Detection of Potassium.]** LER. W. MCCAY (*J. Amer. Chem. Soc.*, 1923, **45**, 2958).—A solution of 31 g. of crystallised chrome alum in 100 c.c. of water forms an excellent light filter for use in the detection of potassium. When this filter is used potassium may be detected by the flame test in the presence of sodium, lithium, strontium, barium, and calcium. The rays from rubidium and caesium, however, are not cut off. J. F. S.

**A Volumetric Micro-method for the Estimation of Sodium.** HANS MÜLLER (*Helv. Chim. Acta*, 1923, **6**, 1152—1161).—The method described has been worked out especially for the deter-

mination of sodium in serum. It can be used for ordinary or micro-estimations. For the latter, 0.1 c.c. of serum is diluted to 1 c.c. with water in a centrifuging tube, and there are added 1 c.c. of potassium pyroantimonate solution (2 g. per litre) and, drop by drop, 0.4 c.c. of 95% alcohol. After two hours, the tube is centrifuged, the supernatant solution removed, and the precipitate washed three times with 30% alcohol. The precipitate of sodium pyroantimonate is then treated with 1 c.c. of 2% potassium iodide solution, 1 c.c. of concentrated hydrochloric acid solution, and 2 c.c. of water and after ten minutes the free iodine is titrated with 0.01N thiosulphate. The method depends on the reduction of the antimonie acid in the sodium pyroantimonate,  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ , according to the equation  $\text{Sb}_2\text{O}_5 + 4\text{HI} = \text{Sb}_2\text{O}_3 + 2\text{H}_2\text{O} + 2\text{I}_2$ . To obtain a sharp end-point in the titration, the concentration of hydrochloric acid must not exceed the limits 7–9%, and not more than four times the necessary potassium iodide should be used. Magnesium, calcium, and phosphate, in amounts exceeding those likely to be present in serum, do not affect the titration.

E. H. R.

**Determination of Silver in Molecular Solution in Presence of Colloidal Silver.** K. VON NEERGAARD (*Arch. expt. Path. Pharm.*, 1923, **100**, 162–189).—The silver-ions are determined in presence of colloidal silver by means of electrometric titration. Among the results are given the concentration of silver-ions found in a number of therapeutic preparations.

C. R. H.

**Use of Picrolonic Acid for the Micro- and Histological Detection of Calcium.** J. KISSER (*Mikrochemie*, 1923, **1**, 25–31).—Characteristic crystals are obtained when a dilute solution of a calcium salt is treated with picrolonic acid solution; the reaction may be obtained with 0.01 mg. of calcium. The reaction may be used to detect the presence of calcium in tissues, but in this case the form of the crystals obtained is more varied. Calcium oxalate does not react with picrolonic acid.

W. P. S.

**Determination of Calcium in Organic Material by de Waard's Method.** G. HECHT (*Biochem. Z.*, 1923, **143**, 342–346).—With quantities as low as 0.1 mg., de Waard's micro-method for determining calcium (*A.*, 1920, ii, 53) gives results accurate within 5%. The determination is not affected within these limits by the presence of phosphates, magnesium, or iron.

J. P.

**Diphenylcarbazine as a Qualitative Reagent for Metals.** I. M. KOLTHOFF (*Chem. Weekblad*, 1924, **21**, 20–22).—The formation of intensely coloured compounds between diphenylcarbazine and metals (Cazeneuve, *A.*, 1900, ii, 627) is not satisfactory for general identification, since the solutions must always be neutral, but the conditions may be so chosen as to make the reaction specific for particular metals. The bluish-violet colour given with mercury salts in dilutions down to 0.1 mg. of metal per litre is very sensitive to the presence of halogen-ions, but cupric salts give a coloration

(reddish-violet, 0.1 mg. per litre of copper) not affected by halogenions, so that copper may readily be detected in presence of mercury (5 mg. in presence of 2,000 mg. of mercury per litre). Cadmium may also be detected in presence of mercury and copper, if the latter be reduced and halides are added. Magnesium salts give no coloration, but the hydroxide gives an intense red, by which the metal may be identified in presence of the alkaline-earth metals.  
S. I. L.

**Reaction of Potassium Permanganate with Cuprous Oxide in Dilute Sulphuric Acid, and the Determination of Metallic Copper, and Cuprous and Cupric Oxides in their Mixtures.** DENGORO NISHIDA and KEN-ICHI HIRABAYASHI (*J. Chem. Ind. Japan*, 1923, **26**, 1123—1133).—Powdered pure metallic copper is practically insoluble in 3—6*N* sulphuric acid at room temperature by contact for twenty minutes; the addition of potassium permanganate solution to the acid has no influence on the solubility. Cupric oxide is, however, completely dissolved in 6*N* sulphuric acid at room temperature; potassium permanganate in the acid has also no influence on the solubility. When cuprous oxide is stirred in 3—6*N* sulphuric acid at room temperature, it is completely dissolved and potassium permanganate, if added into the acid, is consumed according to the equation:  $2\text{KMnO}_4 + 4\text{H}_2\text{SO}_4 = 2\text{KHSO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + 5\text{O}$  and  $5\text{Cu}_2\text{O} + 5\text{O} + 10\text{H}_2\text{SO}_4 = 10\text{CuSO}_4 + 10\text{H}_2\text{O}$ . One c.c. of 0.1*N* potassium permanganate solution corresponds with 0.007157 g. of the oxide.

For analysis, 0.5 g. of a mixture of metallic copper, cuprous, and cupric oxides is dissolved in nitric acid and the total copper content is determined by iodometry. Another weighed sample is stirred with 100 c.c. of 6*N* sulphuric acid and 1 c.c. of 0.1*N* potassium permanganate solution, to which permanganate solution is gradually added until the pink colour of the solution no longer disappears; the percentage of the cuprous oxide is thus determined. After titration, the residue is dissolved in nitric acid and the metallic copper is determined; the cupric oxide can then be calculated.

K. K.

**Experiments Relative to the Determination of Uranium by means of Cupferron.** J. A. HOLLADAY and T. R. CUNNINGHAM (*Trans. Amer. Electrochem. Soc.*, 1923, **43**, 329—339).—A number of experiments are described dealing with the estimation of uranium by means of cupferron which show that quadrivalent uranium or uranium in a lower state of oxidation can be precipitated completely by means of a freshly prepared solution of cupferron from solutions containing 2—8 c.c. of sulphuric acid (*d* 1.84) in 100 c.c. On ignition, the precipitate is converted quantitatively into  $\text{U}_3\text{O}_8$ . If the amount of sulphuric acid is less than 4 c.c. per 100 c.c., aluminium and possibly phosphorus will be carried down with the precipitate, whilst if the acidity is greater than 8 c.c. per 100 c.c., the uranium will not be completely precipitated. If the acidity is kept between 4 and 8%, preferably at 6%, a sharp separation of uranium from aluminium, zinc, calcium,

magnesium, and phosphorus can be obtained by a single precipitation. Uranium and vanadium can be separated and estimated with a sufficient degree of accuracy in the presence of widely varying quantities of iron, aluminium, calcium, magnesium, and phosphorus by the following method. The iron and vanadium are precipitated by cupferron from a 12% sulphuric acid solution in which the uranium, vanadium, and iron are present, respectively, in the sexavalent, quinquivalent, and trivalent condition. Uranium, aluminium, calcium, magnesium, and phosphorus pass quantitatively into the filtrate. The vanadium in the precipitate is then estimated by any of the usual methods. The filtrate is evaporated with nitric acid to destroy the cupferron and the solution then passed through a Jones's reductor to reduce the uranium. The solution is then diluted to 6% sulphuric acid content and the uranium precipitated with cupferron, filtered, washed, and ignited to  $U_3O_8$ .  
J. F. S.

**Determination of Iridium in Platinum by the Method of Fusion with Lead.** R. GILCHRIST (*J. Amer. Chem. Soc.*, 1923, 45, 2820—2828).—The analytical details of the Deville and Stas method for the estimation of iridium in platinum alloys containing 0.1—20% of iridium have been investigated. It is found that the concentration of nitric acid, the concentration of aqua regia, the proportion of lead, and the time and temperature of the lead fusion can be varied over a wide range without any effect on the determination. The observations of Deville and Stas to the effect that palladium and rhodium have no effect on the determination and that ruthenium separates quantitatively with the iridium, are confirmed. Gold is also found not to interfere with the determination. Iron separates almost quantitatively with the iridium as observed by Deville and Stas. Iron can be separated satisfactorily from iridium by the following method. The alloy is fused with zinc and the excess of zinc removed by treatment with hydrochloric acid. The resulting alloy is then fused with potassium pyrosulphate. The fusion, after cooling, is extracted with dilute sulphuric acid. The iron all dissolves and the insoluble residue contains the iridium and silica. The loss in weight of crystalline iridium during the ignition periods is insignificant, and the weight of the crystalline iridium is not affected by heating and cooling in an atmosphere of hydrogen. Spectrographic examination of samples of iridium from the analyses showed that neither lead nor platinum is present in quantities sufficient to affect the determination. The iridium results tend to be low by a small but variable amount. One factor in this error is a slight dissolution of iridium by aqua regia. A modified method is presented which combines the optimum of speed and accuracy. The modified method is as follows: The alloy is fused with ten times its weight of granular lead for one hour at about  $1,000^\circ$  in a graphite crucible and then allowed to cool. The button is removed and brushed to free it from carbon, placed in a beaker containing 1 volume of nitric acid ( $d$  1.42) to 4 volumes of water, using 1 c.c. of acid per g. of lead. The beaker is kept



at 85° for two hours when the alloy will be disintegrated. The solution is diluted to twice its volume and decanted through a double filter-paper. The residue is washed with hot water and the washings passed through the filters. The filter-papers are returned to the beaker without ignition. To the beaker is now added 15 c.c. of water, 5 c.c. of hydrochloric acid ( $d$  1.18) and 0.8 c.c. of nitric acid ( $d$  1.42) for each gram of sample taken and the mixture heated at 85°; in about one and a half hours the lead platinum alloy will be dissolved. The solution is diluted with twice its weight of water and filtered through a double filter-paper in which the iridium collects in fine crystals. The precipitate and filter-paper are washed with hot water and finally with hot dilute hydrochloric acid (1:100). The iridium and filter-papers are placed in a Rose crucible and dried, the filter-paper is then destroyed, and the residue heated with the full heat of a Tirrill burner. The ignited metal is then heated in hydrogen for five minutes and allowed to cool in the gas. J. F. S.

**The Colorimetric Determination of Cholesterol in Blood-serum.** S. KRASSTEVSKY (*Biochem. Z.*, 1923, **143**, 403—407).—Of the colour reactions of cholesterol, the Salkowski reaction is found to be best suited for determining the substance in blood by colorimetric methods. The colour tone is not affected by the presence of other plasma constituents if water is excluded. One c.c. of the serum from 5—10 c.c. of blood is added to 5 c.c. of absolute alcohol, shaken, and kept in a thermostat at 55—56° for twelve to twenty-four hours. To the dried, powdered residue is added 5 c.c. of chloroform and, after fifteen to twenty minutes, 5 c.c. of pure sulphuric acid ( $d$  1.8388). After shaking, the mixture is left in an ice-chest for six to twelve hours, and the chloroform layer is removed and compared with the standard colours of various known concentrations of pure cholesterol. Solutions of Bayer's Benzobrown and Benzoazurin in aqueous alcohol may be used as standards. The normal cholesterol content of blood-serum is 0.0005—0.0012 g. per c.c. J. P.

**Determination of Dextrose by Oxidation with Iodine.** F. AUERBACH and E. BODLÄNDER (*Z. angew. Chem.*, 1923, **36**, 602—607).—Under the conditions described by Willstätter and Schudel (A., 1918, ii, 337) the oxidation of dextrose by iodine proceeds beyond the gluconic acid stage, and lævulose and sucrose are also to some extent attacked. By adjusting the alkalinity of the reaction medium, however, and the time of reaction, a quantitative oxidation of dextrose is effected without any appreciable reaction taking place with lævulose and sucrose. To the sugar solution, which should preferably contain not more than 100 mg. of dextrose in about 25 c.c., a quantity of an  $N/10$  solution of iodine in potassium iodide is added such that at least one-third to one-half of the iodine remains unchanged. To the solution is then added 100 c.c. of a mixture of equal volumes of one-fifth-molar solutions of sodium carbonate and sodium hydrogen carbonate (having  $p_H$  10.1—10.2), and this reaction mixture is kept in the

dark for one and a half to two hours. It is then acidified with 25% sulphuric acid (12 c.c.) and the unchanged iodine is titrated back with *N*/10 thiosulphate and starch. The quantity of thiosulphate required is subtracted from that required in a blank experiment carried out simultaneously, and of the difference 1 c.c. of the *N*/10 solution is equivalent to 9.005 mg. of dextrose. Under these conditions, lactose also is quantitatively oxidised, 1 mol. requiring two equivalents of iodine, and the same applies, at any rate approximately, to maltose. The method may be used to distinguish between natural and artificial honey, and to detect adulteration of honey with artificial invert-sugar or dextrose. [Cf. *B.*, 107.]

W. T. K. B.

**Comparison of the Action of Chlorine and Chlorine Dioxide on Wood.** E. HEUSER and O. MERLAU (*Cellulosechem.*, 1923, 4, 101—109).—An investigation of the method proposed by Schmidt and Graumann (*A.*, 1921, ii, 912) for the removal of incrustive substances from plants, for example, lignin from wood, by means of chlorine dioxide. It is shown that the method is serviceable as a means for the rapid separation of raw-cellulose, so-called "skeleton-substance" from wood, and that under certain conditions it is a useful alternative method for the quantitative analysis of wood. When wood is treated by the Schmidt and Graumann method, hexosans remain in the "skeleton-substance" whereas pentosans are found in both the cellulose and the lignin portions. For instance, spruce wood, freed from ash and resin, and containing 10.80% of pentosans and 6.38% of mannose, yielded 62.71% of "skeleton-substance," which contained 4.4% of pentosans, 5.43% of mannose, and 52.84% of pure cellulose. By dialysis and subsequent evaporation of the lignin extract obtained by treatment of wood with chlorine dioxide and aqueous sodium sulphite, 70% of the lignin originally present in wood was obtained in a dry state, and this contained 8.16% of pentosans. Hence in the determination of pure cellulose and lignin in wood by means of the method of Schmidt and Graumann, allowance must be made for the presence of mannose and pentosans in the "skeleton-substance" and the lignin extract. The pure cellulose-content of wood as determined by the methods of Schmidt and Graumann, and of Cross and Bevan, was 52.2% and 52.8%, respectively, and the lignin content as determined by the former method and by Willstätter and Zechmeister was 30.3% and 29.01%, respectively.

Chlorine dioxide has an appreciable action on xylan, but not on pure cellulose and cotton. Pentosans present in wood are partly removed by treatment with hot water and hot dilute solutions of sodium sulphite (cf. Euler, following abstract), but this solubility is not dependent on simultaneous processes of oxidation or hydrolysis. Methods for carrying out the analysis of wood by the method of Schmidt and Graumann are fully described and also an improved form of Gooch crucible for use with these methods.

A. J. H.

**Determination of Lignin in Wood by the Method of Schmidt and Graumann.** A. C. VON EULER (*Cellulosechem.*, 1923, 4, 109—113).—In view of the considerable difference (9.37%) between the lignin-content of pine wood, as determined by Willstätter and Zechmeister and by the method of Schmidt and Graumann (A., 1921, ii, 912), the latter method has been critically examined. Since albumin is not affected by treatment with an aqueous solution of chlorine dioxide, it is probable that about 0.8% of wood-gum, containing xylose, mannose, and dextrose, will remain in the so-called carbohydrate "skeleton-substance"; the latter also retains about 0.2% of mineral substances so that an error of 1% is possible in the determination of the carbohydrate content. A more serious error arises from the fact that when wood, after successive extraction with benzene and alcohol whereby fats, resins, and turpentine are removed, is subjected to the various processes of washing by means of hot and cold water and aqueous solutions of sodium sulphide as described in the Schmidt and Graumann method, it suffers a considerable loss of weight, due to the solubility, under such conditions, of wood-gum and lignin. For instance, one sample of pine wood, freed from fats, resins, and turpentine, was subjected to thirteen successive treatments comprising steeping in water for twenty-four hours, washing with hot and cold water, extraction with a 2% aqueous solution of neutral sodium sulphite and subsequent washing with water, and the respective losses in weight were 6.5, 2.8, 0.7, 1.5, 1.5, 0.9, 0.7, 1.2, 1.7, 1.2, 0.6, 0.4, and 0.7% (total=20.4%). The Schmidt and Graumann method is therefore likely to give a low carbohydrate-content and a correspondingly high lignin-content. Attention is directed to the apparent solubility of lignin in a neutral aqueous 2% solution of sodium sulphite, but this solubility may be due to the formation of a small amount of sodium hydrogen sulphite during hydrolysis of the wood complex.

A. J. H.

**Detection and Determination of Tartaric Acid.** M. FRANÇOIS and C. LORMAND (*J. Pharm. Chim.*, 1923, [vii], 28, 433—442).—In Kling's method for determining tartaric acid in wine (cf. A., 1910, ii, 359), which depends on the precipitation of the very insoluble calcium racemate by addition of *l*-tartaric acid in excess and calcium acetate, incorrect results are liable to be obtained on account of the sparing solubility of calcium *l*-tartrate. The present authors find the solubility of the calcium tartrates in water at 20° to be: calcium *d*-tartrate and calcium *l*-tartrate, both  $C_4H_4O_6Ca, 4H_2O$ , 0.232 and 0.249 g. per l., respectively; calcium racemate, 0.0493 g. per l. The solubility of the *d*-tartrate in alcohol of 32 vol. % strength is, however, sufficiently small (0.038 g. per l., at 20°) to allow of the direct determination of tartaric acid by precipitation of this salt. The sample for analysis should contain about 0.4—0.6 g. of tartaric acid, and is made up to 100 c.c. with water. To this solution is added 20 c.c. of a solution of calcium acetate (32 g. of pure calcium carbonate and 120 c.c. of glacial acetic acid, made up to 1 l. with water), and then, after stirring,

30 c.c. of alcohol of 95 vol. % strength. After keeping the mixture for twenty-four hours, a further 30 c.c. of the alcohol is added. After a further twenty-four hours, the crystals of calcium *d*-tartrate are collected, preferably in a Gooch crucible, dried in the air at room temperature, and weighed. The results are accurate to about 1%. The characteristic appearance of the crystals of calcium *d*-tartrate may be used for the detection of the acid.

W. T. K. B.

**Determination of Malic Acid in Fruit Syrups and other Fruit Products.** F. AUERBACH and D. KRÜGER (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 177—217).—A 25 c.c. sample of the material is acidified with *N*/2-hydrochloric acid, allowing an excess of 0.5 c.c. over the ash-alkalinity. The latter is determined by titration to Methyl-orange.

In the case of (a) natural juices, lemonade, etc. (with small sugar content), 100 c.c. of 96% alcohol is added, and (b) syrups, marmalade, etc. (containing much sugar), 400 c.c. of alcohol is needed. The solution is filtered through a dry filter, and if the volume of the precipitate is considerable, a correction is made for its volume. Ten c.c. of the filtrate is titrated with *N*/10 sodium hydroxide solution (litmus) and the amount of barium carbonate required to neutralise is calculated. Three hundred and fifty c.c. of filtrate (b) or 75 c.c. of filtrate (a), to which 250 c.c. of alcohol is added, is neutralised with the requisite amount of barium carbonate. Two c.c. of 50% barium acetate solution is added, and the liquid heated on a water-bath until precipitation is complete. The precipitate is filtered after twenty-four hours and washed with 95% alcohol and dried in a steam oven. Precipitate and paper are placed in a 50 c.c. graduated flask, 0.1 g. of barium citrate and 0.05 g. of barium tartrate are added and the whole is diluted with water nearly to 50 c.c. After several hours' shaking, the volume of liquid is made up to the mark with a saturated solution of barium citrate and tartrate. The liquid is filtered, and, if necessary, decolorised with animal charcoal. The malate in the solution is determined polarimetrically. For this, 20 c.c. of solution is shaken for four hours with 3.5 g. of uranyl acetate and 2.5 c.c. of *M*/10 disodium citrate solution and diluted to 25 c.c.; or, 10 c.c. of solution is mixed with 2 c.c. of glacial acetic acid and 10 c.c. of saturated aqueous ammonium molybdate solution, decolorised, if necessary, with animal charcoal and diluted to 25 c.c. The necessary corrections are described, and the effect of various sugars, amino-acids, preservatives, etc., on the accuracy of the method detailed.

A. G. P.

**Determination of Hydroxyl Values [of Oils and Fats] by Normann's Method.** W. MEIGEN and O. RAMGE (*Chem. Umschau*, 1924, **31**, 3—4).—Normann's method of determining the hydroxyl values of oils and fats was tested on specially purified samples of mono- and di-hydroxystearic acids and on mixtures of known proportions of these acids with cacao butter and olive oil. In all cases, the values obtained were somewhat higher than

the theoretical, the discrepancies ranging from 1% to 4%. The fact that high values were obtained by this method was confirmed by parallel determinations of the hydroxyl values of castor and rape oils and of the methyl esters of the mixed fatty acids prepared from these oils. In each case, the value obtained for the oils themselves was higher than that calculated from the hydroxyl value of the methyl esters of the mixed fatty acids. According to Grün (*Oel & Fett. Ind.*, 1919, Nos. 13, 14) the theoretical value is obtained by applying Normann's method to the methyl esters. When, however, the hydroxyl value is not too large the error introduced falls within the experimental error, and in such cases Normann's method may be considered applicable in view of its convenience.

H. C. R.

**Quantitative Analysis of Linseed Oil.** A. EIBNER and K. SCHMIDINGER (*Chem. Umschau*, 1923, **30**, 293—302).—The linseed oil examined was of Dutch origin and was of iodine value 173.6 and acid value 2.3. Its composition was as follows:  $\alpha$ -linolenic acid, 20.1%; isolinolenic acid, 2.7%;  $\alpha$ -linoleic acid, 17.0%;  $\beta$ -linoleic acid, 41.8%; oleic acid, 4.5%; hydroxy-acids, 0.5%; glycerol, 4.1%; saturated acids, 8.3%; phytosterol, 1.0%. By treating the oil with nitrous acid, 0.6% of an elaidin was obtained, which was identified as di-elaidopalmitin. Bromination of the oil in alcoholic solution gave 54.2% of crude solid bromide, which on purification was identified as brominated di- $\alpha$ -linolenic- $\alpha$ -linoleic glyceride. The oil contained about 25% of this mixed glyceride. The form in which the remaining unsaturated acids were combined was not determined. [Cf. *B.*, Feb.]

H. C. R.

**The Determination of Cineole in Essential Oils.** G. WALKER (*J. Soc. Chem. Ind.*, 1923, **42**, 497—498T).—It is suggested that the percentage of cineole in essential oils may be determined from the freezing point and density of a mixture of the oil with  $\alpha$ -naphthol. To make such determinations possible, measurements have been made of freezing points and densities at 20°/4° of mixtures of 3.6 g. of  $\alpha$ -naphthol and 3.85 g. of artificial eucalyptus oil, containing from 65 to 95% of cineole. These oils were prepared by adding pure cineole to various eucalyptus oils free from cineole. Curves are given showing the change of density with the percentage of cineole for each variety of oil used, namely pinene, *Eucalyptus radiata*, *E. nova angelica*, *E. citriodora*, *E. dives*, and *E. cinerifolia* residues.

E. H. R.

**Microchemical Identification of  $\alpha$ -Monoamino-Acids.** O. WERNER (*Mikrochemie*, 1923, **1**, 33—46).—A microchemical method for the separation and identification of the more important  $\alpha$ -mono-amino-acids is described and also outlined in tabular form; it consists essentially in the sublimation of certain of the substances in a special apparatus. The operation is carried out under reduced pressure, and means are provided for cooling the receiver. The character of the crystalline sublimates (in those cases where the substance sublimes), and of the crystals, etc., obtained when the

sublimates and residues are treated with cupric hydroxide reagent or phosphotungstic acid, affords a means of identifying the amino-acids. W. P. S.

**Amylolytic Enzymes.** R. FABRE and H. PÉNAU (*J. Pharm. Chim.*, 1923, [vii], **28**, 289—304, 341—348).—The causes of the variations observed in determining the amylolytic activity of pancreatin and diastase preparations with commercial potato starches are critically examined, and they are shown to be principally influenced by the character of the water employed in the manufacture of the starch (cf. A., 1923, ii, 512). Water with a  $p_H$  on the alkaline side activates the pancreatic diastase and inhibits malt diastase, whilst the reverse is the case with water having a  $p_H$  on the acid side. In order, therefore, to obtain comparable results, it is recommended to prepare the starch employed for such determinations under standard conditions of maceration to avoid influences which tend to produce an extensive demineralisation of the starch granules, and that the water employed in its preparation should be absolutely neutral, and to adopt as analytical method, either that of Bertrand or that of Grimbert's modification of Lehmann's method (A., 1913, ii, 254), both of which are more exact than the method of direct reduction. Twenty-five to 30% of the sugar produced during the saccharification under the conditions required by the pharmacopœia is soluble in absolute alcohol. With malt diastase, maltose is the only sugar produced, whilst in the case of pancreatic diastase, which contains maltase, small quantities of dextrose are also formed. [Cf. B., 27.] D. R. N.

**The Inorganic Elements of Blood Plasma.** A. P. BRIGGS (*J. Biol. Chem.*, 1923, **57**, 351—357).—A system of analysis of the inorganic constituents of blood has been developed by means of which determinations may be made of the sodium, potassium, calcium, magnesium, chloride, and phosphate content of blood, using one small sample. The important point is the choice of an anti-coagulant which will not interfere with the subsequent determinations. Lithium citrate has been selected as the most suitable for this purpose. Nine to 15 c.c. of plasma obtained from blood treated with this anti-coagulant is sufficient for the complete analysis. Proteins are precipitated with 20% trichloroacetic acid and the potassium is determined in a portion of the filtrate by a colorimetric method based on its precipitation as cobaltinitrite and the determination of the latter by Griess's nitrite method. Separate portions of the filtrate are used for determining the remaining constituents, slight modifications of existing methods being used for this purpose. The method has been applied to a number of pathological bloods. E. S.

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## General and Physical Chemistry.

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**Continuous Spectrum of Hydrogen.** H. B. LEMON (*Nature*, 1924, **113**, 127—128).—The continuous spectrum of hydrogen is developed with unusual intensity when discharge takes place through tubes provided with hot cathodes and operated at low potentials of the order of 100 v. The emitted light extends to the yellow-green region. This continuous spectrum seems to have no sharp limits; it bears no relation to the secondary or to the series lines, and in this respect differs entirely from similar spectra in the X-ray region. A. A. E.

**Ultra-violet Line Spectrum of Chlorine.** E. V. ANGERER (*Z. wiss. Phot.*, 1924, **22**, 200—209).—The ultra-violet line spectrum of chlorine has been measured over the range 3522.0—2070.8 Å. Some 322 lines have been measured and tabulated, and compared with Jevons' value (A., 1923, ii, 274). The spectrum obtained by Jevons contained oxygen lines due to impurities in the discharge tube. To obviate this in the present work the author has adopted a streaming method. The spectrum measurements were made with a Steinheil spectrograph which gave a dispersion of 15 Å. at 3000 Å. and 4.4 Å. at 2000 Å. The line 2300 Å. of the iron arc was used as a standard. A group of six lines lying between 2093 and 2086 Å. is found to give four pairs of lines with constant frequency difference. Attention is directed to the fact that a very large number of lines between 2400 and 2100 Å. recorded by Jevons, are absent in the author's photographs. J. F. S.

**Extension of the Spark Spectra of Lead, Bismuth, Antimony, and Thallium to the Extreme Ultra-violet.** L. BLOCH and E. BLOCH (*Compt. rend.*, 1924, **178**, 472—474).—In continuation of previous work (cf. A., 1924, ii, 4), the authors have measured the wave-lengths of new lines in the spectra in question. The measurements have been extended to wave-lengths of about 1300 Å. Results have been obtained for 23 new lines for lead, 11 for bismuth, 20 for antimony, and 14 for thallium. Most of the new lines are situated in the extreme region; others, of feeble intensity, are situated amongst lines previously observed. A. B. H.

**Singlet Series in the Spark Spectrum of Aluminium.** H. N. RUSSELL (*Nature*, 1924, **113**, 163).—A number of the strongest lines in the spark spectrum of aluminium which do not fit into Paschen's system (A., 1923, ii, 672) are considered. Five of the seven lines of intensity 10 or more are found to show a close correspondence with lines in the arc spectrum of magnesium. A. A. E.

**Mass-spectrum of Indium.** F. W. ASTON (*Nature*, 1924, **113**, 192).—The mass-spectrum of indium shows only one line

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at 115, no deviation from the whole number rule being observed, although its intensity was not sufficient to exclude the possibility of the presence of a small percentage of a second isotope. A. A. E.

**Wave-length Standards in the Extreme Ultra-violet.** J. J. HOPFIELD and S. W. LEIFSON (*Astrophys. J.*, 1923, **58**, 59—63).—A careful determination has been made of the wave-lengths of thirty-seven characteristic lines, between  $\lambda$  800 and  $\lambda$  1800, which occur in condensed discharge spectra of impure hydrogen, oxygen, nitrogen, helium, and air. The results, which are accurate to  $\pm 0.1 \text{ \AA.}$ , are intended to serve as reference standards. A. A. E.

**Resonance and Ultimate Lines in the Flash Spectra obtained at different Levels in the Solar Atmosphere.** F. CROZE (*Compt. rend.*, 1924, **178**, 200—202).—Resonance lines which represent combinations derived from lines belonging to one and the same series are remarkable for their persistence. Such lines can be detected at relatively very high levels in the solar atmosphere. On the other hand, resonance lines which represent combinations derived from lines belonging to different series are much less persistent. The resonance line  $\lambda$  4571 of magnesium and the lines  $\lambda$  5432.6 and  $\lambda$  5394.7 of manganese are of the latter type and are only shown by flash spectra obtained at relatively low elevations. Whether resonance lines are ultimate lines depends therefore on the character of the resonance lines (cf. this vol., ii, 1). E. E. T.

**The Mass of the Particles which Emit the several Band Spectra attributed to Nitrogen.** M. DUFFIEUX (*Compt. rend.*, 1924, **178**, 474—476).—The limiting orders of interference fringes produced by the various band spectra emitted by nitrogen under the electric discharge have been studied to determine the masses of the particles giving rise to the emission. The second positive group has been previously (Hamy, *Compt. rend.*, 1913, **157**, 142) attributed to the nitrogen atom. The bands of the second negative group, and those said to be due to cyanogen, have now also been attributed to the atom, whilst those of the first positive group must be due to the nitrogen molecule. A. B. H.

**Observations of the Doppler Effect in Canal Ray Line and Band Spectra.** H. RAU (*Ann. Physik*, 1924, iv, **73**, 266—271).—Particulars are given of a method of observation of the Doppler effect in the canal ray discharge in various gases. In oxygen, the effect was clearly observed in the case of the lines 4368 and 3947. In front of the cathode, all the "negative" bands in the nitrogen spectrum included between 5000 and 3900  $\text{\AA.}$  showed the effect at all values of the exciting potential drop employed, ranging from 3000 to 35,000 v. Behind the cathode the Doppler effect was first observed at a somewhat higher voltage drop of about 9000 v. The observed effect increased with increase of voltage drop and decrease of pressure in the discharge tube. The results indicate that the "negative" nitrogen bands are attributable to the presence of positively-charged nitrogen molecules ( $\text{N}_2^+$ ), in accordance with the result obtained by Wien (A., 1923, ii, 349). The effects observed



with the nitrogen arc lines 4110 agreed with the assumption that the arc lines are attributable to the presence of neutral nitrogen atoms. The Doppler effect was not observed in the case of the positive nitrogen bands. In the multilinear spectrum of hydrogen, the effect was observed behind the cathode in the case of the lines 4723, 4634, 4573, 4568, 4213, 4177, 4171.5, and 4063 Å. The results indicate that the multilinear spectrum is attributable to neutral hydrogen molecules. A relatively weak Doppler effect was observed behind the cathode in the case of the helium line 4686, but none in front of the cathode. J. S. G. T.

**The Zeeman Effect of the Multiplets of Molybdenum.** M. A. CATALÁN (*Anal. Fis. Quím.*, 1923, **21**, 527—532).—Calculated values for the Zeeman effects of the lines of the multiplets of molybdenum show complete agreement with observed values. G. W. R.

**The Theory of Multiplets and their Zeeman Effects.** A. SOMMERFELD (*Ann. Physik*, 1924, iv, **73**, 209—227).—In continuation of previous work (A., 1923, ii, 355), the author discusses mathematically, and principally from the arithmetical and geometrical points of view, the character of the inner quantum numbers associated with the various classes of multiplet spectral lines. It is shown, *inter alia*, that in the case of the even terms in the multiplet series, *i.e.*, doublets, quartets, etc., the inner quantum number associated therewith is an odd multiple of 0.5, whilst in the case of the odd terms the associated inner quantum number is a whole number. Landé's formula relating to anomalous Zeeman effects (*Z. Physik*, 1923, **15**, 189) is applicable, as a special case, to the magneto-mechanical anomaly investigated, amongst others, by Barnett. Rydberg's rule concerning the character of the multiplicity of the lines in the spectrum of an element is re-stated as follows. In the spectra of elements arranged according to the periodic classification, odd and even number spectral terms occur alternately, and the maximum multiplicity of the lines in any given case is greater by unity than the number expressing the maximum valency of the element concerned. Magneton numbers characterising the elements are, in like manner, when expressed in Bohr quantum units, alternately odd and even, and the maximum number characterising any element is equal to the number expressing the maximum valency of the element. It is assumed that the *s*-condition represents the normal or fundamental state of an atom.

J. S. G. T.

**Arrangement of the Vanadium Lines in Multiplets.** O. LAPORTE (*Physikal. Z.*, 1923, **24**, 510—515).—Lines additional to those already classified in multiplet series by the author (*Naturwiss.*, 1923, **11**, 779) are classified as quartets and sextets and a combination of these two systems. The existence of the system of sextets is in accordance with anticipation based on the application of Rydberg's rule to the position of vanadium in the periodic classification. The quartet system is characterised by two groups of terms, between which a cyclical combination relation exists, such that the frequencies of the lines in a fourth quartet may be calculated from the frequencies

of the lines composing three quartets. An approximate evaluation of terms in the series is effected by consideration of two series of the type  $d-np$  in the respective sextet and quartet systems. The occurrence of widely separated super-Bergmann terms  $F^*$  in the series representative of the spectrum of vanadium is confirmed by the existence of a multiplet, which must, according to its structure and characteristic Zeeman effect, be classified as belonging to the combination  $FF^*$ .  
J. S. G. T.

**The Relation between the Spectra and the Sizes of the Alkali Metal Atoms.** L. A. TURNER (*Astrophys. J.*, 1923, 58, 176—194).—It is shown that the differences between the spectra of the different alkali metals can be related to the differences of the sizes of the structures immediately underlying the valency electron. Atomic models in accord with modern theories of atomic structure are assumed, the nucleus (so far as the outer orbits are concerned) being regarded as having a charge  $+9e$ , and being surrounded by eight electrons and a valency electron; the configuration of eight is assumed to have a mean field of force which is geometrically similar, but differs in size, for the various atoms. The application of the theory developed on these lines leads to a fairly good co-ordination of the spectra of the alkali metals in terms of the assumed (and apparently reasonable) sizes of the atomic kernels. Results are also obtained which confirm the quantum numbers of the  $p$ ,  $d$ , and  $b$  terms as given by Bohr.

The radii of some of the electron orbits and the approximate mean field of force in the outer parts of the orbits of the valency electron have been calculated. The radii ( $\times 10^{-8}$ ) are found to be as follows: lithium, 2.38; sodium, 2.72; potassium, 3.45; rubidium, 3.61; caesium, 3.94. The results also indicate that in the crystalline form the atoms are present as positive ions, the electrons fitting into the structure rather than following their usual orbits. The application of the method to the  $4b$  terms of the alkaline-earth metal spectra shows that the kernel of each must be much smaller than that of the corresponding alkali metal.  
A. A. E.

**Intensity Distribution, Series Formulæ, and Excitation Function in reference to the Spectra of the Alkalis.** H. BARTELS (*Z. Physik*, 1924, 20, 398—412).—A theoretical paper, in which the relative intensities of series lines are discussed with reference to the so-called excitation function  $F(V)$ . This affords a measure of the percentage of inelastic impacts which occur in the collisions between atoms and electrons, and its value depends on the electron velocity (measured in volts by  $V$ ). On the assumption that for these inelastic impacts, azimuthal quantum numbers can be determined according to the principles of selection which are applicable to the emission of radiation, the author deduces a relation between the excitation functions characterising the various energy levels of the atom and the various terms in the series formulæ for the corresponding spectrum. The result is shown to be in approximate agreement with observations on the distribution of intensities in the spectra of the alkali metals.  
J. S. G. T.

**The Characteristic Vibration Frequency of an Element.** J. E. P. WAGSTAFF (*Phil. Mag.*, 1924, vi, 47, 84—90).—A simple method of deducing Einstein's relation between the characteristic frequency  $\nu$ , the compressibility  $\kappa$ , the atomic volume  $V$ , and the atomic weight  $M$ , of an element, in the form  $\nu = \beta V^{1/6} / \kappa^{1/2} M^{1/2}$ , where  $\beta$  is theoretically a constant equal to  $2.56 \times 10^7$ , is given. Values of  $\nu$  calculated by means of this equation are shown to be in fair agreement with those given by Einstein and Lindemann in the case of fourteen elements. It is shown that substances for which the Einstein law holds are those in which the atomic energy is due to a state of strain. Elements characterised by values of  $(\rho \kappa \nu^2 V^{2/3})^{1/2}$  large compared with  $2.54 \times 10^7$  possess atomic energy in excess of that attributable to strain energy. By plotting values of  $(\rho \kappa \nu^2 V^{2/3})^{1/2}$  as ordinates against the respective values of the atomic numbers of the elements as abscissæ, a periodic curve closely following the Mendeléev classification of the elements is obtained. In this curve, in contrast with the atomic volume curves of Meyer, the halogen elements occupy the peaks. A well-defined line drawn through the positions indicating the alkali metals separates the non-metals above the line from the metals. Silicon is the only exception amongst the elements considered, and lies below the line. J. S. G. T.

**Energy of the Characteristic  $K$ -radiation from certain Metals.** E. C. UNNEWEHR (*Physical Rev.*, 1923, 22, 529—538).—The author has investigated the  $K$ -characteristic emission from silver, rhodium, copper, and chromium in order to ascertain the dependence of energy of emission on applied voltage and upon the atomic number, the relation of the energy of the  $K$ -characteristic emission to the energy at that wave-length in the continuous spectrum, and the ratio of the energies of the  $\alpha$  and the  $\beta$  characteristic emission. Suitably corrected values for the intensities were linear functions of the square of the applied voltage. The ratios of the intensities of the  $\alpha$  and  $\beta$  radiations were: silver, 4.65; rhodium, 4.75; copper, 6.53; chromium, 7.36. The absorption coefficient of rhodium for its  $K$ -radiation is 222 per cm. ( $K\alpha$ ) and 178 per cm. ( $K\beta$ ). The absorption coefficients of mica for  $K$ -radiation from chromium, copper, rhodium, and silver are 227, 89.2, 7.7, and 5.1 per cm. for  $K\alpha$  and 171, 66, 5.5, and 3.6 per cm. for  $K\beta$ , respectively. A. A. E.

**A Re-investigation of the  $\beta$ -Ray Spectrum of Radium-B and Radium-C.** C. D. ELLIS and H. W. B. SKINNER (*Proc. Roy. Soc.*, 1924, A, 105, 165—184).—In continuation of previous work (A., 1924, ii, 85), the authors have determined the energy values and approximate relative intensities of thirty-one lines in the  $\beta$ -ray spectra of radium-B, and of sixteen lines in the  $\beta$ -ray spectra of radium-C, for values  $H\rho$  up to 2390,  $H$  denoting the strength of the magnetic field and  $\rho$  the curvature of the rays in the field. The results are tabulated, and confirm the conclusion that the groups are due to the conversion of  $\gamma$ -rays in the various electronic levels. Although the majority of the  $\beta$ -ray lines from radium-B (atomic number 82) are due to conversion in atoms of this atomic number,

a group of lines of low energy has been found to be due to conversion in atoms of atomic number 83. The relative absorbing powers of the different *L* sub-groups are found to depend on the frequency of the absorbed  $\gamma$ -ray. J. S. G. T.

**The Interpretation of  $\beta$ -Ray Spectra.** C. D. ELLIS and H. W. B. SKINNER (*Proc. Roy. Soc.*, 1924, **A**, **105**, 185—198).—Measurements of the frequencies of  $\gamma$ -rays emitted by radium-*B* and radium-*C* (see preceding abstract) confirm the conclusion that these rays are due to transitions between stationary states in the nucleus. The probable energy levels which are involved in these transitions in the two substances are discussed. The two sets of levels exhibit striking similarities, and the evidence on the whole is strongly in favour of the hypothesis that the dynamics of the nucleus can be interpreted in terms of the quantum theory. The change in the relative absorbing powers of the *L* sub-groups is shown to be in agreement with Robinson's results derived from analysis of the electrons ejected from a target by homogeneous X-rays in a magnetic field (*A.*, 1923, ii, 818). J. S. G. T.

**The Absorption Spectra of Mixed Metallic Vapours.** S. BARRATT (*Proc. Roy. Soc.*, 1924, **A**, **105**, 221—225).—A new series of bands, each consisting of fine lines separated in the middle by intervals of a few Å. but much more closely packed near the heads of the bands, has been observed in the absorption spectrum of a mixture of sodium and potassium vapours. The respective wave-lengths of the heads of these bands are: 5955.0, 5931.8, 5867.0, 5846.0, 5824.6, 5803.7, 5783.5, 5764.3, 5746.1, 5728.6, 5712.1, 5696.0, 5680.9, 5667.4, 5654.1, and 5645.2 Å. The intensity of absorption decreases considerably at the short wave-length end of the group of bands. It is suggested that the bands are attributable to sodium-potassium molecules present in the mixed vapour. Absorption of the magnesium line 4571 Å., which is excited by low-voltage electrons, was consistently observed in a column of mixed vapours in which a little magnesium vapour was present (cf. McLennan, *A.*, 1916, ii, 591). J. S. G. T.

**Distribution of Electrons between the *L* Levels of Elements.** A. DAUVILLIER (*Compt. rend.*, 1924, **178**, 476—479).—From measurements of the coefficients of absorption of gold, as obtained with a Bragg spectrometer, it is concluded that in the gold atom the electrons in the *L* levels are:  $2L_3$ ,  $2L_2$ , and  $4L_1$ . Other results, using different methods, will be published later, and are in agreement with the above. E. E. T.

**The Influence of Variation in Concentration on the Absorption Spectra of Dye Solutions.** W. C. HOLMES (*Ind. Eng. Chem.*, 1924, **16**, 35—40).—The variation in the wave-length of maximum absorption in the spectra of more than one hundred dyes with variation in concentration of the solution was studied. In the majority of cases displacement of this wave-length with increasing dilution towards the red end of the spectrum was observed. A shift towards the blue occurred in a few cases. An example of the dependence of this phenomenon on chemical constitution is given by the triamino-

derivatives of triphenylmethane, in which it appears only in cases of substitution within the amino-groups. In such cases, measurements of solutions of intermediate concentration show that two widely separated absorption bands exist, the relative intensity of which depends on concentration. It was shown that variations in hydrogen-ion concentration, temperature, or chemical purity could not account for these results. Whilst change in the state of molecular aggregation or similar colloidal phenomena may explain cases of symmetrical shifting of the absorption band in very dilute solution, the discontinuous modification referred to above appears rather to be due to molecular tautomerism. C. I.

**Absorption Spectra of Amino-acids.** L. MARCHLEWSKI and A. MOROZ.—(See i, 272.)

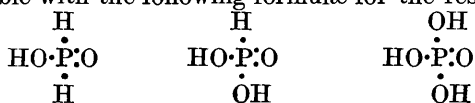
**Absorption of Ultra-violet Light by Organic Compounds.** F. W. WARD.—(See i, 274.)

**Absorption Spectra of Indole Derivatives.** F. W. WARD.—(See i. 314.)

**Absorption Spectra of Kynuretic Acid and Related Quinoline Derivatives.** F. W. WARD.—(See i, 315.)

**Ultra-violet Absorption Spectrum of Gaseous Ammonia.** FERRIÈRES (*Compt. rend.*, 1924, **178**, 202—205).—The absorption spectrum of gaseous ammonia shows a large band beginning sharply at 2265 Å., and extending, with increasing intensity, towards the region of shorter wave-length. Narrower bands are superposed on the broad band, and the first five of these have been resolved into the following triplets (in each of which the two rays of shorter wave-length are the most intense): 2247, 2245, and 2239; 2213, 2211, and 2206; 2171, 2167, and 2163; 2129, 2126, and 2122; 2086, 2083, and 2079 Å. Excepting the first pair, the differences between the mean frequencies of the triplets bands are about 900. E. E. T.

**Chemical Constitution and *K* Absorption Spectra. I. The Investigation of certain Compounds of Phosphorus.** O. STELLING (*Z. anorg. Chem.*, 1923, **131**, 48—56).—The author has examined the *K* Röntgen absorption spectrum of phosphorus in its various modifications, and in combination as hypophosphite, phosphite, and phosphate. The wave-lengths of the limits of *K* absorption for the black and violet modifications of phosphorus are identical, within the limits of error of the experiment, but are greater than for yellow phosphorus. In the hypophosphites, phosphites, and phosphates, a progressive displacement takes place in the direction of lower wave-length. The salts of any one acid and the acid itself give identical results, which are, however, different from those given by organic derivatives of the same acid in which different numbers of hydrogen atoms are replaced. These results are compatible with the following formulæ for the respective acids:



The gradual displacement of the absorption limit corresponds with the replacement of hydrogen atoms by hydroxyl groups directly attached to the phosphorus. W. H.-R.

**The Absorption of X-Rays by Iron, Cobalt, Nickel, and Copper.** F. K. RICHTMYER and F. W. WARBURTON (*Physical Rev.*, 1923, 22, 539—545).—Thin, uniform sheets of the metals were examined by means of a spectrometer, and the X-ray absorption coefficients of iron, cobalt, nickel, and copper, for wave-lengths below the *K* absorption limit, were measured. The sequence of values of the atomic coefficients is found to be that, not of the atomic weights, but of the atomic numbers, according to the relation  $\mu_a = 22.4 \times 10^{-27} N^4 \lambda^3 + \sigma_a$ , which holds within the limits of experimental error for all the ten elements for which results have been obtained, except iron, the experimental value for which is 3% too low. A. A. E.

**Action of Red and Infra-red Radiations on Photoluminescent Substances.** M. CURIE (*J. Chim. physique*, 1923, 20, 437—463; cf. A., 1923, ii, 812).—A continuation of previous work in which the author has investigated the influence of temperature on the luminescence of fluorite and other substances subjected to the action of light from a quartz mercury lamp which has passed through a nickel oxide light-filter. It is found that some varieties of fluorite are fluorescent, whilst others, particularly the colourless and rose-coloured varieties, are non-fluorescent. Most varieties commence to show a feeble luminescence at 50°, which increases in intensity slowly to a maximum and then decreases with increasing temperature. The maximum is often only reached at temperatures above 200°. The luminescence of fluorite shows two bands; at the ordinary temperature a violet band only is observed, but the range of this band depends on the intensity of excitation. At low temperatures, below -100°, an intense band extending from red to green is observed. The change of intensity of the two bands with temperature has been determined and plotted, and the curves have been compared with similar curves obtained for zinc sulphide, zinc oxide, calcium and barium sulphide, willemite, and synthetic ruby. The curves are extremely diverse, the phosphorescence disappearing at very different temperatures. The interpretation of the curves is discussed, and it is pointed out that there are indications of a common electronic mechanism operating in fluorescence, phosphorescence, and thermoluminescence. The index of refraction of the phosphorescent alkaline-earth sulphides has been determined for light of different wave-lengths, and it is shown that the relation  $\lambda/\sqrt{K} = \lambda_0 = \text{constant}$  cannot be confirmed. J. F. S.

**Corpuscular Radiation Excited by X-Rays.** C. G. BARKLA and A. E. M. M. DALLAS (*Phil. Mag.*, 1924, vi, 47, 1—23).—Investigation of the energy of the corpuscular radiation emitted by metal plates exposed to X-radiation of various frequencies has afforded results differing substantially from those obtained by Sadler (A., 1910, ii, 251), Bragg and Porter (A., 1911, ii, 683), and Beatty (A.,

1911, ii, 245). Two independent discontinuities are indicated in corpuscular emission due to  $\alpha$ - and  $\beta$ -constituents of the  $K$  radiation when this was used to excite corpuscular emission. Only few  $K$  electrons, *i.e.*, those emitted in exclusive association with the  $K$  characteristic radiation, whatever their origin, have energy of the order  $hn$ , where  $n$  is the frequency of the exciting radiation. From silver and tin these electrons are insufficient in number to account either for the whole  $K$  ionisation observed when the substance is in the gaseous form, or for the full energy of characteristic radiation on the basis of one quantum of characteristic radiation for one high-speed electron. The results are interpreted as indicating the importance of the part played by electrons with energy equal to  $h(n-n_k)$  as found by de Broglie (Solvay Conference, Brussels, 1921).

J. S. G. T.

**Impact Effects in Nitrogen and Nitric Oxide.** C. B. BAZZONI and A. T. WALDIE (*J. Franklin Inst.*, 1924, **197**, 57—72).—Theoretical and practical difficulties connected with the interpretation of experimental data for the ionisation and resonance potentials of gases are briefly referred to. The authors show that at pressures ranging from 0.1 mm. to 10 cm. of mercury, nitric oxide is not dissociated either by heat radiation or by ultra-violet radiation. Hot metals, *e.g.*, nickel, cause dissociation of the gas, the oxygen liberated combining at once with the metal. It is shown that the virtual free path of electrons in nitrogen must be several times that predicted by the kinetic theory, and that the dimensions of the apparatus employed in the ionisation experiments, more especially the grid distance, determine the appearance of the higher critical voltages of nitrogen. All the critical potentials observed by Brandt for nitrogen (A., 1922, ii, 186) have been confirmed in the present experiments. The evidence suggests that the resonance potential at about 8 v., and the lowest ionisation potential, 17.7 v., are characteristic of the nitrogen atom, whilst the higher potentials, particularly the critical potential at 24 v., are connected with the ionisation of the molecule. The results are in accord with those obtained by Smyth (A., 1923, ii, 602).

J. S. G. T.

**Radiation Potentials of Atomic Hydrogen.** P. S. OLMSTEAD and K. T. COMPTON (*Physical Rev.*, 1923, **22**, 559—565).—Radiation potentials of atomic hydrogen, produced by thermal dissociation of molecular hydrogen with a tungsten furnace which could be maintained at 2800° K, were observed at 10.15, 12.05, 12.70, 13.00, 13.17, and 13.27 v., with additional radiation at the ionising potential 13.54 v. The results, which are liable to an error of less than 0.05 v., are in agreement with the Lyman spectral series and Bohr's theory.

A. A. E.

**The Protective Action of Anti-oxygenisers against the Changes due to Light on Dyed Fabrics.** A. GILLET (*Bull. Soc. chim.*, 1923, **33**, [iv], 1602—1606; cf. A., 1923, i, 675, also Gillet and Giot, A., 1923, ii, 527).—A claim to priority over Sisley (A., 1923, ii, 717).

H. J. E.

**The Validity of Ohm's Law in the Case of Electrolytes subjected to very strong Fields.** M. WIEN (*Ann. Physik*, 1924, iv, 73, 161—181).—Experiments are described showing that Ohm's law is valid to within the limit of experimental error (estimated as about 1%) in the case of conduction by electrolytes, in which the potential gradient is as high as 500,000 v. per cm. This result confirms qualitatively the conclusions of Lenard relating to electrolytic conduction (A., 1920, ii, 349). J. S. G. T.

**The Magnetons of Weiss and of Bohr and the Constitution of the Atom.** B. CABRERA (*Anal. Fis. Quím.*, 1923, 21, 505—526).—The author discusses the relationship between the magnetic moments and magnetons in the case of ions of elements of the iron group, criticising in particular the conclusions of Sommerfeld (A., 1923, ii, 734). In the case of the rare earth metals the magnetic moments are multiples of the Weiss magneton, and not of the Bohr magneton, calculated by Pauli's formula. The latter formula is compared with that of Langevin. The hypothesis that changes can occur in the orbits of electrons may justify Langevin's law.

G. W. R.

**Discovery and Separation of the Isotopes of Chlorine and the Whole Number Rule.** W. D. HARKINS and T. H. LIGGETT (*J. Physical Chem.*, 1924, 28, 74—82).—Using a process of diffusion of hydrogen chloride into air through a membrane of porous porcelain and making a cut of 8000, the atomic weight of chlorine was increased by 0.044 unit. If the process of separation had an efficiency of 100%, the increase of atomic weight should be 0.086 unit, from which it follows that the efficiency of the actual separation was 51%. This agrees well with the efficiency of 60% obtained by Harkins and Broeker (*Nature*, 1920, 105, 230), with the same porous material, but is higher than that of 35% obtained by Harkins and Hayes (A., 1922, ii, 140), who used material with larger pores. The efficiency obtained in a cut of 400 was also 51%, which is in perfect agreement with that for a cut of 8000. Such an agreement could not be attained unless the process described had actually separated the isotopes, for the material separated after each diffusion was purified before the next diffusion was commenced, and in consequence any impurities could not have a constant effect. The atomic weights were determined by precipitation of the chlorine as silver chloride, and are in good agreement with those obtained in independent separations by Harkins and Broeker and by Harkins and Hayes, who used a density method for the atomic-weight determinations. J. F. S.

**An Experimental Determination of the Rate of Decay of the Short-life Product Radium-C'.** J. C. JACOBSEN (*Phil. Mag.*, 1924, vi, 47, 23—31).—A method of preparation of pure radium-C' is described. By observation of the numbers of scintillations produced on a zinc sulphide screen placed at various distances from the pure radioactive material, the value of the transformation constant,  $\lambda$ , of radium-C' was found to be  $8.4 \times 10^5 \text{ sec.}^{-1}$ . A comparison of this result with the value  $5 \times 10^7 \text{ sec.}^{-1}$  deduced from



the formula,  $\log \lambda = a + b \log R$ , suggested by Geiger and Nuttall (A., 1911, ii, 953), in which  $R$  denotes the range of the  $\alpha$ -rays and  $a$  and  $b$  are constants, and the consideration of results relating to other products of the uranium-radium sequence, suggest a modification of this formula.

J. S. G. T.

**Researches on Cellular Disintegration.** A. NODON.—(See i, 347.)

**Remarks on the Preceding Note.** D. BERTHELOT.—(See i, 348.)

**Rare Earths. XV. Search for Element Sixty-one.** L. F. YNTEMA.—(See ii, 185.)

**Chemical Valency and Luminous Radiation. I. The Pictet-Trouton Rule.** J. DUCLAUX (*J. Chim. physique*, 1923, 20, 403—410).—A theoretical paper in which the Pictet-Trouton rule is discussed. The deviations from the normal value of  $Q/T$  exhibited by associated liquids are interpreted by application of the conception of quanta to vaporisation.

J. F. S.

**Statement of the Third Law of Thermodynamics.** E. D. EASTMAN (*J. Amer. Chem. Soc.*, 1924, 46, 39—43).—A theoretical paper in which it is argued that there is in the ideal case no sharp dividing line between the crystalline and the (supercooled) liquid states. If the conclusion of Lewis and Gibson (A., 1920, ii, 585) is accepted that glasses possess finite entropy at the absolute zero, it is necessary to believe that complicated crystals also do. Following Lewis and Gibson, "randomness" is regarded as the source of the entropy differences among glasses and crystals at the absolute zero, and the minimum number of atomic positions necessary to define the state of any system is adopted as a measure of its randomness. From the results of certain plausible assumptions as to the form of the relationship between entropy and randomness, it appears possible that measurable entropy effects may be found in real crystals of the more complex types. Finally, a statement of the third law of thermodynamics in the following terms is in keeping with the above ideas. "At the absolute zero entropy changes in all reactions of the same type are equal, and in reactions in which the system does not change in type the entropy changes are zero."

J. F. S.

**The Systematic Doctrine of Affinity. XXIV.** W. BILTZ. XXV. W. BILTZ and E. MEINECKE.—(See ii, 168, 165.)

**Crystallisation [Crystal Structure] of Sodium Chlorate and Sodium Chloride.** J. BECKENKAMP (*Z. Physik*, 1923, 20, 414).—The crystal structure suggested by Kiby (A., 1923, ii, 687) for sodium chlorate requires modification in order that the optical activity of this substance may be accounted for. According to the amended structure, the two oxygen atoms in the formula  $\text{NaOCl} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix}$ , which are connected by double bonds with the chlorine atom, are separated in the crystal from the chlorine atom by a

distance which differs from the distance between the chlorine atom and the third oxygen atom. This difference, which is responsible for the optical activity of sodium chlorate, cannot be detected by X-ray measurements.

J. S. G. T.

**Determination of the Vapour Pressures of Cæsium and Rubidium, and a Calculation of their Chemical Constants.** D. H. SCOTT (*Phil. Mag.*, 1924, vi, 47, 32—50).—The respective vapour pressures of cæsium and rubidium at various temperatures between 50° and 130° have been determined by means of a slightly modified form of Haber's vibrating quartz-fibre manometer (A., 1914, ii, 534) with which observations were made of the time taken for the amplitude of vibration of the fibre to diminish to a definite fraction of its original value. The following empirical relations were deduced between  $p$ , the vapour pressure measured in mm. of mercury, and  $T$ , the absolute temperature: for cæsium,  $\log p = 7.256 - 3753/T$ ; for rubidium,  $\log p = 7.331 - 4209/T$ . The corresponding values of the respective chemical constants,  $C$ , are: cæsium,  $1.64_0 \pm 0.16_4$ ; rubidium,  $1.36_6 \pm 0.18_4$ . The values of the absolute chemical constant,  $C_0$ , calculated from the equation  $C = 1.5 \log M + C_0$ , where  $M$  is the molecular weight of the element, are: cæsium,  $-1.54_5 \pm 0.16_4$ ; rubidium,  $-1.53_2 \pm 0.18_4$ . Possible reasons why these values are greater than the theoretical value  $-1.608$  are discussed. The respective values of Trouton's coefficient,  $L_{T_B}/T_B$ ,  $T_B$  denoting the boiling point of the element, are: cæsium, 18.2; rubidium, 19.9.

J. S. G. T.

**Vapour Pressures of Nitric Oxide.** F. A. HENGLEIN and H. KRÜGER.—(See ii, 170.)

**Coagulation and Surface Tension.** J. AMAR (*Compt. rend.*, 1924, 178, 522—525).—Investigation is made of the effect of time on the coagulum obtained by the addition of citric acid to goat's milk and of hydrochloric acid to sodium silicate solution. In both cases, dehydration proceeds according to an asymptotic curve. A study of the effects of various coagulants shows that the velocity of coagulation is proportional to the lowering of surface tension by the coagulant.

A. B. H.

**The Molecular Association of Liquids and Highly-compressed Gases. I and II.** E. E. WALKER (*Phil. Mag.*, 1924, vi, 47, 111—126).—A theoretical paper in which it is shown that the critical coefficient  $RT_c/P_cV_c$  of non-associated substances is a function of the length of the molecule. A Dieterici equation of state is proposed which is modified by the introduction of a function of  $l$ , the length of the molecule. The constants  $\alpha$  and  $\beta$  in this equation are additive quantities both for associated and non-associated substances. The effect of association on the critical constants may be calculated with the aid of the modified equation.

W. E. G.

**The Velocity of Sound in Gases and Vapours, and the Ratio of the Specific Heats.** H. B. DIXON and G. GREENWOOD (*Proc. Roy. Soc.*, 1924, A, 105, 199—221).—The authors have determined

directly the respective values of the velocity of sound in various gases and vapours contained in a lead pipe of 25 mm. internal diameter, and have deduced therefrom the corresponding values of the velocity in the free gas or vapour. From the results, the values  $C_p - C_v$  have been calculated by means of the equation  $C_p - C_v = R(1 + 27\pi\tau^3/16)$ , in which the symbols have the customary significance, and the values of  $\gamma$  by means of Berthelot's equation  $C_p/C_v = V^2M[1 - 9\pi\tau(1 - 6\tau^2)/64]/RT$ . Combination of these data gives  $C_p$  and  $C_v$ . The following are the respective values of  $\gamma$ ,  $C_p - C_v$ ,  $C_p$ , and  $C_v$  recorded at different temperatures: ethyl ether: 80°, 1.086, 2.202, 27.81, 25.61; pentane: 86°, 1.086, 2.202, 29.50, 27.31; hexane: 80°, 1.080, 2.323, 31.36, 29.03; ethyl alcohol: 90°, 1.129, 2.138, 18.72, 16.57; methyl alcohol: 77°, 1.203, 2.120, 12.56, 10.44; benzene: 90°, 1.097, 2.245, 25.39, 23.15. Values of  $\gamma$ ,  $C_p - C_v$ , and  $C_v$  for ammonia and ethylene at the temperatures stated are as follows: ammonia: 16.5°, 1.3144, 2.062, 6.56; 41°, 1.3095, 2.045, 6.61; 63.5°, 1.3062, 2.034, 6.64; 86°, 1.3021, 2.025, 6.70; ethylene: 12°, 1.2562, 2.0494, 8.20; 41.5°, 1.2380, 2.0327, 8.45; 63.5°, 1.2295, 2.0246, 8.82; 89°, 1.2213, 2.0162, 9.12. For ammonia, the values of  $C_v$  at temperature  $t^\circ$  agree very closely with those calculated by means of the formula  $C_v = 6.525 + 0.002t$ . The corresponding relation for ethylene is  $C_v = 8.06 + 0.0119t$ .  
J. S. G. T.

**The Ratio of the Specific Heats of Nitrogen and of Oxygen.** J. R. PARTINGTON and A. B. HOWE (*Proc. Roy. Soc.*, 1924, **A**, 105, 225—243).—In continuation of previous work (A., 1914, ii, 529; 1921, ii, 621; 1922, ii, 191), measurements of the specific heat ratio  $\gamma$  for nitrogen and oxygen have been made by the method of adiabatic expansion. The results, corrected for radiation and for deviation from the ideal gaseous state, are nitrogen,  $1.4045 \pm 0.0003$ ; oxygen,  $1.3946 \pm 0.0002$  at 20° and 760 mm. The value for nitrogen is in close agreement with that found by Dixon, Campbell, and Parker (A., 1921, ii, 621).  
J. S. G. T.

**Relation between Vapour Pressure and Vapour Composition in Binary Mixtures of Volatile Liquids.** W. K. LEWIS and E. V. MURPHEE (*J. Amer. Chem. Soc.*, 1924, **46**, 1—7).—A theoretical paper in which an approximate integration is presented for the Duhem-Margules equation. With the aid of this, it is possible to calculate the vapour-liquid composition curve from the isothermal total pressure curve. The method outlined has been tested in the case of the binary mixtures, methyl alcohol-water, ethyl alcohol-water, carbon disulphide-water, and acetone-chloroform. For only one of these mixtures is the divergence between the experimentally determined composition and the calculated value as great as 2%.  
J. F. S.

**Attempt to Correlate certain Theories of Solution.** T. W. JONES (*Chemistry and Industry*, 1924, **43**, 4—6).—A theoretical paper in which, after outlining J. J. Thomson's theory of solution and ionisation, the author shows in what respects this is in agreement with the views of H. E. Armstrong and Lowry. The points of

divergence are also indicated, and it is shown that the three theories are agreed on the point that the active constituents of solutions do not exist unattached, but form complexes with the molecules of the solvent. J. F. S.

**Two Attempts to Replace the Ionic Theory by a Theory based on the Molecular Condition of Water.** V. AUGER (*Compt. rend.*, 1924, **178**, 330—332).—The author points out certain obvious difficulties in connexion with the anti-ionic theories advanced, respectively, by Armstrong (cf. A., 1923, ii, 542) and by Kling and Lassieur (*ibid.*, 543). He regards Armstrong's two main premises as hypothetical and arbitrary, and directs attention to the exiguity of detail in connexion with the other authors' formulæ for the two modifications of water which are postulated. E. E. T.

**Mixed Crystals of Alloys.** F. SAUERWALD.—(See ii, 189.)

**The Law of Definite Proportions in the Light of Modern Research.** U. R. EVANS (*Trans. Faraday Soc.*, 1923, **19**, 420—429).—The author reviews briefly metallographic evidence in reference to the law of definite proportions, paying special attention to the hardness and stability of alloys, and re-states the present metallographic position concerning the variable composition of alloys from a point of view somewhat different from that adopted by Kurnakov (*Z. anorg. Chem.*, 1914, **88**, 109). It is claimed that Kurnakov's contention, which is tantamount to a revival of Berthollet's doctrine of the variable composition of homogeneous bodies, may be extended to compounds between metals and non-metals. A "compound" is, in many cases, merely a particularly stable member of a continuous series of solid solutions; the fact that maximum stability within the series occurs at a composition expressible by a simple formula may often be explained from the physical point of view. J. S. G. T.

**Mixed Crystals.** G. TAMMANN and W. KRINGS.—(See ii, 175.)

**The Structure of Solid Solutions.** A. WESTGREN and G. PHRAGMÉN (*Nature*, 1924, **113**, 122—124).—By the use of a precision camera, the main features of which are indicated, it is found that the face-centred elementary cube of steel quenched at 1100° has an edge of 3.629 Å., whilst that of steel quenched at 750° has an edge of 3.601 Å. The lattice thus appears to increase in size with increasing content of carbon, although the carbon atoms are smaller than the iron atoms; the solid solution is hence not formed by a simple substitution. In the case of a homogeneous austenitic manganese steel, it is evident that the lattice is formed only by iron and manganese atoms, the carbon atoms being distributed uniformly between them. If less than 8% of aluminium is dissolved in copper, the copper lattice is unchanged in type, but it increases in size with increasing content of aluminium. These solid solutions would appear to be formed by simple substitution of copper atoms by aluminium atoms. In the range 16—25% Al, the lattice dimensions decrease with increasing content of aluminium. The edge of the elementary cube varies from 8.701 Å. to 8.656 Å., and it

appears that three copper atoms in the lattice are replaced by two aluminium atoms. The groups of atoms present in the elementary cube correspond very nearly with the formulæ  $\text{Cu}_{36}\text{Al}_{16}$ ,  $\text{Cu}_{33}\text{Al}_{18}$ ,  $\text{Cu}_{30}\text{Al}_{20}$ , and  $\text{Cu}_{27}\text{Al}_{22}$ .

The powder photograph of a zinc-copper alloy containing 65% Zn bears an unexpectedly close resemblance to those of aluminium-copper alloys containing 16–25% Al; these would appear to be formed by simple substitution of one metal for the other in the lattice framework.

A. A. E.

**Double Decomposition in Absence of Solvents.** A. G. BERGMANN.—(See ii, 178.)

**Displacement of Acids by Diffusion.** E. DEMOUSSY (*Compt. rend.*, 1924, **178**, 208–211).—The displacement of a strong acid (hydrochloric) by a weaker one (formic) in contact with a membrane (cf. Li Shou Houa, *Ann. Physique*, **17**, 475) is shown to be due to the greater speed of diffusion of the strong acid. The phenomenon is observed in the absence of a membrane. If a solution containing barium chloride (1 mol.) and formic acid (2 mols.) is introduced into the lower part of a tall vessel containing water, hydrochloric acid diffuses upwards more rapidly than formic acid, and the original state of equilibrium is continuously displaced.

E. E. T.

**Displacement of Acids by Diffusion.** P. GIRARD (*Compt. rend.*, 1924, **178**, 389–391).—The simple explanation offered by Demoussy (cf. *supra*) of results obtained by Li Shou Houa and by Girard (cf. A., 1914, ii, 718) is shown to be insufficient. The interposition of a membrane between a salt solution and water inverts, but does not create, the electrostatic field (at the junction of the two media), and it is the latter which is responsible for the effects observed by all three authors.

E. E. T.

**Method of Determining Micromiscibilities.** N. PERRAKIS and A. MASSOL (*Compt. rend.*, 1924, **178**, 322–323).—Micromiscibilities are readily determined by a titration method, the end-point being determined by the appearance of cloudiness. Two mixtures of water, alcohol, and an oil were examined, the water or the oil being present in traces only (cf. A., 1923, ii, 836).

E. E. T.

**Esterification Equilibria in the Gaseous Phase.** G. EDGAR and W. H. SCHUYLER (*J. Amer. Chem. Soc.*, 1924, **46**, 66–75).—The equilibrium in the gaseous state between ethyl alcohol, acetic acid, ethyl acetate, and water has been examined. The method of procedure adopted consisted in determining the composition of the vapour which distilled at measured temperature and pressure from the liquid equilibrium mixture. The temperature varied from 52.2° to 77.6° and the pressure from about 0.5 to 1.0 atmosphere. The manipulation at atmospheric pressure is simpler than at reduced pressure, and in consequence the results of the individual experiments (12) at this pressure are in better agreement. The results show that the equilibrium in the gaseous phase is in general different from that in the liquid phase and in the present case it is widely different. From the results it is calculated that at 150°

the equilibrium corresponds with about 95% esterification. The results obtained by Reid and Mulliken were in all cases less than this, and the suggestion that the experiments in question afford evidence of the displacement of the equilibrium by the contact catalyst can therefore not be accepted. J. F. S.

**Dissociation Constant of Boric Acid.** E. B. R. PRIDEAUX and A. T. WARD.—(See ii, 171.)

**Faraday's Law for Lithium Hydride.** K. PETERS.—(See ii, 174.)

**Electrolytic Conductivity of Molten Scandium Chloride.**—(See ii, 184.)

**Determination of the Degree of Dissociation of a Binary Electrolyte from Conductivity [Measurements].** E. CHERBULIEZ (*J. Chim. physique*, 1923, 20, 464—470).—A theoretical paper in which the author discusses the probable errors in the value of the degree of ionisation calculated from the equation  $\alpha = \lambda/\lambda_\infty$ . These errors are much reduced with increasing ionisation and with increasing ratio between the two dilutions. More accurate values of  $\alpha$  are obtained by determining the variation of the conductivity with the dilution, and equations are given showing the relationship between these. J. F. S.

**Influence of Gelatin on the Transport Numbers of Hydrochloric Acid.** W. G. FRANCE and W. H. MORAN (*J. Amer. Chem. Soc.*, 1924, 46, 19—30).—The transport numbers of 0.1N- and 0.01N-solutions of hydrochloric acid have been determined at 25° by an *E.M.F.* method in the presence of gelatin. It is shown that the transport number of the anion varies from 0.1699 in the absence of gelatin to 0.77718 in the presence of 20% of gelatin. The addition of gelatin reduces the effective hydrogen-ion concentration of 0.1N- and 0.01N-hydrochloric acid solutions and alters the conductivity. The relative change in the conductivity of 0.01N-solutions is greater than for 0.1N-solutions. In the case of a 10% gelatin solution, the conductivity of a 0.1N-solution is reduced almost to zero; a similar change occurs in 0.01N-hydrochloric acid with 2—3% of gelatin. These facts suggest that not only is the hydrogen-ion concentration reduced, but that the acid is removed as a whole by the gelatin. In agreement with this view, evidence has been obtained that gelatin reacts with acids to form a dissociable adsorption complex or additive chemical compound. This is in agreement with the hypothesis put forward by Loeb. J. F. S.

**Hydrofluoric Acid Solutions.** C. W. DAVIES and L. J. HUDLESTON.—(See ii, 167.)

**Influence of Neutral Salts on the Potential of Metal Electrodes.** G. POMA (*Z. physikal. Chem.*, 1923, 107, 329—332).—A claim for priority over Ārkadiev (A., 1923, ii, 369), Sachanov (Diss. Odessa, 1915), Harned (A., 1916, ii, 8), and Åkerlöf (A., 1922, ii, 134) in connexion with experimental work on the influence of neutral salts on the potential of metal electrodes and of hypotheses put forward to explain the effects observed (A., 1912, ii, 323;

1914, ii, 440). The matter contained in the previous papers is briefly discussed.

J. F. S.

**Effect of a Magnetic Field on the Potential of Hydrogen Occluded in Iron.** T. W. RICHARDS and W. T. RICHARDS (*J. Amer. Chem. Soc.*, 1924, **46**, 89—104).—The potential of pure iron in ferrous sulphate, in mixtures of ferrous and ferric sulphate, and in mixtures of ferrous sulphate and sulphuric acid of various concentrations has been measured against a normal calomel electrode at 25°. The effect of a magnetic field on the potential of pure iron and of spongy iron charged with hydrogen in ferrous sulphate solutions has also been examined. It is found that the potential of iron in ferrous sulphate is changed only very slightly (0—1.0 millivolt) by the application of a magnetic field. This small alteration is probably to be attributed in part to diffusion in the electrolyte under magnetic influence. On the other hand, the potential of hydrogen occluded in iron is found to be lowered distinctly (0.5—5.1 millivolts), the change being roughly proportional to the strength of the magnetic field employed. With a given magnetic field, the decrease of "overvoltage" is approximately proportional to the "overvoltage" itself, amounting, with the strongest magnet used, to about 5% of the "overvoltage" value. The results appear to indicate that occluded hydrogen is in the atomic condition, but not ionised, and that a magnetic field affects its potential, not because of any change in affinity between hydrogen and iron, but rather because of some change in the texture of the occluding metal due to magnetostriction.

J. F. S.

**Effect of Various Preparations of Mercurous Sulphate on the Electromotive Force and Hysteresis of Weston Standard Cells.** W. C. VOSBURGH and M. EPPLEY (*J. Amer. Chem. Soc.*, 1924, **46**, 104—111).—Weston cells have been prepared with mercurous sulphate of variously sized particles ( $3\mu$  —  $360\mu$ ) and the *E.M.F.*'s measured at 25° after varying periods of time. It is shown that cells with finely divided mercurous sulphate have *E.M.F.* values which are from 40 to 100 microvolts higher than those of cells made with coarser mercurous sulphate. The hysteresis of the cells varied greatly with the characteristics of the mercurous sulphate, being largest in the case of a coarse-grained, white mercurous sulphate and practically zero in the case of a fine-grained, grey mercurous sulphate. Both the smallness of the particles and the presence of finely divided mercury appear to influence the prevention of hysteresis. The addition of acid to cells lowers the hysteresis considerably. In setting up a standard cell, it is important therefore that the mercurous sulphate should be sufficiently large-grained. Digestion with sulphuric acid solution at the boiling point is a wise precaution, but this cannot be depended on to correct a very finely divided, uniform mercurous sulphate. Low hysteresis cannot be taken as indicating trustworthiness in cells of low acid content. On the contrary, a cell with a fairly high hysteresis is more trustworthy for use as a primary standard. When it is more important that a cell should have low hysteresis rather than that the *E.M.F.* should

have the established value, a higher acidity and a fine-grained mercurous sulphate may be used. J. F. S.

**Concentration Cells in Methyl Alcohol.** J. GRANT and J. R. PARTINGTON (*Trans. Faraday Soc.*, 1923, **19**, 414—417).—Contrary to the conclusion of Wilson (A., 1906, ii, 144), the authors find that the values obtained for the *E.M.F.*'s of concentration cells, in which solutions of silver nitrate in methyl alcohol with a concentration range from  $N/10$  to  $N/640$  were contained, agree with the corresponding values calculated by means of Nernst's formula. Wilson's discordant results are attributed to experimental error. J. S. G. T.

**The Electrochemical Behaviour of Chromium.** N. BOUMAN (*Rec. trav. chim.*, 1924, **43**, 1—29).—The determination of the potential of chromium in acid solution is attended with great difficulty, on account of the tendency of the metal to become passive. Many previous workers have experimented with metal prepared by Goldschmidt's method, which is now shown not to give reproducible results, on account of the presence of traces of impurity. Constant results have, however, been obtained with electrolytic chromium, obtained by Sargent's method (*Trans. Amer. Electrochem. Soc.*, 1920, **37**), activated in 24% hydrochloric acid at 100°. The potential measured in 1.0*N*-sulphuric acid is  $-0.546$  volt. This potential is independent of the metal on which the chromium is deposited, and also of the method of activation. It is also independent of the ratio of  $\text{Cr}^{++}$  to  $\text{Cr}^{+++}$ -ions in solution. It is curious that, with increasing hydrogen-ion concentration, the potential becomes more positive in sulphuric acid, but more negative in hydrochloric acid solution. Chromium remains active only when the acidity is above a certain limit, about 0.001*N*. In the passive state, the potential of chromium in potassium chloride solution depends on the previous treatment which it has received, and this is shown to be equally true of other metals, including platinum. Consequently no conclusions can be drawn from such measurements relative to the state of the metal. The potential of passive chromium varies with the metal on which it is deposited. When chromium is polarised anodically, the potential varies in the same way with the acidity as the potential of the unattackable electrode. The polarisation tension is therefore governed by the reaction  $\text{Cr}^{+++} + 4\text{H}_2\text{O} = \text{CrO}_4^{--} + 8\text{H}^+ + 3\ominus$ . The phenomenon of "after-anodic polarisation" was investigated, and was found to be less general than Aten supposes (A., 1919, ii, 8). The behaviour of chromium is explicable by the theory of allotropy. E. H. R.

**The Electromotive Behaviour of Magnesium and Magnesium Amalgams.** R. MÜLLER and W. KNAUS (*Z. anorg. Chem.*, 1923, **130**, 173—180).—The potentials of the metal and its amalgams have been measured in solutions of magnesium chloride, potassium chloride, sodium hydroxide, and hydrochloric acid in dilutions from 1.0*N* to 0.0001*N*, using the calomel normal electrode. The values for the amalgams are in all cases considerably higher than for the metal. The values for the latter do not alter when it



is filed under the solution, except in the case of the sodium hydroxide solutions, in which a skin of hydroxide forms very rapidly. The values in acid solution are of no significance, since both metal and amalgam react vigorously. The potential of the metal in *N*-magnesium chloride solution, calculated with reference to the hydrogen electrode, is 1.49 v., and of the liquid amalgam (10–20 atoms% magnesium) 1.8 v., but the latter value is uncertain, as the amalgams react vigorously with the solutions. Determinations were therefore made with saturated solutions of magnesium bromide in anhydrous pyridine, measuring against the half-element  $\text{Ag}|\text{AgNO}_3$ , 0.1*N* in pyridine; the potential for pure magnesium is 1.33 v., which value remains constant for amalgams up to 50 atoms% of mercury; at this point a sudden rise to 1.72 v. occurs. The amalgams rich in magnesium are solid, very brittle, and considerably harder than pure magnesium. Above 50 atoms% of mercury the potential remains at 1.72 v. until only 10 atoms% of magnesium is present. The potential falls slightly for less than 10 atoms% of magnesium, then suddenly for 1 atom%, the potential for pure mercury being 0.427 v. The alloys very poor in magnesium are liquid. The potential curve is exceptional, the sudden change indicating the compound  $\text{HgMg}$ , which is formed with liberation of heat.

Magnesium may be separated electrolytically from the pyridine solution of the bromide on a platinum or mercury cathode, the potential for platinum being 1.35, and for mercury 1.65 v. S. I. L.

**Amphoteric Elements.** J. KASARNOWSKY (*Z. anorg. Chem.*, 1923, **130**, 140).—A note explaining that the difference in the values of the potential  $\phi_h$  given in an earlier paper (A., 1923, ii, 824, 828) is due to alternative methods of calculation. S. I. L.

**Intermittent Current Electrolysis. III. The Measurement of Overvoltage.** S. GLASSTONE (*J. Chem. Soc.*, 1924, **125**, 250–260).—The true potential of the electrode at the instant of switching off the polarising current is determined by measuring the rate of fall of the potential of a polarised electrode after the current is switched off, and extrapolating the P.D.–time curve. The overvoltage at the electrode is determined from these potentials, obtained at various current densities. The results show that for small values of polarising current, the overvoltages measured by the direct method and by the extrapolation method are almost the same, hence the existence of transfer resistance is very doubtful. For very low current densities the direct method is the only method available, since the repeated make and break of the polarising current prevents the electrode from reaching its equilibrium value. At greater current densities the results obtained by the direct method are appreciably higher than the extrapolated values. This difference is probably due to the resistance of a metal–gas–electrolyte system at the surface of the electrode. Variation in the size of the electrode, and of the dilution and temperature of the electrolyte, give results which strongly support this view. The “surface resistance” at a lead electrode 1 sq. cm. area in a *N*/1-solution of sodium hydroxide or sulphuric acid is not greater than 4 ohms. J. B. F.

**The Dependence of Polarisation-overvoltage on Hydroxyl and Hydrogen-ion Concentration. I. Polarisation-overvoltage of an Antimony Cathode in Aqueous Alkaline Solution.** H. J. S. SAND and E. J. WEEKS (*J. Chem. Soc.*, 1924, 125, 160—168).—The polarisation overvoltage  $\omega$  of an antimony cathode in alkaline solution is determined by the commutator method and obeys with considerable accuracy the empirical equation:  $\omega = a - 2h$ , in which  $h$  (the so-called  $p_H$  voltage) is the potential difference between a standard calomel electrode and a hydrogen electrode in the solution examined, and  $a$  is a constant depending only on the temperature. The relation holds for most varied electrolytes and hence such factors as sodium-ion concentration are without measurable influence. In explanation of these results it is suggested that ions of the formula  $H(OH)_2''$  are formed in solution with a very high velocity. When these ions, which have a definite solubility and also a definite supersolubility limit, have accumulated in a sufficient number (in the liquid or solid state) they undergo decomposition and furnish thereby the energy required for the formation of a gas bubble. It is suggested further that polarisation overvoltage is determined by the concentration of hydrogen dissolved in, or adsorbed by the surface of the electrode, that the hydrogen dissolved in the working cathode is in thermodynamic equilibrium with hydrogen dissolved in the layer of electrolyte immediately outside the double layer separating the metal from solution, and that hydrogen is de-ionised simultaneously on the electrode throughout the double layer and immediately beyond it, *i.e.*, free electrons travel directly from the cathode into the solution over this range during the passage of the current. The conclusion is drawn that identical relations should be found with other metals which act as indifferent cathodes in alkaline solution.

J. B. F.

**Free Energy of Antimony Trioxide and the Reduction Potential of Antimony.** R. SCHUHMANN (*J. Amer. Chem. Soc.*, 1924, 46, 52—58).—The *E.M.F.* of the cells of the type  $Sb, Sb_2O_3(s) | HClO_4(c) | H_2$  has been measured at 25° for concentrations of perchloric acid lying between 0.1*M* and 1.0*M*. The solubility of antimony trioxide in perchloric acid solutions of this range of concentrations was also measured at 25°. The value of the *E.M.F.* is found to be -0.152 volt for the cell. From this value the free energy of formation of antimony trioxide from its elements at 25° is found to be -148,600 cal. with an error which probably does not exceed  $\pm 300$  cal. The results of the solubility determinations indicate that the dissolved antimony exists mainly in the form of  $SbO^+$  at the concentrations of perchloric acid employed. From the solubility data and the *E.M.F.* of the cell the molecular reduction potential corresponding with the electrode reaction  $Sb(s) + H_2O + 3\oplus = SbO^+ + 2H^+$  is found to be -0.212.

J. F. S.

**Activity of Perchloric Acid in Aqueous Solution.** R. SCHUHMANN (*J. Amer. Chem. Soc.*, 1924, 46, 58—60).—The *E.M.F.*

of cells of the type  $H_2|HCl|HClO_4|H_2$  has been measured at  $25^\circ$  for concentrations of the two acids between 0.1*N* and 1.0*N*. In all combinations, the concentrations of the two acids were very nearly the same. The liquid junction potential, resulting from the slight difference between the mobilities of the chloride and the perchlorate ions, was very small, and was estimated as 0.00047 v. The corrected *E.M.F.* values obtained are so small as to be negligible in determining the relative activities of the two acids at the same concentration. Thus the largest value, 0.00017 v., would correspond with a difference of only 0.7% in the value of the activity coefficient of the hydrogen-ion. The conclusion may be drawn therefore that the activity coefficient of perchloric acid is substantially the same as that of hydrochloric acid for concentrations up to 1.0*N*, and the values derived for the latter acid (see Lewis and Randall, "Thermodynamics") may therefore be employed in mass action and thermodynamic expressions relating to perchloric acid. This conclusion is of interest, since it indicates that the behaviour of these acids, including the pronounced minimum in their activity coefficients in the neighbourhood of 0.5*N*, is primarily determined by the hydrogen-ion, the effects of the two anions being apparently relatively small and nearly equal.

J. F. S.

**Free Energy of Aqueous Sulphuric Acid.** D. F. SMITH and J. E. MAYER (*J. Amer. Chem. Soc.*, 1924, **46**, 75—83).—The equilibrium conditions of the reversible reaction  $H_2SO_4(5.4-6.8M) + 6HI(0.1-1.0N) = 3I_2 + 4H_2O + S(\text{rhomb})$  have been determined at  $80^\circ$ . The *E.M.F.*'s of cells of the type  $Pt, H_2|H_2SO_4(C_1) + HCl(C_2)|H_2SO_4(C_1) + HI(C_2) + I_2(C_3)|Pt$  were also measured at the same temperature. By combining the data obtained, the partial free energy of sulphuric acid (5.441 molar) was calculated to be -169,850 cal. at  $80^\circ$ . Making use of already known heat data, the corresponding value for  $25^\circ$  was calculated as -175,010 cal. By means of the activity data of Lewis and Randall ("Thermodynamics") the free energy of the sulphion  $SO_4^{--}$  at 1*M* concentration was found to be -176,540 cal. at  $25^\circ$ , thus confirming the provisional value of -176,500 cal. derived by Lewis and Randall. By combining this new value for the free energy of the sulphion with the values given by Lewis and Randall for other sulphur compounds, the reduction potentials of various combinations which have considerable practical significance have been worked out for  $25^\circ$  and tabulated. J. F. S.

**The Variation of Surface Tension with Temperature and some Related Functions.** S. SUGDEN (*J. Chem. Soc.*, 1924, **125**, 32—41).—Equations put forward by various observers showing the variation of surface tension with temperature are discussed. If *B* is given the value 1.20, then from van der Waals' equation  $\gamma = k_1\theta_c v_c^{-\frac{2}{3}}(1-m)^B = k_2\theta_c^{\frac{2}{3}}p_c^{\frac{1}{3}}(1-m)^B$  and Katayama's modification of the Ramsay and Shields equation,  $\gamma[M/D-d]^{\frac{2}{3}} = A\theta_c(1-m)$ , it is possible to derive Macleod's relation between surface tension and density. The results of Ramsay and Shields (*A.*, 1894, **ii**, 179) are too low owing to inadequate correction for capillary rise and are corrected, as also are the results of Walden and

Swinne (A., 1912, ii, 628). From the data thus obtained for six non-associated liquids, it is shown that (a) the variation in surface tension with temperature is represented accurately by the equation  $\gamma = \gamma_0(1 - \theta)^{1.2}$ , where  $\theta$  is the reduced temperature and  $\gamma_0$  a constant, (b) Macleod's relation  $\gamma = C(D - d)^4$ , where  $C$  is a constant and  $D$  and  $d$  are the densities of liquid and vapour, respectively, holds accurately for non-associated liquids up to  $40^\circ$  below their critical temperature. In the van der Waals equation the universal constants  $k_1$  and  $k_2$  vary several units % among the different liquids, whilst the relations connecting  $\gamma_0$  and the critical constants are shown to hold only approximately. The method of correcting the data of Ramsay and Shields is described. J. B. F.

**The Determination of Surface Tension from the Maximum Pressure in Bubbles.** II. S. SUGDEN (*J. Chem. Soc.*, 1924, 125, 27—31).—An improved form of apparatus is described, which consists essentially of three parts, the vessel holding the liquid under examination (called the bubbler) into which pass two tubes, one a capillary and a tube of about 4 mm. diameter, a pressure gauge, and a small mercury aspirator. To avoid direct measurement of the radius of the capillary tube, the surface tension of pure benzene, which is known with sufficient accuracy, may be taken as a reference liquid for the purpose of calibration. A table giving the surface tension of benzene for every degree between  $10^\circ$  and  $30^\circ$  is given. The equation  $\gamma = AP(1 + 0.69r_2gD/P)$  may be used for the sizes of tubes generally employed.  $A$  is a constant for the particular apparatus,  $P$  the difference between the pressures required to liberate bubbles from the two tubes,  $D$  the density of the liquid, and  $r_2$  the radius of the wide tube. J. B. F.

**Surface Tension at the Surface of Separation of Water and an Organic Liquid, in Presence of Aliphatic Acids, and of Alkalis.** R. DUBRISAY and P. PICARD (*Compt. rend.*, 1924, 178, 205—208; cf. A., 1923, ii, 741).—Solutions of aliphatic acids in benzene have been examined by the drop method (Donnan, A., 1900, ii, 201), the volume of 10 drops (of benzene solution) formed in (a) *N*/1250-sodium hydroxide, (b) *N*/2500-sodium hydroxide, and (c) *N*/2500-sodium hydroxide containing 1% of sodium chloride being measured. This volume decreases in the order: (a) lauric, myristic, oleic, palmitic, erucic, ricinoleic, stearic acid; (b) lauric, myristic, ricinoleic, oleic, erucic, palmitic, stearic acid; (c) lauric, ricinoleic, myristic, oleic, erucic, palmitic, stearic acid. Similar experiments have been carried out with different concentrations of stearic, oleic, and ricinoleic acids. With increasing concentration, the volume of the 10 drops at first diminishes, and then increases. E. E. T.

**Permeability of Precipitated Copper Ferrocyanide Membranes for Non-electrolytes.** R. COLLANDER (*Koll.-Chem. Beihefte*, 1924, 19, 72—104).—The permeability of precipitated copper ferrocyanide membranes for non-electrolytes has been investigated. It is shown that these membranes behave towards non-electrolytes in the same way as an ultra-filter. Compounds of which the molecules do not exceed a certain size pass more or less

easily through such membranes, whilst larger molecules are held back. In the present experiments, the upper limit of size at which the molecules are able to pass through the membrane lies at a molecular volume of 80—100. Adsorption and solution processes in the membrane, if they are present at all, are of small importance in comparison with this dominating sieve action. J. F. S.

**Electrification by Adsorption of Membranes and Colloids.**

F. CHOUCROUN (*J. Chim. physique*, 1923, **20**, 411—436).—The author gives a *résumé* of the present state of knowledge on electrification by adsorption, and he points out that in all cases of electro-osmosis an opposing electromotive force of filtration is set up. The electro-endosmosis of distilled water, dilute acids and alkalis across membranes of ferric oxide, arsenic sulphide, ferric ferrocyanide, and copper ferrocyanide has been investigated, and it is shown that the phenomena observed are the result of two different actions, the one generally observed depending on the action of acids and alkalis, and the other a specific action due to superficial ionisation of the wall. Attention is directed to a group of liquids with properties which suggest that they are neither suspensions nor true colloidal solutions; these are the opalescent liquids in which the particles are in static equilibrium with a liquid in which they are soluble. It is shown that the micellæ when travelling in an electric field draw with them the intermicellar liquid in certain cases. J. F. S.

**Method of Determining the Detergent Action of Soaps.**

J. W. MCBAIN, R. S. HARBORNE, and A. M. KING (*J. Soc. Chem. Ind.*, 1923, **42**, 373—378T).—A method has been developed and standardised for the direct and rapid determination of the amount of finely divided carbon which various soaps carry through filter-paper. This gives a "carbon number" characteristic of each soap solution, which may be taken as a measure of the detergent action of the particular material. The carbon number is defined as the number of grams of carbon carried through by 1 kg. of solution under standard conditions. The method of determination consists of the following: One g. of "Auk" carbon black is weighed to within 1%, placed in a large test-tube containing 20 c.c. of soap solution, thoroughly shaken and placed in a thermostat for twenty-three hours, shaken again and kept for a further hour in the thermostat, and then poured on an 11.3 cm. No. 31 Whatman filter-paper. The filtration is carried out in the thermostat, and when about 10 c.c. of filtrate have been collected this is analysed and the amount of carbon determined. It is shown that by a slight variation of the conditions the detergent action of a soap may be enormously increased. There is an optimum concentration in moderate dilution for which the effect is a maximum; very slight addition of either acid or preferably alkali greatly enhances the detergent power. With rise of temperature the detergent power diminishes rapidly at first and then more slowly. There is surprisingly little difference between soaps as different as oleate and myristate. J. F. S.

**Colloidal Vanadium Pentoxide.**—A. V. DUMANSKI.—(See ii,

**Colloidal Nature of Clay.** A. FODOR and B. SCHOENFELD (*Koll.-Chem. Beihefte*, 1924, **19**, 1—46).—The behaviour of electrolytes towards suspensions of clay has been investigated with particular reference to the rate of sedimentation, coagulation, peptisation, cataphoresis, adsorption, and swelling. It is shown that the behaviour of different alkalis is fundamentally different. In small concentrations, ammonia increases the stability of clay suspensions, although in larger quantities it causes an ultramicroscopic aggregation of the particles without effecting a macroscopic coagulation. Sodium hydroxide, however, in small quantities effects the coagulation of the coarser particles, and in large quantities causes quantitative precipitation. The critical alkali concentrations are not only dependent on the hydrogen-ion concentration, but also on the quantity of clay contained in unit volume. Alkali hydroxide is adsorbed by clay and the adsorption isotherm is found to be of normal type. Relatively small quantities of calcium hydroxide bring about considerable coagulation; with increasing concentration of calcium hydroxide, the volume of the coagulate increases. This the authors attribute to peptisation and subsequent adsorption. In support of this is the fact that, in general, lime behaves as a dehydrating agent and applied to the soil has a disintegrating action. The form of the adsorption isotherm of calcium hydroxide by clay is in keeping with this view, and further support is afforded by the rapidity with which equilibrium is reached. Clay which has adsorbed calcium hydroxide never regains its previous power of adsorbing this substance, even after the most thorough washing.

The precipitation of clays by alkalis differs noticeably from that produced by acids. This difference is seen in the relatively greater density of the coagula produced on the addition of acids. Small amounts of acid increase the stability of the suspension, but large amounts bring about immediate coagulation.

Salts in small quantities increase the stability of suspensions; in larger quantities coagulation is accelerated. Humus-acids and phosphates exercise a protective action on clay suspensions. The peptising action of phosphate is independent of the hydrogen-ion concentration and in keeping with its adsorption by clay; phosphates tend to stabilise the suspensions. The above results are all obtained from experiments of a qualitative character. J. F. S.

**Composition of Micellæ. II. Colloidal Iron Oxide.** R. WINTGREN and M. BILTZ (*Z. physikal. Chem.*, 1923, **107**, 403—422; cf. A., 1922, ii, 78).—With the object of controlling the method previously described (*loc. cit.*) for determining the composition and the equivalent aggregation, that is, the number of molecules in a single colloidal particle per unit of electric charge, the authors have measured the electrical conductivity of a series of ferric oxide hydrosols and that of the liquid obtained from them by ultra-filtration. In this way, a value is obtained for the conductivity of the micellæ. In addition, the migration of the sols in an electrical field has been studied. The results show that the composition of the micellæ is not changed by ultra-filtration. The amount of chlorine present in the sols, which were prepared from a commercial dialysed

product, was determined gravimetrically, and the chlorine-ion electrometrically. Using the method of calculation previously described, it is shown that in a sol containing chlorine and iron in the ratio 0.0605, and containing 1.601 g. of iron in 100 c.c., a single micelle contains  $7.63 \times 10^5$  molecules of ferric oxide, whilst in a sol with the ratio  $\text{Cl} : \text{Fe} = 0.1236$  and 2.869 g. of iron in 100 c.c. the micelle contains  $3.31 \times 10^5$  molecules of ferric oxide. On dividing the number of molecules in the ionic micelle by the equivalent aggregation, the valency is found to be 10,230 and 6494 in the two cases mentioned. Assuming that the micelle is  $\text{Fe}_2\text{O}_3$  of density 5.1, the radius of the particle is 21.1 and  $16.0 \mu\mu$ , respectively. This assumption is probably unjustifiable, in that the colloidal particles may have a spongy structure in which there is a considerable amount of water.

J. F. S.

**The Formation of Anomalous Liesegang Bands.** F. G. TRYHORN and S. C. BLACKTIN (*Trans. Faraday Soc.*, 1923, **19**, 433—441).—The authors find that the slow diffusive reaction in gelatin gels between mercuric chloride and potassium iodide, and between potassium dichromate and silver nitrate results in the production of anomalous Liesegang bands in which the normal bands are accompanied by secondary bands, similar to those described by Hatschek for the reaction between lead acetate and potassium chromate or dichromate (*Proc. Roy. Soc.*, 1921, **A**, 96, 496). The substances formed in these three reactions crystallise from the respective gels more readily in the light than in the dark. This observation affords an adequate explanation of the formation of the anomalous bands, and a tentative suggestion, according to which the possibility of the formation of Liesegang bands depends on the stability of the ion-gelatin complex taking part in the reaction involved, is advanced to explain the mechanism of the process.

J. S. G. T.

**Rhythmic Formation of Precipitates. Liesegang's Rings.** C. K. JABLONCZYNSKI (*Bull. Soc. chim.*, 1923, **33**, [iv], 1592—1602).—Measurements by Morse and Pierce (*A.*, 1904, ii, 14) of the rate of formation of Liesegang's rings have been interpreted by these authors in support of Ostwald's theory. This method of interpreting the results is criticised on the ground that these can be explained by reference to the rate of diffusion of one of the reacting substances. The author's treatment of the problem leads to the relation  $(r_2^3 - r_1^3)/(t_2 - t_1) = 3kDC_0/\pi\beta$ , where  $r_1$  and  $r_2$  are the radii of two rings in order of formation,  $t_1$  and  $t_2$  the corresponding times of formation,  $D$  is the coefficient of diffusion of silver nitrate in the gelatin, and  $C_0$  its concentration,  $\beta$  being the thickness of the gelatin layer. If the last two quantities are constant the expression on the right assumes a constant value. New measurements have given results which are in agreement with the calculated values. The mechanism of the ring-formation is interpreted on the assumption that the growth of the larger particles of silver chromate is at the expense of the smaller. This view is preferred to Ostwald's theory of metastable conditions on the ground that the changes observed

are gradual at all stages. The analogy between ring-formation in precipitates and the annular structure of tree-trunks suggested by Küster is shown to be superficial only, but Liesegang's application to ring-formation in agates is valid.

H. J. E.

**Formation of Periodic Precipitates. II.** N. R. DHAR and A. C. CHATTERJI (*J. Physical Chem.*, 1924, **28**, 41—50; cf. A., 1922, ii, 627).—A continuation of the investigation of periodic precipitates. It is shown that gelatin previously mixed with dichromate has a better peptising effect on silver chromate than that which is previously mixed with silver nitrate. In the formation of lead chloride rings in silicic acid jelly by the action of lead nitrate on sodium chloride, the rings are more closely packed as the concentration of the jelly is decreased, and, other conditions being constant, the rings are less closely packed the lower the concentration of the lead nitrate. Similar results are obtained for silver chloride rings in silicic acid. Rings of silver chloride and iodide are affected by diffused light, whilst those of lead chloride and iodide are not. Tubes containing mercuric iodide rings show more rings when exposed to diffused daylight than in the dark. The theories explaining the formation of Liesegang rings put forward by Ostwald and Bradford are found to be unsatisfactory. It has been frequently observed that sols can be more or less completely adsorbed and coagulated by freshly precipitated solids. Based on the foregoing observations, a hypothesis of the formation of Liesegang rings is put forward in which a layer of coagulated material is assumed to be followed by a space free from the precipitated material. Mercuric iodide rings in gelatin and agar consist of a layer of coagulated and crystalline mercuric iodide which is red, followed by a layer of colloidal mercuric iodide which is yellow. An explanation of the formation of rings consisting of a layer of coagulated and crystalline material followed by a layer of the peptised substance has been put forward, in which the adsorption of the second product of the chemical change is the dominant factor. It is pointed out that there is the possibility of the occurrence of two distinct classes of Liesegang rings. In the one class, a layer of precipitate is followed by a zone practically free from the substance, whilst in the other class, the rings consist of a layer of coagulated sol, which in course of time may crystallise, followed by a layer of the peptised sol. The authors are of the opinion that under suitable conditions all sparingly soluble substances are capable of forming Liesegang rings.

J. F. S.

**Calorimeter for Heats of Mixing at Elevated Temperatures.** B. H. CARROLL and J. H. MATHEWS (*J. Amer. Chem. Soc.*, 1924, **46**, 30—36).—A calorimeter is described which is suitable for the measurement of the heat of mixing at temperatures up to the boiling point of the mixture concerned. This calorimeter has been employed for measuring the heat of mixing of carbon tetrachloride with ethyl acetate, benzene with ethyl alcohol, acetone with ether and chloroform, respectively, and ethyl alcohol with water. The curves obtained by plotting the heat of mixing per g.-mol. against the molar composition, deviate in all cases appreciably from a straight line. The curve



for benzene-ethyl alcohol shows a strong minimum at  $-360$  cal. at  $0.351$  mol. benzene. The curve for chloroform-acetone shows a well-defined maximum at  $400$  cal. for the mol. fraction  $0.5$ . In this case the curve is taken to indicate the formation of an equimolecular compound. The absorption of heat on dilution of ethyl alcohol with benzene may be attributed to the decrease in the association of the alcohol. The heat changes observed with the other mixtures do not afford conclusive evidence of any clearly defined molecular change. J. F. S.

**Rapid Method for the Determination of Heats of Adsorption and some Values for Hydrogen on Nickel and Copper.** R. A. BEEBE and H. S. TAYLOR (*J. Amer. Chem. Soc.*, 1924, **46**, 43—52).—A rapid method for measuring heats of adsorption of gases on metallic catalysts is described. The catalyst mass is placed in the inner tube of a vacuum vessel and an insulated platinum-iridium wire, distributed evenly throughout the mass, serves as a resistance thermometer. A wide tube carrying a Beckmann thermometer is placed in the middle of the catalyst mass, and this, with the aid of cement, closes the inner tube of the vacuum vessel. The hydrogen is admitted by a suitable tap, and the amount adsorbed measured by the method of Taylor and Burns using nitrogen as reference gas (A., 1921, ii, 630). The integral value for the heat of adsorption of hydrogen on nickel varies from  $13,500$  to  $20,500$  cal., depending on the past history of the adsorbent. Corresponding values for the same samples are in good agreement, and although the authors do not claim an accuracy greater than about  $10\%$ , yet the results generally are much closer than this. The magnitude of the heat of adsorption shows that the phenomenon is not a simple condensation. The differential values of the heat of adsorption remain nearly constant with increasing partial pressure, and this suggests that a specific adsorption effect is involved. With copper as adsorbent of hydrogen, the results are more concordant. The magnitude of the heat of adsorption is in this case  $9600$  cal. J. F. S.

**Formation of Ozone at Low Temperature and Pressures.** A. EUCKEN (*Z. physikal. Chem.*, 1923, **107**, 436—452).—When the concentration of oxygen in discharge tubes is below  $5$  millimol. per litre a very much smaller yield of ozone is obtained at high temperatures than at the temperature of liquid air. A similar variation is found when the gas is subjected to ultra-violet light of short wave-length. These observations indicate that the mean persistence of the primarily excited oxygen molecules decreases rapidly with increase of temperature. The decreased formation of ozone is accompanied by a change in the band spectrum. J. F. S.

**The Mechanism of Chemical Reaction.** A. JOB (*Bull. Soc. chim.*, 1923, **33**, [iv], 1561—1591).—A lecture delivered before the Société Chimique de France, 10th March, 1923. H. J. E.

**The Causation of Organic Reactions by Alumina, and Theories of Catalysis.** H. ADKINS and B. H. NISSEN (*J. Amer. Chem. Soc.*, 1924, **46**, 130—145; cf. A., 1922, i, 422; ii, 834).—Two series of experiments have been conducted using alumina

prepared either from hydrated alumina, aluminium hydroxide, or various aluminium alkoxides. In one series of experiments, the behaviour of esters, alcohols, etc. has been studied when passed over the various aluminas at temperatures from 350° to 490°. It is believed that the aluminas differ in the spacial relationships of the "active points" of the alumina.

In another series of experiments, the effect on the decomposition of an ester of introducing water, alcohols, heptane, ethylene, acetic acid, acetone, or other esters has been observed.

The relative stabilities or reactivities of the members of even a homologous series cannot be determined by comparing the speeds of reaction or decomposition of the members of the series, because even the relative speeds are a function of the surface at which the reaction occurs.

The formation of ketones from acids, of nitriles from amides, and of olefines from alkyl halides is not affected by modifications in the spacial configuration of the alumina catalysts. The reactions of esters and alcohols are very sensitive to such modifications.

No experimental evidence has been obtained to support the idea that the function of the catalyst is to remove one member of an equilibrium, or that the catalyst reacts with the substance catalysed to form compounds such as aluminium acetate or ethoxide. It is believed that in every case the substance catalysed unites chemically with the catalyst with a resultant rearrangement of the electrons of the substrate followed by vaporisation of the products. The nature of the rearrangement and subsequent reaction is determined primarily by energy relationships and electronic configuration, and in most cases by the spacial configuration of the catalyst.

Esters attach themselves directly to the catalyst without any preliminary rupture of the molecule, and then rearrange and react with adjacent molecules, to give various proportions of acid, ketone, olefine, alcohol, carbon dioxide, and water depending on the spacing of the atoms of the catalyst.

Alcohol and ether are equally stable towards alumina, and react by a mechanism similar to that of the esters. Acetic acid attaches itself to the surface of the catalyst, and then reacts with a second molecule impinging on it to give acetone, carbon dioxide, and water. Formic acid rearranges, as do the esters, to give either water and carbon monoxide, or carbon dioxide and hydrogen. It also gives formaldehyde and carbon dioxide by the mechanism suggested for the formation of acetone from the acetic acid. Amides must be affixed to some surface before they give nitriles and water, but the character of this surface is relatively unimportant. Alkyl halides probably give olefines and halogen acid by a similar mechanism. It appears that the rate of reaction of the two latter classes of compounds is determined by their rates of adsorption. F. A. M.

**Catalytic and Induced Reactions.** (i) **In the Presence of Salts of Cerium.** (ii) **In the Presence of Salts of Iron.** A. K. GOARD and E. K. RIDEAL (*Proc. Roy. Soc.*, (i) 1924, **A**, 105, 135—148; (ii) 1924, **A**, 105, 148—164).—(i) The theories of induced

oxidation proposed respectively by Schönbein (*Pogg. Ann.*, 1857, **100**, 1) and Bach (*Compt. rend.*, 1892, **16**, 411) are briefly referred to, and in connexion with the conditions under which an induced reaction is transformed into a continued or catalytic reaction, details are given of an experimental investigation of the action of cerous salts in effecting (1) the induced oxidation of potassium arsenite dissolved in a concentrated solution of potassium carbonate, (2) the catalytic oxidation of five reducing sugars, viz., dextrose, lactose, arabinose, galactose, and lævulose. The oxidising powers of the solutions employed were deduced from measurements of oxidation potentials, and a special type of electrode is described for measuring the potentials of substances which behave irreversibly towards the platinum electrode. In the case of the oxidation of potassium arsenite, the observed potentials arranged in the order of increasing "oxygen pressure" are: cerous salt (inductor)—arsenite (acceptor)—equilibrium mixture—perceric salt. In the case of the catalytic oxidation of the sugars the corresponding order is: reducing sugar—cerous salt—perceric salt.

(ii) Schönbein's reaction, viz., the separation of iodine from a solution of potassium iodide in the presence of hydrogen peroxide and ferrous salts, has been similarly studied from the point of view of oxidation potentials, and the results are shown to accord with the authors' views on the nature of coupled and catalytic reactions. Direct evidence has been obtained of the formation of a peroxide of iron,  $\text{Fe}_2\text{O}_5$ , by the action of hydrogen peroxide on ferrous sulphate in neutral solution, and its decomposition, which takes place in agreement with the equation for a unimolecular change, has been followed by means of potential measurements. J. S. G. T.

### **The Influence of the Support on the Activity of Catalysts.**

K. W. ROSENMUND and P. LANGER (*Ber.*, 1923, **56**, [B], 2262—2264).—In order to study the effect of varying the nature of the support on which a catalyst is deposited, a series of experiments was carried out on the rate of catalytic reduction of cinnamic acid by hydrogen with the aid of a palladium catalyst deposited on various supporting materials, in presence or absence of arsenic oxide or carbon monoxide which act as "poisons." Kieselguhr-palladium catalysts show the least activity and greatest sensitiveness to poisoning of all the catalysts examined, whilst blood-charcoal and palladium represents the most active and most resistant catalyst. In both cases the activity of the catalyst runs parallel to its resistance to poisoning, but this behaviour is not invariably observed.

The general conclusion drawn from the experiments is that the influence of a third substance on a catalyst varies according to the nature of the supporting material on which the catalyst rests. The following figures indicate the results obtained using as carriers (a) crude kieselguhr, (b) purified kieselguhr, (c) purified pumice powder, (d) barium sulphate, (e) purified bone charcoal, (f) purified blood-charcoal, respectively. (The numbers represent the average rate at which hydrogen is absorbed): I. Normal experiments: 1.90; 0.70; 2.05; 2.30; 1.25; 6.20. II. Arsenious oxide poisoning:

0.00; 0.00; 0.40; 0.23; 0.43; 4.25. III. Carbon monoxide poisoning: 0.80; 0.25; 1.65; 0.45; 1.00; 5.45. F. A. M.

**Velocity of the Hydrogen Electrode Reaction on Platinum Catalysts.** L. P. HAMMETT (*J. Amer. Chem. Soc.*, 1924, **46**, 7—19).—The polarisation of the hydrogen-hydrogen-ion reaction on platinum electrodes of a wide range of catalytic activity has been investigated. An equation has been developed on general grounds which represents the data satisfactorily for small polarisations. The results are in keeping with the hypothesis that the reaction proceeds in two stages, a rapid electrochemical reaction consisting in the discharge of hydrogen-ions to atoms, followed by a much slower combination to form molecules, and similarly for the reverse reaction. The deviations from the theoretical equation have been discussed, and certain possible causes eliminated. An empirical equation has been formulated to represent the data. The equation used by Haber and Russ (A., 1904, ii, 309) to represent their results on the polarisation of the quinone-quinol electrode has been shown to be unsatisfactory in that it is incapable of giving both positive and negative polarisations with a single equation. A more satisfactory equation is proposed, and it is suggested that the intermediate hydrogen mechanism for the quinone reduction is incorrect. J. F. S.

**Catalytic Activity.** C. O. HENKE and O. W. BROWN (*J. Physical Chem.*, 1924, **28**, 71—73).—The authors discuss Rideal's statement (A., 1920, ii, 220) that metals with low overvoltages are catalytically active, whilst metals with high overvoltages are catalytically inactive. The authors' experimental results (A., 1922, i, 586, 1196; this vol., ii, 31) show that tin and lead have high overvoltages and are excellent catalysts, whilst the well-known catalysts nickel and platinum have relatively low overvoltages. This difference indicates that there is no relationship between catalytic activity and overvoltage. In the reduction of nitrobenzene the catalysts act specifically. Their activity and even the product obtained may be varied, if only within certain limits. There seems to be a relationship between the atomic weight of a metal and its capacity to act as a catalyst in the formation of azobenzene. The behaviour of iron and antimony catalysts suggests oxidation of the metal by the nitrobenzene and subsequent reduction of the oxide by hydrogen. J. F. S.

**Photochemical Sensitisation of the [Molecular] Transformation of Maleic Esters effected by Bromine.** J. EGGERT (*Physikal. Z.*, 1923, **24**, 504—506).—The author has investigated the mechanism of the photochemical transformation of maleic acid into fumaric acid, employing for this purpose the ethyl esters of maleic acid in place of the free acid used by Wislicenus in his investigation of this phenomenon (*Ber. d. Sächs. Akad. d. Wiss.*, 1895, **47**, 491). The transformation was effected by bromine in the presence of carbon tetrachloride, and the radiation employed was of wave-length 557, 436, or 365  $\mu\mu$ . Although the amount of ester transformed was, under these conditions, proportional to the total number of quanta of radiation absorbed, the photochemical

equivalence law was not obeyed. The transformation is attributable to the activation of bromine by the absorption of radiation. The fact that the amount of substance transformed increases exponentially with the temperature, a rise of  $10^{\circ}$  doubling the amount transformed, is attributable to the circumstance that the activated bromine molecule can only transform such molecules of the ester as possess more than a certain critical amount of energy.

J. S. G. T.

**The Radiation Hypothesis of the Velocity of Chemical Reaction. II. Theory and Experiment in Gas Reactions.**

A. KISS (*Chem. Weekblad*, 1924, **21**, 26—31).—A discussion of the radiation hypothesis, giving a bibliography of recent work.

S. I. L.

**Extraction Apparatus for Liquids.** E. MURMANN (*Oesterr. Chem.-Ztg.*, 1924, **27**, 3).—An apparatus is described for use in the continuous extraction of a liquid with light solvents such as ether and benzene. The extracting liquid should be immiscible with the liquid to be extracted. The apparatus containing the latter is inserted between the flask containing the boiling solvent and a reflux apparatus, and consists of a glass cylinder into which two tubes lead, one from the flask and the other from the reflux apparatus. The tube from the reflux apparatus, down which the condensed solvent flows, dips below the liquid and reaches nearly to the bottom of the extraction apparatus. The vapour of the solvent passes up the other tube, which projects 5—8 mm. above the level of the liquid to be extracted, and reaches the condenser through a perforation at the top of the other tube. The extracting solvent after passing up through the liquid forms a layer on the top which continuously overflows back into the flask.

G. W. R.

**Geber (Jabir ibn Hayyan).** ANON. (*Chemistry and Industry*, 1924, **43**, 87).—A summary of views expressed by Ruska (*Arch. Gesch. Med.*, 1923, **15**) in general agreement with those of Holmyard (*Proc. Roy. Soc. Med.*, 1923, **16**, 46). It is definitely held that Geber is Jabir ibn Hayyan, the great Muslim chemist of the eighth century, and that although the Latin works ascribed to Geber may not be authentic, they represent for the most part the state of Arabic chemistry at the time they were written. (Cf. A., 1923, ii, 148, 314, 628, 683.)

A. A. E.

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### Mineralogical Chemistry.

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**The Analysis of the Interior of the Earth.** G. TAMMANN (*Z. anorg. Chem.*, 1924, **131**, 96—100).—From our knowledge of the composition of the earth's crust, and assuming that the composition of the outer silicate layer has not changed greatly during solidification, it is possible to draw conclusions with regard to the composition of the middle sulphide layer, *d* 5·6, and of the metallic

core, *d* 9.6. Since the three layers must have been in equilibrium in the liquid state, it is possible to apply the proposition that the division of metals between a fluid silicate layer and a liquid metal layer occurs in such a way that the less noble, more electropositive metals dissolve in the silicate, the more noble in the metallic layer. The order of metals from least to most noble (most to least electropositive) is the order of the heats of formation of their chlorides; when the metals are so arranged, and against each is placed the percentage extent to which it occurs in the earth's crust, it is obvious that of the metals more positive (less noble) than iron, only traces can occur in the earth's metallic core, whilst the metals more noble than iron may occur to a much greater extent in the core than in the crust.

Nickel is the next most common metal to iron in the crust, but being more positive must occur in relatively greater proportion in the core; the composition of meteorites (90% Fe; 10% Ni) may thus correspond approximately with the composition of the earth's core, for the proportion of noble metals (lead, bismuth, silver, mercury, gold, platinum, etc.) in the crust is so small that if it were a thousand times greater in the core, it would still be below 1% of the core.

The density of the middle sulphide layer may correspond with a mixture, Fe 20%, FeS 70%, FeO and silicate 10%, which has *d* 5.2 at 20° and 1 atm. The small sulphur content of eruptive rocks may be due to the presence of phosphorus, silicon, etc. in the middle layer, which would reduce the sulphur content of the silicate layer (slag).

S. I. L.

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### Inorganic Chemistry.

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**Attempted Separation of the Isotopes of Chlorine by Adsorption on Charcoal.** J. SAMESHIMA, K. AIHARA, and T. SHIRAI (*J. Chem. Soc. Japan*, 1922, **43**, 761—766).—Dry hydrogen chloride is passed into a tube filled with bamboo charcoal (*A*). When the gas is absorbed by *A*, the tube is heated at 110° and the evolved gas is absorbed in a second tube filled with the same charcoal (*B*). *A* is heated further and the gas evolved between 150° and 220° is absorbed in a third tube (*H*). The same process is repeated until *B* is saturated, then *B* is heated and the gas evolved below 110° is absorbed in a fourth tube, then to the fifth tube (*D*). The gas evolved between 150° and 220° from *H* is absorbed in a seventh tube (*L*) through the sixth tube. The gases in *D* and *L* are then transferred to two tubes containing sodium hydroxide solution at room temperature and converted into sodium chloride. The atomic weight of the chlorine in the two samples of sodium chloride (*D* and *L*) and in ordinary sodium chloride was determined by a modification of Richards' method (*Carnegie Inst. Washington Publ.*, No. 28, etc.) the results being 35.4612, 35.4588, and 35.4608 respectively.

K. K.

**Isotopes of Chlorine.** W. D. HARKINS and T. H. LIGGETT.—(See ii, 142.)



**Solubility of Iodine in Chloroform.** L. GRIMBERT, M. MALMY, and G. POIROT (*J. Pharm. Chim.*, 1924, **29**, 5—9).—The weight of pure iodine dissolved by 100 g. of pure chloroform is 1.314 g. at 0°, 1.483 g. at 5°, 1.805 g. at 10°, 2.176 g. at 15°, 2.630 g. at 20°, and 3.200 g. at 25°. Traces of alcohol contained in the anæsthetic have no appreciable influence on the solubility of iodine, whilst the impurities present in commercial rectified chloroform tend to increase it slightly. W. T. K. B.

**Kinetics of the Formation of Iodine from Iodide and Periodate.** E. ABEL and A. FÜRTH (*Z. physikal. Chem.*, 1923, **107**, 313—328).—The kinetics of the reduction of potassium periodate by potassium iodide in an acetic acid-sodium acetate solution have been investigated at 25°. The reaction, which may be represented,  $\text{IO}_4' + 2\text{I}' + 2\text{H}' = \text{IO}_3' + \text{I}_2 + \text{H}_2\text{O}$ , follows the laws of bimolecular reactions, namely,  $-d[\text{IO}_4']/dt = -0.5d[\text{I}']/dt = d[\text{I}_2]/dt = k[\text{IO}_4'] \cdot [\text{I}']$ . The concentrations of the various substances were varied in the following proportions in different experiments: periodate 4 : 1, iodide, 20 : 1, acetate, 480 : 1, acetic acid, 3000 : 1. It is shown that with a low concentration of acetate (0.1*N*) the value of *k* is independent of the acetic acid (*H'*) concentration, but it depends on the concentration of the acetate itself, in the sense that with increasing acetate concentration the value increases. The value of the constant for the unrealisable acetate-free solution is about 380 and for 0.1*N*-acetate about 545 (time in minutes and concentrations in mols. per litre). With higher concentrations of acetate a dependence on the acetic acid concentration is found and this is the more noticeable the more concentrated is the acetate. This dependence is of such a kind that the constant, *k*, with increasing acetic acid concentration at first increases and then decreases, that is, it passes through a maximum. In the range of concentrations examined the value of *k* varies between 239 and 1024, and for the concentrations, acetic acid 0.1*N*, acetate 0.4*N*, it has the value 707. The mechanism of the reaction  $\text{IO}_4' + \text{I}'$  on the basis of the above results, is shown to be  $\text{IO}_4' + \text{I}' = \text{IO}_3' + \text{IO}'$  (determined by time) followed by  $\text{IO}' + \text{I}' + 2\text{H}' = \text{I}_2 + \text{H}_2\text{O}$ . J. F. S.

**The Systematic Doctrine of Affinity. XXV. The Behaviour of certain Halides with respect to Halogen.** W. BILTZ and E. MEINECKE (*Z. anorg. Chem.*, 1923, **131**, i, 1—21).—The action of liquid halogen on some halides of elements of the fourth and fifth groups has been examined, to see whether complex compounds are formed when the halide and halogen are completely miscible. The general conclusion is drawn that no chemical action takes place. Freezing-point diagrams have been constructed on the basis of thermal analysis (cooling curves), supplemented in some cases by vapour-pressure determinations.

Lead dichloride, cerium trichloride, zirconium tetrachloride, and thorium tetrachloride are all insoluble in liquid chlorine, whilst tungsten hexachloride is very slightly soluble. Arsenic trichloride and the tetrachlorides of silicon, titanium, and tin are all completely miscible with liquid chlorine, forming simple eutectic systems with

no evidence of the formation of any compound. Carbon tetrachloride is completely miscible with liquid chlorine, and the equilibrium data suggest that a compound may be formed. It is possible, however, that the observed results may be due to the transformation of carbon tetrachloride, which is found to exist in two forms with a transition temperature at  $-44^{\circ}$ . The system carbon tetrabromide-bromine is similar to that of carbon tetrachloride-chlorine. Lead tetrachloride is completely miscible with liquid chlorine, and a method is described for its preparation by means of a new substance—*lead pyridine hexachloride*. W. H.-R.

**The Formation of Periodate by the Action of Permanganate on Various Iodine Compounds.** R. LANG (*Z. anorg. Chem.*, 1923, **130**, 141—150).—Excess of potassium permanganate in the cold, in presence of 5*N*-sulphuric acid, converts iodic acid quantitatively into periodic acid. The excess of permanganate is destroyed by addition of nitrite, and the latter by carbamide, after which the periodic acid formed may be determined by reduction with hydriodic acid and titration of the liberated iodine. The results are about 1% too low, since the nitrite effects slight reduction of the periodate, as does also oxalic acid under these conditions, although it does not reduce periodic acid alone even at the boiling-point. The oxidation of iodates by permanganates is influenced by hydrogen-ion and chlorine-ion concentrations; the latter inhibits the oxidation at normal concentrations ( $N/1\text{-Cl}$ ), and renders it incomplete at lower concentrations. Hydriodic acid is also oxidised to periodic acid by sufficient excess of permanganate. Iodine monochloride is incompletely oxidised; the chlorine-ions formed prevent complete oxidation of the iodic acid. Iodine cyanide is also oxidised to periodic acid, although the reaction is not quite complete.

The permanganate in these reactions is reduced only to the manganic stage, as is to be expected from the normal potentials, and from the observation that periodic acid will oxidise manganous salts. If, however, the solutions be very strongly acid, periodic acid is not reduced by manganous salts, although, on the other hand, it is not oxidised by manganic salts; the effect of hydrogen-ion concentration on the potentials involved is discussed. At the boiling point the oxidation is completely reversed, manganese salts in boiling, strongly acid solutions being oxidised by periodic acid to permanganate; this observed result is contrary to the result to be expected from the reaction constants at low and high temperatures calculated from the potentials and the heats of formation. An explanation of this discrepancy is suggested in the formation of ozone in hot solutions of periodic acid, which might be accelerated by the presence of an acceptor such as a manganese salt. S. I. L.

**Kinetics of the Reduction of Periodate by Arsenious Acid.** E. ABEL and A. FÜRTH (*Z. physikal. Chem.*, 1923, **107**, 305—312).—The reduction of potassium periodate by arsenious acid in the presence of acetic acid has been investigated at  $25^{\circ}$ . It is shown that the reduction takes place according to the equation

$-d[\text{IO}_4']]/dt = -d(\text{AsO}_2')/dt = 5.5[\text{IO}_4'](\text{AsO}_2')$ , where  $[\text{IO}_4']$  is the periodate-ion concentration,  $(\text{AsO}_2')$  the analytically determined total concentration of arsenious acid in mols per litre, and  $t$  the time in minutes. The velocity is independent of the concentration of hydrogen-ions. The initial concentrations in the various experiments were varied in the proportions of 4.5 : 1 for the periodate, 5 : 1 for the arsenious acid, and 4000 : 1 for the hydrogen-ion concentration.

J. F. S.

**The Early History of Hydrofluoric Acid.** J. R. PARTINGTON (*Mem. Manchester Lit. and Phil. Soc.*, 1922—3, 67, 73—87).

**Transference Numbers and Ionic Complexity of Hydrofluoric Acid Solutions.** C. W. DAVIES and L. J. HUDLESTON (*J. Chem. Soc.*, 1924, 125, 260—268).—Transference measurements were made at 25° for hydrofluoric acid solutions varying from 0.016 to 2.3*N*. The transport number of the anion increases uniformly from 0.13 in the most dilute to 0.338 in the most concentrated solutions, thereby indicating the formation of a complex ion. The results thus obtained were combined with the conductivity values obtained by Deussen (A., 1905, ii, 311) and the mobilities of the hydrogen-ion and fluoride-ion by Kohlrausch. For solutions of great dilution the equilibrium constant for  $\text{HF} = \text{H}' + \text{F}'$  has a value  $K = 7.4 \times 10^{-4}$ , whilst for the reaction  $\text{HF}_2' = \text{F}' + \text{HF}$  the equilibrium constant  $K_2 = 4.7$ , which increases slightly with dilution. The mobility of the hydrofluoride-ion has an approximate value of 75. The concentrations of these three ions ( $\text{H}'$ ,  $\text{F}'$ , and  $\text{HF}_2'$ ) in solutions over the range 0.03—2*N* were also determined. J. B. F.

**Formation of Ozone at Low Temperatures and Pressures.** A. EUCKEN.—(See ii, 159.)

**Disulphur Difluoride.** M. CENTNERSZWER and C. STRENG (*Ber.*, 1923, 56, [B], 2249—2253).—When a mixture of well-dried silver fluoride (1 g.) and sulphur (4 g.) is heated in a vacuum, a gas (about 100 c.c.) is evolved which does not condense at the ordinary temperature, and is believed to be disulphur difluoride,  $\text{S}_2\text{F}_2$ . The surface of the mercury becomes blackened owing to the formation of mercuric sulphide. On exposure to the atmosphere, sulphur is deposited from the gas.

The molecular weight of the gas calculated from the density was found to be about 97.33 (mean of two experiments), and on analysis by absorption in a solution of potassium hydroxide and hydrogen peroxide, the following figures were obtained: S, 64.04%, F, 35.17%. It is assumed that the discrepancies were due to the presence of a little sulphur dioxide, as the gas has not yet been obtained quite pure; it is also formed on heating mercurous fluoride with sulphur. The gas is colourless and has an odour similar to, but even more objectionable than, that of disulphur dichloride. It is at once decomposed by moisture with deposition of sulphur. F. A. M.

**The Systematic Doctrine of Affinity. XXIV. The Power of Crystallised Salts to Combine with Ammonia.** W. BILTZ (*Z. anorg. Chem.*, 1923, 130, 93—139).—The results obtained in

the twenty-three previous investigations are examined and compared in the present paper. An exhaustive table has been drawn up showing for the ammoniates obtained by direct combination of ammonia with the crystalline halides of the alkali and alkaline-earth metals, magnesium, zinc, tin, lead, copper, silver, thallium, manganese, iron, cobalt, and nickel: (1) the decomposition temperatures at 100 mm. pressure, (2) the heat of formation per mol. of ammonia from the next lower compound, (3) the total heat of formation from the ammonia-free salt, per mol. of ammonia, and (4) the affinity at  $300^{\circ}$ , *i.e.*, the work produced when 1 mol. of ammonia at that temperature and normal pressure combines with the pure salt to form the respective ammoniate. Curves showing the dissociation pressures at various temperatures are also given. From the tables and curves for the 167 ammoniates considered, it appears that apart from 34 monoammoniates, the commonest compounds have the Werner co-ordination numbers, 2, 4, 6, and 8. By plotting the total heats of formation against the co-ordination numbers, the valency isobars are obtained, the inclination of which is a measure of the decomposition temperature, and therefore of the stability; compounds with a small ammonia-affinity form one or few ammoniates, although where one only is formed it may have a high ammonia content, as in barium octamminechloride. As a general rule, the heat of formation (2) becomes smaller as the saturation with successive molecular increments of ammonia increases. The decomposition interval, *i.e.*, the region enclosed by the dissociation curves of the highest and lowest ammoniates, also brings out the relations between the various groups.

The constitutions of the ammoniates formed from solid salts are by no means simple, and they fall into various classes, *e.g.*, those in which the anion is included in the complex, the molecular ammoniates; the normal kationammoniates; the double-shell ammoniates, mixed compounds, etc. It is impossible to deduce laws of complete application, although general rules may apply for various groups.

The ability to form ammoniates is also considered with regard to the general physical and chemical properties of the salts. The molecular volumes of the halides of the metals considered obey fairly generally the linear relationship; the atomic volumes of barium and strontium have been redetermined, and are given as 39 and 33, respectively. Silver, thallium, zinc, lead, and univalent copper do not obey the linear rule. The atomic volumes of the halogens deduced by applying Kopp's law agree fairly well amongst themselves, and with the values at absolute zero calculated by Herz (A., 1919, ii, 220). With the group II metals, and tin and lead, the values indicate a contraction on combination; with manganese, zinc, copper, and thallium there is an expansion. When the molecular volumes are compared with the heats of formation of the halogen salts, it appears that the iodides and bromides, which have the lowest heats of formation, occupy the greatest space; with the alkali and alkaline-earth halides, the heat of formation is greater as the contraction is greater, but in other groups this is reversed.

The melting points show no general regularity, and only rules of limited application can be applied to the solubility. The space lattice measurements are of great interest, the closeness of the atoms in the copper and silver halides explaining their anomalous solubilities, melting points, etc.

Applying these tabulated data for physical properties of the halides to the collected data for their ammoniates, the following conclusions are drawn : (1) In the group of the alkali and alkaline-earth metals and magnesium, the affinities in the formation of the higher ammoniates are smaller the greater are the weight, atomic volume, and electrolytic potential of the metal-ion, the more strongly negative and the smaller is the anion, and the greater the heat of formation and volume contraction in formation of the salt. (2) The iron group obeys the same rules, but the effects of the weight of the kation and volume contraction are reversed. (3) The copper, zinc, and lead compounds obey the same rules in some cases, but in others inverse rules. (4) High melting point and low solubility of the ammonia-free salt influence the stability of the ammoniates.

Examination of the lattice structure of the ammoniates by X-ray spectrum methods shows that for the hexammine-compounds of the halides of the iron metals, manganese, and zinc, the ammonia molecules are very closely packed, there being practically no free space in the metal-hexammine complex; the spaces occupied by the halogen atoms are in agreement with those observed for normal polar binary compounds. The formation of the ammonia compound is in these cases accompanied by a separation of the metal from the halogen-ion, involving mechanical work,  $E$ , which may be calculated. The total heat of formation of the ammoniate involves this value,  $E$ , and the energy concerned in the association of the ammonia molecules with the kation; where  $E$  is small, *i.e.*, where the kation and anion are already somewhat separated, as in the iodides, the ammoniate will be more stable for the same kation. The differences in affinity in the formation of the ammoniates are therefore bound up with space considerations; the instability of the ammoniates of the alkali metals, for example, depends not so much on the low energy involved in association of the kation with ammonia molecules as on the high value of  $E$ .  
S. I. L.

**Catalytic Oxidation of Ammonia by Air in Contact with pure Palladium.** E. DECARRIÈRE (*Bull. Soc. chim.*, 1924, [iv], 35, 48—58; cf. A., 1923, ii, 631).—The catalytic oxidation of ammonia by air, in contact with pure palladium, has been studied in a manner similar to that used in the case of platinum (A., 1919, ii, 463). The palladium is a more effective catalyst as foil than as wire, wire in turn being more effective than sponge. As with platinum, oxidation attains a maximum for a certain temperature range and an ammonia concentration range, the temperature being the more important factor. Palladium is more efficient than platinum with high concentrations of ammonia, 90% oxidation being obtained with concentrations up to 11%. With platinum foil, oxidation is as efficient at 450° as with palladium foil at 650—

700°. Maximum oxidation (92%) occurs, in the case of palladium, at 740–780° and, in that of platinum, at 630° (95%). Increase in the curvature of the surface of the palladium catalyst gives an optimum oxidation temperature of 760°, the effect of surface thus being much less than in the case of platinum. When used as a catalyst as above, palladium disintegrates and loses its activity as a result.

E. E. T.

### Measurements of the Vapour Pressures of Nitric Oxide.

F. A. HENGLEIN and H. KRÜGER (*Z. anorg. Chem.*, 1923, **130**, 181–187).—Pure nitric oxide was obtained by the action of nitrosylsulphuric acid on mercury, and after several distillations the solid was pure white, the liquid having a faint blue colour. The temperature control for pressures of 30 to 800 mm. of mercury was solid mercury, which when preserved in a vacuum rose in temperature 0.05–0.10° per minute; for pressures from 0.01 to 3.0 mm. the manometer arm was immersed in a liquid air bath. Temperatures were measured by an oxygen vapour-pressure thermometer. The results were plotted and are expressed for solid nitric oxide by the formula  $\log p = -867.4/T + 10.1466$ , and for the liquid by  $\log p = -681.1/T + 8.4440$ ,  $p$  being measured in millimetres of mercury and  $T$  on the absolute scale; the m. p. is 109.4° Abs. at a pressure of 165.7 mm., from which and the critical pressure (64 atm.) the heats of sublimation and vaporisation at the melting point are calculated as 3980 and 3080 cal., respectively; the latent heat of fusion is therefore 900 cal. The b. p. at 1 atm. is 122.4° Abs., at which temperature the latent heat of vaporisation is 3024 cal., so that Trouton's coefficient,  $\lambda/T$ , is 24.7, a high value indicating association in the liquid state. The Clausius-Clapeyron function  $\delta p/p \cdot \delta T$  is relatively great; the substance therefore shows a very great change of vapour pressure for a relatively small change of temperature, and is especially suitable for temperature measurements over the range –164° to –145°; at –150°, a change of 1° corresponds with a change of 90 mm. pressure.

S. I. L.

### Catalysis in Homogeneous Gas Reactions. II. Catalysis of Nitrosyl Chloride Formation by Nitrogen Peroxide.

A. KISS (*Rec. trav. chim.*, 1924, **43**, 68–79; cf. A., 1923, ii, 237).—The interaction of nitric oxide and chlorine is not appreciably accelerated by small concentrations (1–2%) of nitrogen peroxide, but the acceleration is considerable with about 10% of that compound. Measurements were made of the reaction velocity with varying concentrations of nitrogen peroxide at 18° in the manner previously described (*loc. cit.*). There is no doubt that the reaction is truly catalytic, with intermediate formation of the compound  $\text{NO}_2\text{Cl}$ , thus:  $2\text{NO}_2 + \text{Cl}_2 = 2\text{NO}_2\text{Cl}$ ;  $2\text{NO}_2\text{Cl} + 2\text{NO} = 2\text{NOCl} + 2\text{NO}_2$ . The former reaction is rapid; the latter is slower, and is a true gas reaction of the second order. The reactions involved are independent of the surface of the reaction vessel and are not influenced by light.

E. H. R.

**The Metaphosphates.** P. PASCAL (*Bull. Soc. chim.*, 1923, [iv], 33, 1611—1627).—A republication in fuller detail of work previously described (A., 1923, ii, 489, 563). H. J. E.

**"Insoluble" Alkali Metaphosphates.** P. PASCAL (*Compt. rend.*, 1924, 178, 211—213).—The decomposition, by heat, of sodium dihydrogen phosphate, or of sodium ammonium hydrogen phosphate, affords the acid pyrophosphate,  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ , some metaphosphate also resulting if the temperature is allowed to rise too rapidly. With control of heating, definite products are always obtainable. At  $250^\circ$ , the acid pyrophosphate first formed begins to pass into an insoluble metaphosphate, this change being complete in an hour at  $355^\circ$ . The metaphosphate is stable up to about  $477^\circ$ , passing into trimetaphosphate, apparently irreversibly, at higher temperatures. At  $510^\circ$ , 97% of metaphosphate passes into trimetaphosphate in an hour. As shown previously (this vol., ii, 39) hexametaphosphate is formed at still higher temperatures. The metaphosphate is scarcely affected by boiling water or by saline solutions.

A second metaphosphate is formed on heating sodium methyl (or ethyl) phosphate to redness, the friable product being washed with water to remove trimetaphosphate. Crystals so obtained are used to inoculate metaphosphate prepared as follows: hexametaphosphate is superfused at  $550^\circ$ , inoculated with the above crystals, and cautiously heated to aid crystallisation. In this way, a completely crystalline, insoluble metaphosphate is obtained (m. p.  $809\text{--}811^\circ$ ). It is only affected by heat if it contains tri- or hexa-metaphosphate, when fusion affords a soluble salt. The metaphosphate dissolves in water, in presence of traces of soluble pyro- or meta-phosphates to give the viscous, colloidal liquids described previously (*loc. cit.*). The elasticity observed with hexa-, penta-, and deca-metaphosphates by various authors is due to the presence, in these salts, of the metaphosphate. The latter appears to be closely related to the hexametaphosphates, since in the solid or liquid states it gives the same complexes as the latter with iron and uranyl salts, with simultaneous loss of viscosity.

E. E. T.

**The Dissociation Constant of Boric Acid.** E. B. R. PRIDEAUX and A. T. WARD (*J. Chem. Soc.*, 1924, 125, 69—71).—The apparent dissociation constant of boric acid (uncorrected for incomplete ionisation) is calculated from the hydrogen-ion concentrations given in the literature, supplemented with determinations in the more dilute solutions. The constant varies for borax solutions from  $5 \times 10^{-10}$  up to nearly  $1 \times 10^{-9}$  in 0.25*M*- and 0.02*M*-solutions, respectively. The constant diminishes with increase of the degree of neutralisation. Thus for 0.05*M*-solutions 12% and 64% neutralised the constants are  $8.4 \times 10^{-10}$  and  $7.1 \times 10^{-10}$ , respectively. Substituting ionic activities for ionic concentrations, a limiting true dissociation constant should be obtained which for dilute borate solutions is found to be nearly independent of the

degree of neutralisation and has a value  $5 \times 10^{-10}$ , which agrees closely with the apparent constant in 0.2*M* and 0.25*M* solutions.

J. B. F.

**The Nature of Graphite and Amorphous Carbon.** G. ASAHARA (*Sci. Papers Inst. Phys. Chem. Research*, 1922, **1**, 23—29, and *Japan. J. Chem.*, 1922, **1**, 35—41).—The author has established the essential identity of graphite and amorphous carbon by the X-ray analysis of thirty-four different forms of carbon from different sources. The material was ground to a fine powder, compressed to a layer of about 1 mm. thickness, and fixed in front of a small window of a wooden box containing a photographic plate. The interference figure of the material was recorded on the plate as concentric rings, the plate cutting the mantles of cones of the diffracted rays. Six of the cameras, in which the wooden box was placed, were arranged conically, with the vertex in the source of the X-rays, facing the X-rays bulb in a shielded box. The interference figures thus obtained constitute a continuous series, gradually altering from those with six comparatively sharp concentric rings of intensity maxima (Type I) to those with an indistinct halo of distributed intensity (Type III), those where the intensity maxima are not sharply defined but broadened to ill-defined bands (Type II) lying between the two extremes. Certain forms of graphite, such as Ceylon and Korean graphites, etc., gave figures with radial streaks (Type IV), the intensity maxima being common to graphites appearing intact. The streaks are to be attributed to the fact that these graphites are only ground along their flat cleavage faces, and the incident rays fall chiefly and almost perpendicularly on these cleavage faces. The angles corresponding with the six concentric rings, which the diffracted rays make with the incident rays, are approximately 14°, 18° 50', 22° 20', 25° 40', 31°, and 36° 30', respectively.

The natural and artificial graphites, however finely they may be powdered, have a crystalline structure, as they plainly show sharply defined interference rings. Amorphous carbons also gave interference figures, but no distinct maxima were observed owing to the distributed intensity. The estimated maxima are, however, invariably at about 14° and 23°. Carbons produced by the decomposition of certain gases or vapours, such as carbon monoxide, acetylene, or carbon disulphide, or iron carbide and coal, gave no indication of definite crystalline form, but they gave definite interference figures which establish their crystalline nature. The word "amorphous" must therefore be replaced by "very minutely crystalline" (cf. Debye and Scherrer, A., 1917, ii, 437). K. K.

**The Adsorption of Air by Charcoals at Low Temperatures.** K. HAYASHI (*J. Chem. Soc. Japan*, 1922, **43**, 535—544).—The volume of air absorbed at 1 atm. pressure, at -185°, -79°, 0°, and the ordinary temperature, by charcoal from twenty-two different sources, and by silicic acid gel, was measured. The results, together with apparent densities, are tabulated in the original.

K. K.



**The Decomposition of Carbon Monoxide.** G. FESTER and G. BRUDE (*Ber.*, 1923, **56**, [B], 2245—2249).—By the use of a catalytic mass consisting of palladium deposited either on activated charcoal or on activated silicic acid, the authors have shown that the decomposition  $2\text{CO}=\text{C}+\text{CO}_2$  occurs at quite moderate temperatures, either with a mixture of equal volumes of hydrogen and carbon monoxide or with the pure monoxide alone. Using palladium and charcoal and passing a mixture of hydrogen and carbon monoxide over it at  $100^\circ$ , up to 16.1% of carbon dioxide was obtained; using pure carbon monoxide, 1% of carbon dioxide was obtained at  $65^\circ$  and 11% at  $110^\circ$ ; by allowing the monoxide to remain in contact with the catalyst for sixteen hours, the percentage of dioxide obtained was: at  $35^\circ$ , 0.6%;  $100^\circ$ , 12.0%;  $240^\circ$ , 55%. With palladium deposited on activated silica and dried at  $60^\circ$ , the following amounts of carbon dioxide were obtained (using pure carbon monoxide): at  $35^\circ$ , 0.7%;  $65^\circ$ , 3.6%;  $100^\circ$ , 14.6% and 8.8%. In all cases, however, a few per cent. of hydrogen were obtained, due to adsorbed moisture in the silica.

The authors contradict the statement of Orlov (A., 1909, i, 77) that a mixture of hydrogen and carbon monoxide when passed over a nickel-palladium catalyst yields up to 8.3% of ethylene; they regard the reactions obtained as being probably due to small amounts of saturated hydrocarbons together with nickel carbonyl.

F. A. M.

**Gases extractable from Heated Steels, and Reducibility of the Oxides of Carbon.** N. PARRAVANO and C. R. DEL TURCO (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 373—376).—As a general rule, de-oxidation of steel is found to result in diminution of the proportion of carbon monoxide extractable from the hot metal in the usual way. Further, the deoxidising agents commonly used in the steel industry are able to reduce both carbon monoxide and dioxide at high temperatures. [Cf. B., 1924, 176.] T. H. P.

**The Influence of Catalysts on the Production of Potassium Perchlorate by the Action of Heat on Potassium Chlorate.** W. FARMER and J. B. FIRTH (*J. Chem. Soc.*, 1924, **125**, 82—87).—Potassium chlorate, with which 15% of catalyst is intimately mixed, was heated in glass, unglazed porcelain, and quartz tubes, respectively. For temperatures between  $480^\circ$  and  $550^\circ$ , the results were similar, the period of heating being determined by the temperature of the experiment. The yield of potassium perchlorate is not increased by the addition of silver oxide, the whole of the silver oxide being decomposed before any appreciable amount of perchlorate is formed. The addition of cerium and thorium oxides results in almost complete decomposition of the chlorate into chloride and oxygen, whilst zirconium oxide and glass considerably reduce the yield of perchlorate, but increase the yield of chloride and oxygen. Aluminium silicate and potassium dichromate considerably reduce the percentage of chlorate decomposed. The yield of perchlorate is influenced by the nature of the reaction vessel, being greatest for quartz vessels. A mixture of potassium chlorate with 15%

of powdered quartz heated in a quartz tube at  $500^{\circ}$  for seventy five minutes resulted in the conversion of 59.3% of chlorate into perchlorate, 3% of the chlorate being unchanged. J. B. F.

**Revision of the Atomic Weight of Sodium.** E. MOLES and J. M. CLAVERA (*Z. physikal. Chem.*, 1923, **107**, 423—435).—The authors have converted sodium azide into sodium nitrate, and as the result of eight experiments the ratio  $\text{NaNO}_3 : \text{NaN}_3$  is found to have a value which lies between the extreme values 1.30731 and 1.30738. From this the atomic weight of sodium is calculated to  $22.998 \pm 0.002$  on the basis that nitrogen has the atomic weight 14.008. The present value is in full agreement with the value found by Richards and Wells (A., 1905, ii, 450) and all other modern determinations. The ratio  $\text{NaNO}_3 : \text{NaN}_3$  confirms the value 14.008 accepted for the atomic weight of nitrogen. The present work confirms once more the statement that the atomic weights of carbon (12.005) and sulphur (32.060) derived on the basis  $\text{Na} = 22.995$  by Richards and Hoover and adopted by the International Atomic Weight Commission since 1916, are incorrect. The values  $\text{C} = 12.000$ ,  $\text{S} = 32.070$  are to be preferred. J. F. S.

**Heat of Formation of Sodium Silicate.** C. MATIGNON (*Bull. Soc. chim.*, 1924, [iv], **35**, 29—31).—The heat of formation of sodium silicate has been determined from the interaction of sodium silicate and dilute hydrochloric acid, the following equation being obtained :  $\text{Na}_2\text{SiO}_3$  (solid) +  $2\text{HCl}$  (dissolved) =  $\text{SiO}_2$ , aq. (precipitate) +  $2\text{NaCl}$  +  $\text{H}_2\text{O}$  + 32.8 cal., whence  $\text{SiO}_2$ , aq. (precipitate) +  $\text{Na}_2\text{O} = \text{Na}_2\text{SiO}_3$  + 51.1 cal.;  $\text{SiO}_2$ , aq. (precipitate) +  $\text{Na}_2\text{CO}_3 = \text{Na}_2\text{SiO}_3$  +  $\text{CO}_2$  - 24.7 cal.; and  $\text{Si}$  (crystalline) +  $3\text{O}$  +  $2\text{Na} = \text{Na}_2\text{SiO}_3$  + 331.4 cal. (Cf. Mulert, A., 1912, ii, 626.) E. E. T.

**A Confirmation of Faraday's Law for Lithium Hydride.** K. PETERS (*Z. anorg. Chem.*, 1924, **131**, 140—172).—The work of Moers (A., 1921, ii, 200) which showed that on electrolysis of lithium hydride hydrogen is evolved at the anode, has been repeated and extended quantitatively, the results being in agreement with Faraday's law. The m. p. of the hydride was found to be  $697^{\circ}$ ; it diffused readily through the walls, 3 mm. thick, of the steel tube used for the cell, and mechanical difficulties were experienced from the great adhesive power of the molten hydride, from attack of the iron vessel, and from dissociation at the high temperature. Finally, it was found that the solid crystalline hydrate can be electrolysed at temperatures much below the melting point, and measurements of pressure increases due to hydrogen evolved at  $558^{\circ}$  with a current of 2 ampères at 10 v., after allowance for the volume formed by dissociation, showed that Faraday's law is obeyed for a short time, although the evolution rapidly fell off for a number of reasons. By an ingenious arrangement, in which the hydrogen evolved was allowed to escape into a relatively large space, the pressure in which gave by reference to curves previously constructed the volumes of gas, it was possible to obtain truly quantitative results at temperatures of  $630$ — $675^{\circ}$ , the average of

many experiments giving a yield on the current of 99.5%, and many giving the exact figures demanded by theory.

Metallic lithium free from hydride could not be obtained from the cathode, but analyses of the mixtures of hydride and metal obtained from the cathode rod showed percentages of lithium varying from 55% to 74%.

The acidic character of hydrogen in lithium hydride is thus proved, confirming the work of Moers (*loc. cit.*) and the results of the X-ray spectrum examination by Bijvoet and Karssen (A., 1922, ii, 499, 569; 1923, ii, 857).

In the course of the work, it was observed that, after remaining for a few minutes in contact with iron, molten lithium very rapidly penetrates it; hence the dissociation of the hydride at high temperatures in iron vessels is greatly increased by removal of the lithium set free, a phenomenon attributed by Ephraim and Michel (A., 1922, ii, 58) to the supposed reaction  $\text{LiH} + \text{Fe} = \text{LiFe} + \text{H}$ . After remaining for some time in contact with iron, melted lithium or its hydride completely removes carbon, sulphur, silicon, phosphorus, etc. from the iron, which accounts for the difficulties encountered by earlier workers, who observed abnormal evolution of hydrogen from the hydride heated in steel tubes. From observations carried out with knowledge of these facts, it is clear that the dissociation pressures observed are abnormal, being influenced by the solubility of lithium in its melted hydride. S. I. L.

**Lithium Perborate.** (MLLE.) R. BEZNER LÖWY (*Bul. Soc. Chim. România*, 1923, 5, 81—82).—Lithium perborate has been prepared both by the hydrogen peroxide and the electrolytic methods. In the former, lithium metaborate,  $\text{LiBO}_2 \cdot 8\text{H}_2\text{O}$  (prepared by fusing lithium carbonate with boric acid, and dissolving the mass in boric acid solution), is treated in aqueous solution with an excess of hydrogen peroxide at 0°; absolute alcohol is then added to the solution. Evaporation in a vacuum at 40° yields the perborate as a white, amorphous powder. In the electrolytic method, the electrolyte is a solution of 4.5 g. of lithium metaborate and 13.5 g. of potassium carbonate in 100 c.c. of water, the anode a platinum spiral, and the cathode a tube of tin through which water at 15° is circulated. A current density of 2 amps./cm.<sup>2</sup> at 6 v. is employed. The maximum yield is obtained after one and a half hours. Analysis shows the perborate to possess the formula  $\text{Li}_2\text{B}_2\text{O}_5 \cdot 2.5\text{H}_2\text{O}$ . It is stable at the ordinary temperatures, but decomposes above 50°. It is soluble to the extent of 10–13 g. in 100 c.c. of water at the ordinary temperature. J. W. B.

**The Differences between Mixed Crystals obtained from Melted Salts and from Solutions.** G. TAMMANN and W. KRINGS (*Z. anorg. Chem.*, 1923, 130, 229—245).—The study of the differences in properties of mixed crystals according to whether they are obtained from mixtures of the pure salts in the melted state or from solutions (Tammann, A., 1919, ii, 398) has now been extended to the investigation of the heats of solution. The methods of obtaining and analysing the mixed crystals and the

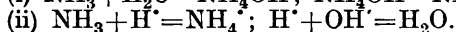
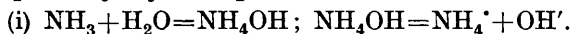
calorimeter devised for the measurements are described, mixtures of potassium chloride and bromide, potassium and rubidium chlorides, and barium and lead nitrates being employed. By interpolation of the results to allow of comparison of mixtures of the same compositions, the following conclusions are drawn: (1) Mixed crystals obtained from the melted salts (melt crystals) have appreciably lower heats of solution than those of the same composition from solutions (solution crystals); for mixtures of potassium chloride and bromide the differences are 0.4–0.9 cal./g. (1–1.5% of the total), for potassium and rubidium chlorides, 0.5–2.0 cal./g. (1–4%). For the pure salts potassium chloride and potassium bromide, fusion has no effect on the heats of solution. (2) The heats of solution of mechanical mixtures of the salts do not agree with those calculated from the simple mixture rule, but are appreciably lower; they are equal to the value for the solution crystals for mixtures of potassium and rubidium chlorides and lead and barium nitrates, but 1.3 cal./g. smaller for mixtures of potassium chloride and bromide. (3) The anomalous double refraction of mixed crystals of lead and barium nitrates is not connected with the heats of solution, for the latter remain unaltered by heating at 340°, whilst the optical anomaly disappears after heating at 340°, and does not reappear on cooling.

From the fact that the solution crystals were generally cloudy, and from results obtained by other workers, it appears probable that such crystals are not homogeneous in structure: this view is strengthened by a consideration of the conditions under which separation from solution occurs, especially in view of the fact that the composition both of the crystals and of the solution alters during the separation. The various examinations which have been made of the X-ray spectra of mixed crystals, including hitherto unpublished investigations by Wever, show that interference-spectra are observed which are identical, not only for solution and melt crystals, but also for mechanical mixtures of the components, so that these give no information on the differences under discussion. The specific gravities of mixed crystals from the melted potassium chloride and bromide are considerably lower than those calculated from the simple mixture rule (Retger's rule); owing to inclusions, this property has not been determined for the solution crystals. The m. p. curves have been constructed for the systems potassium chloride and bromide and potassium and rubidium chlorides; the latter system shows a distinct crystallisation interval, the former definite solidifying points; the curves for the latter fall continuously; that for the former has a minimum at 740°, 70–80% of potassium bromide. Curves have also been constructed to show the wide variations in composition between the mixed crystals and the solutions from which they separate.

S. I. L.

**Henry's Law as Applied to Aqueous Ammonia Solutions and the Hydrolysis of Ammonium Salts.** E. KLARMANN (*Z. anorg. Chem.*, 1924, 132, 289–300).—The partial pressures of

aqueous ammonia solutions were determined by a modification of the dynamic method, for concentrations ranging from 0.5*N* to 0.0083*N*. The results are in agreement with Henry's law. The formation of an aqueous solution of ammonia is represented according to the "quinquevalent" and "quadrivalent" theories, respectively, by the equations:



The two theories are developed from the point of view of the law of mass action, and the degree of hydrolysis of ammonium acetate is calculated. From conductivity measurements of dilute aqueous ammonia and dilute acetic acid at 0°, the dissociation constants are  $K^0_{\text{C}_2\text{H}_3\text{O}_2} = 1.68 \times 10^{-5}$  and  $K^0_{\text{NH}_4\text{OH}} = 1.52 \times 10^{-5}$ . The conductivity and freezing point of aqueous solutions of ammonium acetate were also determined. The former is determined exclusively by the ions present in solution, whilst the depression in the freezing point is determined by the total effect of undissociated salt, electrolytic and hydrolytic products. The results for the depression of the freezing point exhibit anomalies, and it is not possible to combine the results in order to establish the degree of hydrolysis. Partial pressure measurements of ammonium acetate solution at 0° show that Henry's law applies for the hydrolytic ammonia formed. J. B. F.

#### Electrolytic Preparation of Ammonium Persulphate.

J. SALAUZE (*Bull. Soc. chim.*, 1923, **33**, [iv], 1738—1761).—An extensive investigation of the electrolytic preparation of ammonium persulphate by different methods. The preparation may be effected either in acid or in neutral solution (chromate method, Müller, A., 1912, ii, 895, etc.). The second method gives the higher yield (80—85%), but has many disadvantages. The chromium hydroxide diaphragm formed on the cathode (which must be of platinum) is very fragile, and dissolves if the solution becomes slightly acid. Temperature has little effect on the yield, which is as good at 22° as at 8°, whilst the yield is improved if chlorides are added in traces. The process can only be followed by measuring (1) the gas evolved, or (2) the cathode potential, which necessitates continued attention. Another drawback to the method is due to the great solubility of ammonium persulphate in neutral or alkaline solution. Prolonged electrolysis is needed before the salt separates.

Electrolysis in acid solution does not require much attention, and the ammonium persulphate separates readily. Electrolysis may be effected in presence or in absence of potassium ferrocyanide, addition of the latter increasing the yield, but giving a product slightly contaminated with Prussian-blue, which is difficult to remove. The conditions for a good yield (70—75%) are as follows: (1) a low temperature, (2) a concentration of sulphuric acid corresponding with the presence of ammonium hydrogen sulphate, (3) a fresh platinum anode (anodic current density, 50 amps. per sq. dm.), (4) a platinum cathode and (this being very important), the largest possible cathodic current density, and (5) the presence of a trace of chloride-ion.

E. E. T.

**Double Decomposition in the Absence of Solvents. V.**

A. G. BERGMANN (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 625—637; cf. A., 1923, ii, 568, 636, 761, 764).—1. The system silver chloride—mercuric iodide. The systems previously investigated included those formed by mercury halides with the nitrates of a variety of metals; such an investigation is rendered difficult by the fact that mercuric nitrate decomposes on melting and its behaviour towards the chlorides of other metals cannot be studied. The system now investigated does not suffer from this disadvantage; the thermal effect of the double decomposition is practically zero, and, moreover, both mercuric iodide and silver iodide are coloured and thus facilitate observation. It has been found that the system does not form complex compounds; there is a simple eutectic at 136°. The components appear to interact below this temperature in the solid state, as evidenced by the change of colour from reddish to orange-yellow. The reason for the absence of interaction is to be sought in the low ionisation of mercuric iodide; this is proved by the results obtained with the system silver iodide—mercuric chloride. It is found that the liquidus and solidus curves are in this case identical with those previously obtained with silver chloride and mercuric iodide, as also is the colour etc. Carefully dried silver iodide and mercuric chloride interact on mixing in the cold, the colour gradually changing from pale yellow to orange-red.

2. A new type of reciprocal system. Four-component systems can be divided into three categories, of which the most common is formed by four independent components (the simplest of these is one of four elements). The diagram of state of such a system is represented by a regular tetrahedron (Jänecke, A., 1908, ii, 808, 841; 1912, ii, 750, 762). The second category includes reciprocal systems in which there is an equilibrium  $MX + NY \rightleftharpoons MY + NX$  in the liquid state and also, apparently, in the solid state. These systems can be formulated as three-phase systems (Jänecke, *loc. cit.*); the best-known examples are those of potassium chloride—magnesium sulphate and sodium chloride—potassium sulphate.

It is now proposed to distinguish a third category, the irreversibly reciprocal systems. The difference from the second category consists in the fact that the reaction is complete in one or other direction, the system  $2AgI + HgCl_2 \rightarrow 2AgCl + HgI_2$  affording a good example. The systems formed by mercury halides with silver and thallium nitrates can also be referred to this group, although they could not be examined completely owing to the instability of mercuric nitrate. A method of graphic representation of such systems is given, and it is pointed out that the three categories have the following morphological characteristics: the first gives rise to one quaternary, four ternary, and six binary systems; the second to one quaternary and four binary, and the third to two ternary and five binary systems.

G. A. R. K.

**The Energy of Crystallisation of Ignited Gypsum. M. VON**

GLASENAPP (*Z. anorg. Chem.*, 1923, **130**, 246—252).—The author has already shown that the setting of ordinary gypsum which has

been ignited at temperatures of  $130\text{--}200^\circ$  is due finally to the recrystallisation of the soluble hemihydrate,  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ , in the form of the relatively insoluble dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Burnt gypsum in the form of small plates or cubes allowed to stand with one surface in water, recovered in two hours about one-third more than the water originally driven off by heating; after fully drying, the increase was exactly equal to the amount originally driven off. Microscopical examination before ignition and after regeneration (burning and then keeping in water, and finally drying) showed that the relatively coarse crystalline structure before ignition had been converted into a fine leaf structure, whilst in the powdered condition the addition of water results in fine needles. Material regenerated in lump form is much harder than the original, but has a lower specific gravity; originally clear lumps become cloudy. If alum solution is used instead of water for the regeneration, the final material has a hardness approaching that of marble. These changes are attributed to the difficult conditions of recrystallisation in the solid lump.

Small lumps of ignited material exposed to an atmosphere saturated with water vapour in a closed space, required from forty to seventy-five days to recover the original weight. Microscopical examination showed that recrystallisation occurs in this case in extremely fine needles, with a greater change in the specific gravity. The hardening of pavement gypsum, a variety obtained by heating to  $1000^\circ$ , which is accompanied by some loss of sulphur trioxide, is very different from the above, the alteration in form of crystal being less, and complication is introduced by the formation of carbonate from the free lime.

S. I. L.

**Thermal Effects on the Heating Curves of Barium, Strontium, and Calcium Oxides and their Carbonates in Graphite Tubes.** G. TAMMANN and K. F. GREVEMAYER (*Z. anorg. Chem.*, 1923, **130**, 205—208).—During the heating of the oxides in graphite tubes, an acceleration in the rate of rise of the temperature was observed between  $700^\circ$  and  $900^\circ$  with barium and strontium oxides, followed in each case by a marked reduction in the rate at higher temperatures; the first effect is at temperatures at which carbon monoxide and dioxide are formed by oxidation of the graphite tube, but the second effect occurs at temperatures  $100^\circ$  or more below those at which the respective carbonates have a dissociation pressure of 1 atm. If, however, the carbonates be mixed with soot or charcoal, the temperature at which the reduction in the rate of rise occurs is considerably reduced, *i.e.*, the carbonate decomposes at lower temperatures by reason of the diminution of the partial pressure of the carbon dioxide due to the formation of carbon monoxide; industrially, charcoal is added to barium carbonate in order to causticise it at lower temperatures. The acceleration and subsequent decrease in the rate of rise of temperature on heating the oxides in graphite tubes are therefore due to formation and subsequent dissociation of the carbonates.

S. I. L.

**Hydrates in Aqueous Solution. I. The Beryllium-ion.**

R. FRICKE and H. SCHÜTZDELLER (*Z. anorg. Chem.*, 1924, **131**, 130—139).—Examination of solutions of beryllium chloride confirms that of all bivalent metallic ions in aqueous solution the beryllium-ion is the most highly hydrated. Solutions prepared by neutralising the pure hydroxide with the equivalent quantity of hydrochloric acid have abnormally high conductivities, possibly from the presence of some uncombined hydroxide in colloidal solution. The measurements were therefore made with solutions prepared from the sulphate by double decomposition with the equivalent quantity of barium chloride. Measurements of the viscosity at 25° of solutions from 0.053*N* to 0.526*N* gave values greater than for solutions of magnesium, zinc, and ferrous salts. Similarly, the molecular depression of the freezing point for aqueous solutions has a pronounced minimum at a concentration of about 0.103*N*, which is considerably less than the corresponding concentrations for solutions of ferrous and magnesium chlorides. The mobility of the beryllium-ion at 25°, as determined from conductivity measurements, is about 30, the lowest value yet observed for a metallic ion, with the possible exception of the thorium-ion.

The great degree of hydration of the beryllium-ion indicated by these measurements is in agreement with the marked deliquescence of the chloride, its great heat of solution, and the stability of the tetrahydrate,  $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$ , which was found to suffer no loss in weight even after remaining for six weeks over phosphoric anhydride. On the other hand, the volume contraction on dissolution of the chloride in water is very small, as calculated from determinations of the specific gravity of the anhydrous chloride and of the aqueous solutions; in this property, the beryllium-ion is closely analogous to the lithium-ion.

S. I. L.

**Properties of Magnesite.** T. NISHIMURA and M. MURACHI (*Rikwagaku Kenkyujo Iho*, 1923, **2**, 408—419).—The material contained  $\text{MgCO}_3$  97.43%,  $\text{CaCO}_3$  0.68%, mineral matter insoluble in acids 1.06%; the salt  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  was also used. The mode of hydrolysis of magnesite in water can be observed under a microscope by the adsorption of fluorescent dye, such as fluorescein, eosin, or curcumin. Crystallised magnesite adsorbs the dye and emits fluorescence, whilst the hydrolytic product does not. With the synthetic compound, the difference is not distinct. The solubilities of the natural and synthetic compounds, respectively, in water at 20° saturated with atmospheric air (I) and carbon dioxide (II) at 1 atm. pressure are: (I) 0.084 g. and 1.56 g. per litre of solution and (II) 0.156 g. and 25.70 g. per litre. The solubilities of the magnesite in 0.530*N*-hydrochloric acid, 0.507*N*-nitric acid, and 0.547*N*-sulphuric acid were measured at 16—19°; the products of the velocity constant and a definite surface of the sample are 0.0193, 0.0095, and 0.0014, respectively. For 0.589, 1.034, 1.526, and 2.585*N*-hydrochloric acid, the products are 0.0182, 0.0102, 0.0073, and 0.0056, respectively. The velocity of hydrolysis of the magnesite is less than its velocity of solution in about 0.5*N*-



hydrochloric and nitric acids, but larger than that in sulphuric acid of almost the same concentration. When the magnesite is covered with the hydrolytic product, the solubility velocity in 1.034*N*-hydrochloric acid is one-half to one-third of that of the unhydrolysed substance. The presence of 2 mols. of sodium chloride or ammonium chloride or 1 mol. of calcium chloride only slightly decreases the solubility velocity in about 0.5*N*-hydrochloric acid. In the case of magnesium chloride, if the concentration of the salt is less than 27%, the solubility velocity of the magnesite in about 0.5*N*-hydrochloric acid is moderately decreased; if, however, the concentration is above 28%, a double salt is formed as in the case of the synthetic salt (cf. A., 1923, ii, 689), which is practically insoluble in about 0.5*N*-hydrochloric and sulphuric acids. K. K.

**Preparation of Chemically Pure Zinc.** (MILLE.) A. DRESCHER (*Bul. Soc. Chim. România*, 1923, 5, 80—81).—A saturated solution of chemically pure zinc sulphate is treated with sodium amalgam at 81°; the zinc amalgam obtained becomes, on cooling, a semi-solid, crystalline mass. The crystals are washed and dried, and the mercury is removed by slow distillation at 400° in a vacuum. Zinc of 99.95% purity remains. J. W. B.

**The Action of Hydrogen Peroxide on the Precipitation of Zinc Salts with Sodium Metasilicate.** A. H. ERDENBRECHER (*Z. anorg. Chem.*, 1924, 131, 119—129).—Solutions of sodium metasilicate in 30% hydrogen peroxide may be obtained containing very high proportions of sodium silicate, but cannot be made to deposit crystals. If sodium silicate be added to concentrated solutions of zinc salts in presence of 30% hydrogen peroxide, products are obtained in which the proportion of oxygen varies according to the concentration from 2.3 to 7.9%; they are to be regarded as mixtures of zinc peroxide and silicic acid, admixed with zinc silicates and other products of reaction, as shown by the similarity of the dissociation curves with those of zinc peroxide and silicic acid mixtures made up for comparison. Precipitation with sodium carbonate gave products containing up to 12.1% of oxygen. Since precipitated zinc silicate does not combine with hydrogen peroxide, the latter may be used to distinguish zinc oxide in presence of the silicate.

S. I. L.

**Combining Weight of the Lead of a Vesuvian Cotunnite.** A. PRUTTI and D. MIGLIACCI (*Atti R. Accad. Lincei*, 1923, [v], 32, ii, 468—472).—If sufficiently pure lead chloride is phenylated in accordance with the procedure given by Hofmann and Wölff (A., 1907, ii, 521), the resulting lead tetraphenyl may be perfectly purified by alternate crystallisations from benzene and chloroform and treatment with absolute alcohol. Treatment with bromine vapour alone suffices to convert the lead tetraphenyl quantitatively into lead bromide. By this means it is found that the combining weight of ordinary lead is 207.192, and that of the lead obtained from a sample of Vesuvian cotunnite originating in the eruption of 1906, 207.050. From these results, together with those of Ross

(A., 1908, ii, 9), the conclusion is drawn that the lead of the cotunnite consists of a mixture of ordinary lead with about 12% of uranium-lead.

No explanation is advanced for the slight divergence of the value found for the combining weight of ordinary lead from the accepted value, namely, 207.20 (cf. A., 1915, ii, 455, 456). T. H. P.

**The Solubility of Lead Chloride and Lead Bromide in Aqueous Solutions of the Chlorides of the Alkali and Alkaline-earth Metals.** W. HERZ and M. HELLEBRANDT (*Z. anorg. Chem.*, 1923, **130**, 188—198).—As a preliminary to the work, various methods for the determination of lead in presence of alkali and alkaline-earth metal halides were examined, and precipitation with sodium cyanide in the cold was found most suitable; the precipitate was dissolved on the filter with cold nitric acid, and the metal precipitated as sulphide by ammonium sulphide and weighed as sulphate. The solubility of lead chloride in solutions of the chlorides and bromides of sodium, potassium, calcium, strontium, and barium, in concentrations up to about  $4N$ , was found to obey the same general rule, declining to a minimum in solutions of concentrations about or below  $N/1$ , and then rising again (cf. von Ende, A., 1901, ii, 241); it is greater in solutions of the bromides than in those of the chlorides of equivalent concentrations. The curves plotted from the results lie very close together for the interval of diminishing solubility, i.e., the kation plays only a small part, but as the solubility increases again the curves diverge. The effect of the kation in solutions of the chlorides up to  $3.6N$  is in the order K, Ca, Na, Sr, Ba, and above  $3.6N$ , K, Ca, Sr, Na, Ba, the last being most effective; for solutions of the bromides the effect is the same as in the second order, but greater, so that the solubility of lead chloride in a strong bromide solution may be greater than in pure water. The solubility of lead bromide in these solutions is very similar. S. I. L.

**The Equilibrium between Lead Chloride and Iodide and some Alkali Chlorides and Iodides in Aqueous Solution.** (MME.) N. DEMASSIEUX (*Ann. Chim.*, 1923, [ix], **20**, 233—296).—The systems previously studied, lead chloride-potassium chloride-water (A., 1914, ii, 185), lead chloride-ammonium chloride-water (A., 1913, ii, 409), lead chloride-sodium chloride-water (A., 1914, ii, 271), lead iodide-potassium iodide-water, and lead iodide-ammonium iodide-water (A., 1923, ii, 565), are dealt with in detail and supplemented by a description of the system lead chloride-lithium chloride-water, which behaves in an analogous manner to the system lead chloride-sodium chloride-water (*loc. cit.*). A general survey of the results obtained shows that, from the point of view of double salt formation, the alkali chlorides form two distinct groups. Potassium and ammonium chlorides each form two compounds with lead chloride, one series having the general formula  $2PbCl_2.MCl$ . The second pair of compounds do not possess the same type of composition, their formulæ being  $PbCl_2.KCl, \frac{1}{3}H_2O$  and  $PbCl_2.2NH_4Cl$ , respectively. Moreover, the latter substance is

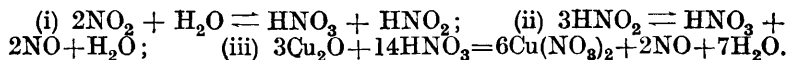
stable only above  $75^{\circ}$ , whilst the former can exist at a considerably lower temperature. The potassium analogue of the compound  $\text{PbCl}_2 \cdot 2\text{NH}_4\text{Cl}$  has been prepared by other methods (cf. Lorenz and Ruckstuhl, A., 1906, ii, 853), but was not detected in the course of the work described. The chlorides of sodium and lithium are differentiated from those of potassium and ammonium in their action on lead chloride in that they do not yield with that substance compounds capable of detection by solution methods. However, the solubility of lead chloride increases considerably in the presence of a concentrated solution of sodium or lithium chloride, a possible explanation being the formation of complexes in solution. The compounds of lead iodide with the iodides of potassium and ammonium do not give the characteristic reactions of lead salts or of iodides with the ordinary reagents; in this respect they differ from the double chlorides described, which behave towards reagents as mixtures of chlorides.

H. J. E.

**Evolution of the Molecule of Cupric Hydroxide in Aqueous Suspension.** (MLLE.) S. VEIL (*Compt. rend.*, 1924, 178, 329—330).—The molecular coefficients of magnetisation of the following four substances have been compared: (1) Freshly prepared blue cupric hydroxide; (2) the oxide obtained by igniting (1); (3) the brown hydroxide obtained by warming (1) in presence of water; and (4), the oxide obtained by igniting (3). The coefficients of (3) and (4) are approximately equal and less than that of (2), which is about a third of that of (1). The change of colour from blue to brown is therefore not due, as usually supposed, to simple dehydration.

E. E. T.

**The Reaction between Copper and Nitrogen Peroxide.** J. R. PARK and J. R. PARTINGTON (*J. Chem. Soc.*, 1924, 125, 72—82).—When nitrogen peroxide is passed over specially prepared copper, the latter is oxidised to cuprous oxide, with the evolution of heat, the nitrogen peroxide being reduced to nitric oxide:  $2\text{Cu} + \text{NO}_2 = \text{Cu}_2\text{O} + \text{NO}$ . The cuprous oxide then adsorbs about 33% of nitrogen peroxide. The actual amount of nitrogen peroxide taken up is variable, although the mean value of the atomic ratio O/N is practically 3. The results are consistent with the formation of cuprous oxide and a subsequent adsorption complex  $y\text{NO}_2 \cdot x\text{Cu}_2\text{O}$ . The properties of the substance are not in agreement with the formula  $\text{Cu}_2\text{NO}_2$  as suggested by Sabatier and Senderens (A., 1893, ii, 374) or  $\text{Cu}_2(\text{NO}_3)_2$  as suggested by Tartar and Semon (A., 1921, ii, 336). No oxygen or nitrogen is evolved on the decomposition of the nitro-copper by heat. With water, nitric oxide is evolved and a solution of cupric nitrate with a little nitrite is left, a result which may be explained by the following reactions:



A little cupric nitrite will be formed by the action of undecom-

posed nitrous acid. The residue of copper found by previous workers had evidently escaped reaction, since the product only contained 27% of the nitrogen and oxygen as a maximum. At 65—70°, the whole of the nitrogen peroxide is removed by an inert solvent such as carbon tetrachloride, leaving a residue of cuprous oxide. This indicates that the nitrogen peroxide is adsorbed and not chemically combined.

J. B. F.

**The Reaction between Solutions of Complex Cupric Salts and Potassium Cyanide.** R. LANG (*Z. anorg. Chem.*, 1923, **130**, 151—160).—Two chief factors are involved in the reaction, the first being a reduction of the cupric salt to the cuprous state, and the second the formation of a cyanide complex, in which the ratio CN/Cu may vary from less than 2 to 4; both these factors are strongly influenced by the cyanide-ion concentration, which is in turn effected by the temperature and by the hydroxyl-, hydrogen-, ammonium-, etc. ion concentration, so that no stoichiometric relation exists. The decolorisation of an ammoniacal solution of a cupric salt by addition of potassium cyanide is certainly due to the formation of a complex cuprous cyanide, but no definite complex formula can be deduced; the conclusion of Treadwell (*A.*, 1904, ii, 172) that the variation in the amount of cyanide required, observed in the presence of ammonium salts, is due to back-formation of cyanide varying with the alkalinity of the solution, is not supported. Even in strongly alkaline solutions, it is shown that this back-formation of cyanide is extremely slight, and its effect on the quantitative aspect of the reaction is entirely masked by the factors discussed.

S. I. L.

**Power of Spontaneous Transformation of Yellow Mercuric Iodide.** A. DAMIENS (*Compt. rend.*, 1924, **178**, 326—328).—Crystals of red mercuric iodide, with an area of about 0.7 sq. cm., were heated at 155° until completely yellow, chilled to definite temperatures, and observations made of (a) the time, in seconds, required for the appearance of the first red particle, and (b) the number of red particles visible three seconds later. The lower the temperature of chilling (for temperatures down to 40°), the smaller the value of *a* and the larger that of *b*. Chilling to temperatures a little below 40° made *b* too large to measure. Chilling from 155° to —80° was not accompanied by an appearance of the red form, but on suddenly warming to the ordinary temperature, general conversion to the red form rapidly occurred, this effect being intensified if chilling was effected to liquid air temperatures (cf. also *A.*, 1923, ii, 864).

E. E. T.

**The Electrolytic Conductivity of Molten Scandium Chloride.** W. BILTZ and W. KLEMM (*Z. anorg. Chem.*, 1923, **131**, 22—26).—The scandium chloride was melted under pressure in a quartz apparatus in order to avoid loss by sublimation. The m. p. was 939°. The specific conductivity was found to be 0.51 at 959°, 0.55 at 969°, 0.57 at 981°, and 0.59 at 991°. A marked decrease in conductivity was observed as the molten salt solidified on cooling.

The observed results resemble those of thorium chloride rather than those of aluminium chloride, the conductivity of the last-named being from  $10^{-5}$  to  $10^{-6}$  times as much. W. H.-R.

**Cerium, Mixed Cerium Metals, and Hydrogen.** A. SIEVERTS and G. MÜLLER-GOLDEGG (*Z. anorg. Chem.*, 1924, **131**, 65—94).—The metals examined were (1) cerium, containing 94.9% of Ce, 4.2% of other cerium metals, and the remainder iron and silicon; (2) a mixed metal containing 53.8% of Ce, about 44% of other cerium metals, mostly lanthanum, and the remainder aluminium; (3) a mixed metal containing 10.2% of Ce, 84.3% of other cerium metals (mostly lanthanum), some iron, aluminium and silicon, and (4) a cerium-manganese alloy, Ce : La : Mn = 83.5 : 9.0 : 7.5. These samples absorb nitrogen extremely slowly, even when molten. Hydrogen is not absorbed until the temperature exceeds  $300^{\circ}$ ; if, however, the metal has been previously melted in a vacuum, it absorbs hydrogen very rapidly even at normal temperatures. The mixed metal (3) absorbs hydrogen very rapidly even without previous heating; after previous heating, the absorption is even more rapid, ceasing only when the metal is cooled in mixed ether and solid carbon dioxide, and starting again if the temperature is allowed to rise to  $-10^{\circ}$ . Traces of nitride in the metals reduce the speed of absorption, and larger quantities are inhibitory.

The products saturated with hydrogen at  $20^{\circ}$  are greyish-black powders, that from (1) being spontaneously inflammable. Samples (1) and (2) gave products containing 1.89% of hydrogen; (3) gave a product containing 1.94% of hydrogen; the formulæ  $\text{CeH}_3$  and  $\text{LaH}_3$  require 2.11 and 2.13%, respectively. By plotting the pressures as ordinates against the volumes of gas absorbed at  $800^{\circ}$  as abscissæ, curves are obtained consisting of a slowly rising portion, continuing in an almost horizontal line, and finally rising very sharply; at  $600^{\circ}$  and lower temperatures, the horizontal portion disappears. The volumes absorbed vary with the previous history of the sample, being continuously lessened by repeated heating and cooling. The final sharply rising part of the curves is of the form  $m = K_1 + K_2\sqrt{p}$ , where  $m$  is the volume absorbed by 1 g.,  $p$  the pressure, and  $K_1$  and  $K_2$  are constants depending on the temperature and previous treatment.

The curves are similar to those obtained by Hoitsema and Roozeboom for the system palladium-hydrogen and suggest the formation of two non-miscible solid solutions; they furnish no support for the view that hydrides  $\text{CeH}_3$  and  $\text{LaH}_3$  are formed. S. I. L.

**Rare Earths. XV. Search for Element Sixty-one.** L. F. YNTEMA (*J. Amer. Chem. Soc.*, 1924, **46**, 37—39).—An account of experiments undertaken to detect the presence of an element of atomic number 61 which was shown by Moseley (A., 1914, ii, 326) to lie between neodymium and samarium. The materials investigated were pure neodymium oxide, pure samarium oxide, the oxides of intermediate fractions between the two pure oxides, and

intermediate oxides from a gadolinite fractionation and a fergusonite fractionation. The arc spectrum showed that the five faint lines 3305.8, 3329.1, 3342.5, 3378.0, and 3379.2 Å. were found in both pure neodymium and pure samarium oxides. The X-ray absorption spectra were found to give the *K* absorption limit for samarium easily, but on mixing with 5% of neodymium oxide the corresponding value for this element was not obtained. Consequently, the method was abandoned, since the missing element is not likely to be present to so large an extent as 5%. With the primary X-ray emission spectrum, it is shown that 0.1% of impurity can be detected in the case of the pure oxides of neodymium and samarium, and that if the element 61 is present in these substances it is present to a still smaller extent than 0.1%. Hence whilst the spectroscopic evidence indicates that the element of atomic number 61 may be associated with neodymium and samarium, X-ray analysis of material from various sources has given no evidence of the presence of this element.

J. F. S.

### Constitution and Evolution of Precipitates of Alumina.

P. PASCAL (*Compt. rend.*, 1924, **178**, 481—483).—From measurements of the magnetic susceptibilities of specimens of alumina precipitated under various conditions, the author concludes that (1) the precipitate (a gel) formed by the addition of aqueous ammonia to an aluminium salt consists originally of anhydrous alumina; this at length is converted into the hydrate,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , which is unstable and is not identical with the crystalline hydrate; (2) the aluminium in solutions of aluminate is largely present in the colloidal state; (3) in no case does hydrated alumina consist of the true hydroxide,  $\text{Al}(\text{OH})_3$ . The conclusion is drawn that it is impossible to have more than a certain number of hydroxyl groups attached to the same atom, without the occurrence of dehydration, as with carbon compounds.

A. B. H.

**Clays. V. Action of Heat.** O. BOUDOUARD and J. LEFRANC (*Bull. Soc. chim.*, 1923, [iv], **33**, 1627—1640).—The authors have studied the dehydration of twenty-seven specimens of clay from nine distinct sources. The temperatures of experiment ranged from 182° to 800°, and the results obtained are tabulated to show both percentage and molecular loss of water. Graphic representation of the dehydration as a function of temperature indicates that the loss of combined water occurs between 450° and 500°.

H. J. E.

### The Formation of the Green Manganous Sulphide. A.

MICKWITZ and G. LANDESEN (*Z. anorg. Chem.*, 1924, **131**, 101—118).—The work of Villiers (A., 1914, ii, 658) and of Fischer (A., 1915, ii, 462), whilst confirming that the rose-coloured sulphide is always precipitated first, and is not converted into the green form if precipitation has been effected with sodium or potassium sulphides, has not removed the uncertainty left by earlier workers as to the conditions for obtaining the green form. It is now found that the sole condition is the presence of free ammonia before the

addition of the ammonium sulphide. If no free ammonia be present, the rose-coloured sulphide precipitated by ammonium hydrogen sulphide contains more sulphur than is required by the formula  $\text{MnS}$ , and its composition is better expressed by the formula  $\text{H}_2\text{Mn}_3\text{S}_4$ ; in presence of free ammonia, the formula is  $(\text{NH}_4)\text{HMn}_3\text{S}_4$ , and this rose-coloured precipitate slowly passes into the green form,  $\text{MnS}$ , giving up  $(\text{NH}_4)\text{SH}$  to the mother liquor. S. I. L.

**Mechanism of the Reduction of Permanganate and its Physico-chemical Basis.** VIII. Kinetics and the Hydroxyl-ion Influence in the Stepped Reaction Manganate-Formaldehyde-Formate. J. HOLLUTA (*Z. physikal. Chem.*, 1923, **107**, 333—346; cf. A., 1923, ii, 864; this vol., ii, 115).—A continuation of previous work. The velocity equations have been deduced for the stepped reaction manganate-formaldehyde-formate, for the special case where a tenfold excess of formate is used. The consequence of this condition on the secondary reaction has been deduced; this allows of a simple mathematical treatment, and in consequence of the ease with which the second partial reaction of the whole process can be isolated ( $\text{MnO}_4'' + \text{HCO}_2' = \text{MnO}_2 + \text{CO}_3'' + \text{OH}'$ ), also allows of the calculation of the velocity constant of the first partial reaction ( $\text{MnO}_4'' + \text{H}\cdot\text{CHO} = \text{MnO}_2 + \text{H}\cdot\text{CO}_2' + \text{OH}'$ ) from the concentration of the manganate and from the known velocity constants of the reduction of manganate by formate. The velocity equations obtained have been tested in a series of measurements with different hydroxyl-ion concentrations and found to represent the facts. In addition to the retardation previously found, which is proportional to the square root of the hydroxyl-ion concentration, a second retardation has been found which is directly proportional to the hydroxyl-ion concentration. The two retardations take place side by side. It is probable that the cause of the second retardation is the formation of the anion,  $\text{H}_2\text{C}(\text{OH})\text{O}'$ , which is produced by a neutralisation process with the formaldehyde and reacts more slowly with the manganate than formaldehyde itself. The temperature coefficient of the reduction of manganate by formaldehyde at an alkalinity of 0.1N is found to be 1.85. J. F. S.

**Temperature Periods in the Emission of Occluded Gases from Iron.** G. BORELIUS and F. GUNNESON (*Nature*, 1923, **113**, 82—83).—In addition to properties known to exhibit a periodicity as a function of temperature, the speed with which occluded gases are removed from iron on rise of temperature is also periodic. Experiments with electrolytic iron containing occluded hydrogen or nitrogen showed that an accelerated emission of gas takes place more or less in the neighbourhood of the hundreds on the centigrade scale. A. A. E.

**Decomposition of [Iron] Pyrites by Heat.** (MLLE.) G. MARCHAL (*Bull. Soc. chim.*, 1924, [iv], **35**, 43—47).—A study of the dissociation of iron pyrites (into ferrous sulphide and sulphur) in a vacuum and in an atmosphere of nitrogen. In a vacuum, dissociation begins at  $500^\circ$ , is much more rapid at  $550^\circ$ , and, at

670—680°, is complete in eight hours, large pieces of pyrites undergoing disintegration during the process. At 700—800°, the sulphur condenses in a well-defined form, and possibly could so be extracted from pyrites on the large scale. At 850°, dissociation is complete in two hours. At higher temperatures (1200°), the residue is a mixture of ferrous sulphide and (a little) iron.

In an atmosphere of nitrogen, dissociation is very rapid at 850°.  
E. E. T.

**Definitions of Steel and Cast Iron.** K. HONDA (*Rikwagaku Kenkyujo Ihô*, 1923, 2, 405—407).—The author has defined steel and cast iron from the content of carbon in them. The maximum amount of carbon contained in iron as a solid solution at the ordinary temperature is 0.035%, and that of carbon dissolved in iron at high temperature is 1.7%; this figure has a distinct meaning on the equilibrium diagram of iron and carbon. Steel is therefore defined to be an alloy of iron and carbon, which contains 0.035—1.7% of carbon. Cast iron is defined to be an alloy of iron and carbon, which contains more than 1.7% of carbon.  
K. K.

**The Solidus Curve of Austenite.** G. ASAHARA (*Rikwagaku Kenkyujo Ihô*, 1923, 2, 420—425).—The author has determined the solidus curve of austenite by the quenching method. The sample was prepared from "Armco" iron and sugar carbon, the content of carbon being 0.46, 0.48, 0.58, 0.95, and 1.44%. The sample was quenched at 1134—1408°, cooled rapidly by throwing into cold water, and microscopically examined. The curve occupies a higher position than that of Gutowsky (*Metallurgie*, 1909, 731) and far lower than that of Carpenter and Keeling (*J. Iron and Steel Inst.*, 1904, 1, 224).  
K. K.

**Derivatives and Reactions of Iron Pentacarbonyl.** H. FREUNDLICH and E. J. CUY (*Ber.*, 1923, 56, [B], 2264—2267).—The observations of Dewar and Jones (A., 1906, ii, 89; 1907, ii, 266) on iron pentacarbonyl, iron tetracarbonyl, and iron nonacarbonyl were confirmed, except that the pentacarbonyl was found to react with iodine on exposure to light or on heating in alcoholic solution. All three carbonyls are diamagnetic, the values for their magnetic susceptibilities being:  $\text{Fe}(\text{CO})_5$ ,  $\kappa = -0.51 \times 10^{-6}$ ;  $\text{Fe}_2(\text{CO})_9$ ,  $\kappa = -0.37 \times 10^{-6}$ ;  $\text{Fe}(\text{CO})_4$ ,  $\kappa = -1.3 \times 10^{-6}$  (approx.).

The best method for preparing iron tetracarbonyl was found to be by heating the pentacarbonyl for some time, in absence of air, with a slight excess of concentrated sodium hydroxide or ammonia solution; the carbonyl dissolved to a brown solution, which was treated with excess of ammonium sulphate and extracted with ether. The red, ethereal solution was dried with copper sulphate and the solvent removed by distillation, the characteristic green crystals of iron tetracarbonyl remaining. The brown solution of the pentacarbonyl in alkali was found to contain a number of complex iron compounds which possess strong reducing properties. A red substance was isolated in dichroic needles, but has not yet been obtained sufficiently pure for analysis. It possesses powerful reducing properties.  
F. A. M.



**The Magnetisation of Alloys of Nickel and Electrolytic Chromium.** J. SAFRANEK (*Compt. rend.*, 1924, **178**, 479—480).—The author has studied the magnetic properties of alloys of pure nickel and electrolytic chromium. Accepted values of the constants for nickel were confirmed. For chromium, the susceptibility was found to be independent of the magnetic field between 2000 and 14,000 gauss and of the temperature between 100° and 600°, and to have a value of  $4.31 \times 10^{-6}$ . The reciprocal of the susceptibility of the alloys plotted against temperature gives a straight line becoming concave towards the axis of  $T$  at higher temperatures. The various magnetic constants are found to be linear functions of the composition.

The specific magnetisation at the absolute zero for different alloys has been found by extrapolation, and was zero for 13% chromium content, corresponding with  $\text{CrNi}_6$ . Such a compound has not been isolated, and microscopical observations have shown these alloys to be solid solutions.

A. B. H.

**The Hardness of Mixed Crystals of Copper-Nickel and Iron-Nickel Alloys at Temperatures up to the Melting Point.** F. SAUERWALD [with K. KNEHANS] (*Z. anorg. Chem.*, 1923, **131**, 57—64).—Metallic solid solutions are characterised by an increase in hardness as one metal dissolves in another, the relation between hardness and composition being expressed by a graph with a well-defined maximum in the region of middle composition. The author's experiments show that this rule also applies to the hardness of solid solutions at high temperatures, in the case of copper-nickel and iron-nickel alloys, the hardness being tested up to 910° for the copper-nickel and up to 1230° for the iron-nickel alloys, in both of which cases a single series of solid solutions is present at high temperatures. The hardness is measured by an indentation method, a steel ball attached to a bar being allowed to fall on to the specimens. At low temperatures, the iron-nickel results are complicated by the presence of more than one constituent.

W. H.-R.

**Nickel Hydride and the Mechanism of Hydrogenation using a Nickel Catalyst.** W. SCHLENK and T. WEICHSELFELDER (*Ber.*, 1923, **56**, [B], 2230—2234).—Anhydrous nickel chloride, on treatment with an ethereal solution of a Grignard reagent such as magnesium phenyl bromide, reacts rapidly forming a dark brown sol containing nickel in colloidal solution. This solution absorbs hydrogen readily, the nickel being precipitated as a flocculent, deep black sediment leaving a clear solution. Measurement of the volume of hydrogen absorbed indicates that a compound of the formula  $\text{NiH}_4$  is formed, but on separating the black product and drying it in a current of hydrogen it was found to possess exactly the formula  $\text{NiH}_2$ . On treatment with alcohol, the black precipitate at once begins to evolve hydrogen, although it is quite stable in contact with ether. This is accepted as further evidence that the usual processes of catalytic reduction in presence of nickel

are essentially chemical, due to the formation of nickel hydride, and are not merely adsorption phenomena. F. A. M.

**Chromium-Copper-Nickel Alloys.** E. SIEDSCHLAG (*Z. anorg. Chem.*, 1924, **131**, 173—190).—Of the three binary systems, those of copper-nickel and chromium-nickel have already been investigated; the first shows complete miscibility in both the liquid and solid states, the melting and freezing-point curves running continuously between the melting points of the pure metals, whilst the system chromium-nickel is homogeneous in the liquid phase, with a series of mixed crystals in the solid state, the curves showing a deep minimum at  $1300^{\circ}$ , 40—42% of nickel. The system copper-chromium has now been examined thermally and microscopically; there is only partial miscibility in the liquid state, with a eutectic near the copper end (1.5% Cr,  $1076^{\circ}$ ), the limits within which a mixture of two liquids is formed being 37% to 93% chromium, above  $1470^{\circ}$ . In the solid state only heterogeneous mixtures of two crystal species are obtained, chromium and the eutectic rich in copper.

The triangular and solid diagrams for the ternary system have been worked out, and as might be expected from the binary systems, the heterogeneity of the copper-chromium system is partly removed by addition of nickel. Mixed crystals were obtained from alloys in the following proportions: Cr : Ni : Cu = (1) 10 : 80 : 10; (2) 10 : 60 : 30; (3) 20 : 60 : 20; (4) 30 : 60 : 10, and (5) 40 : 55 : 5. With proportions of nickel below 55%, only heterogeneous systems were obtained. Of the alloys, only (1) showed magnetic properties. The alterations in composition of the liquid and solid phases during crystallisation are worked out in great detail in a number of cases.

Microscopical examination of the ternary mixed crystals showed dendritic inclusions, which may be due to the change from  $\beta$ - to  $\alpha$ -nickel in the solid state. The alloys which solidify as mixtures show under the microscope beautifully-formed chromium-nickel crystals in a cupreous matrix. Alloys in the region of non-miscibility in the liquid state solidify as shown under the microscope in separate layers more or less emulsified.

Alloys of composition (2) and (5) were examined for resistance to acids, but were found to be resistant only to concentrated nitric acid, also to sodium hydroxide; the influence of chromium in the ternary system, therefore, is not apparent in this respect. The alloys forming mixed crystals may be mechanically useful, but as the samples obtained appeared under the microscope to contain inclusions, partly of slag and partly of gas, no detailed measurements were made. These alloys have a high silvery lustre even after exposure to moist air, but on heating become tarnished with a dark green oxide. S. I. L.

**Chromium-Molybdenum and Chromium-Molybdenum-Copper Alloys.** E. SIEDSCHLAG (*Z. anorg. Chem.*, 1924, **131**, 191—202).—Molybdenum dissolves readily in molten chromium until the mass contains 25% of the former; in investigating alloys richer in molybdenum, the finely powdered metals were mixed

and compressed into briquettes, which were then heated, but for proportions of molybdenum above 50%, the initial solidification temperature could not be measured. The curve shows a eutectic at  $1460^{\circ}$ , 22.7% Mo. The liquid is homogeneous, but no mixed crystals are formed below 22.7% Mo, the solid consisting of chromium crystals and the eutectic mixture; above this proportion, the solid consists of molybdenum crystals containing 2.5% Cr, and the eutectic. The alloys are not likely to be mechanically useful; those rich in chromium cut glass with remarkable ease.

The system copper-molybdenum has already been found to be heterogeneous in both the liquid and solid states, whilst chromium and copper form no mixed crystals, and are only partly miscible in the liquid state. In the ternary system, the three metals remain separate in the solid state. Electrolytic copper was melted with powdered chromium and molybdenum, and the thermal analysis carried out in the usual way; no mixed crystals are formed, the solids consisting of the three metals, with the eutectics Cr-Mo and Cr-Cu. The diagram shows that alloys of copper with up to 38% of chromium should dissolve up to 8% of molybdenum, whilst chromium-molybdenum mixtures should dissolve up to 7% of copper.

S. I. L.

**The Ageing of Chromium Hydroxide. Alkali Chromites and their Solutions.** R. FRICKE and O. WINDHAUSEN (*Z. anorg. Chem.*, 1924, **132**, 273—288).—The solubility of pure chromium hydroxide (approximately  $\text{Cr}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ) in sodium hydroxide solution was determined at the ordinary temperature. From the solubility curve and the analysis of the solid phase, the existence of sodium chromite in the liquid is concluded. The formation of chromite precedes the formation of the hydroxide. With sodium hydroxide below 10*N*, primary sodium chromite is formed, whilst above 10*N* the solution contains also tertiary sodium chromite. Potassium chromite is similarly produced; below 8*N*-alkali only the primary chromite is formed, whilst above 8*N* the solution contains also secondary chromite. From solutions of potassium chromite which have stood for a long time, needle-shaped crystals of the formula  $\text{Cr}_2\text{O}_3 \cdot 3\text{K}_2\text{O} \cdot 8\text{H}_2\text{O}$  are obtained.

The ageing of chromium hydroxide was also studied. It is more rapid under alkali solution than under water, and the rate of ageing increases with increase of hydroxyl-ion concentration. Increase of temperature also accelerates the ageing. The ageing is not the result of dehydration, and is analogous to the behaviour of beryllium hydroxide and the so-called crystalline aluminium hydroxide (cf. A., 1920, ii, 387). The development of crystalline structure is not revealed by examination with the micropolariscope, and the ageing is attributed to an increase in the size of the particles. The subsequent separation of chromium hydroxide from clear chromite solutions is the result of the ageing of chromium hydroxide already present in the solution in the colloidal state. From cryoscopic measurements, the lowering of the freezing point by potassium chromite in 1.5*N*-solution increases with the time of standing, and

is due to hydrolysis, resulting in the formation of secondary chromite, colloidal hydroxide, and finally precipitated hydroxide. The existence of chromite in solution is also demonstrated by potential measurements.

J. B. F.

**The Action of Chromisulphuric and Ferrisulphuric Acids on the Decomposition of Hydrogen Peroxide.** J. POIZAT (*Bull. Soc. chim.*, 1923, [iv], **33**, 1606—1611).—The action of chromisulphuric, chromidisulphuric, chromitrisulphuric, and ferrisulphuric acids (cf. Recoura, A., 1892, ii, 783; 1893, ii, 470; 1903, ii, 599, 600) on hydrogen peroxide of various concentrations was studied, and from the results obtained the corresponding values of the velocity constants of the reaction were calculated. The values thus found decreased with the progress of the reaction; this is ascribed to the dissociation of the acids into sulphuric acid and metallic sulphate, with subsequent partial hydrolysis of the latter. In the case of ferrisulphuric acid, an additional effect is produced by reason of the catalytic activity of the liberated ferric sulphate.

H. J. E.

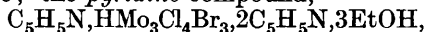
**The Chlorides of Bivalent Molybdenum, Tungsten, and Tantalum. II. Tri-molybdenum Hexachloride ["Molybdenum Dichloride"] and its Derivatives.** K. LINDNER, E. HALLER, and H. HELWIG (*Z. anorg. Chem.*, 1923, **130**, 209—228).—The "dichloride,"  $\text{Mo}_3\text{Cl}_6$ , is obtained in good yield by heating molybdenum powder in carbonyl chloride at 610—620°; approximately 90% of the metal is obtained as dichloride in one operation. Other organic chlorine compounds may be used, but the reaction is less smooth. The powdered mass, on treatment with ether containing 5% of ethyl alcohol in an extraction apparatus and subsequent evaporation in a vacuum, yields the compound  $\text{Mo}_3\text{Cl}_6 \cdot \text{EtOH}$  as a light yellow powder stable in air; the alcohol cannot be removed by heating in an inert atmosphere without decomposition. Addition of alcoholic silver nitrate to the alcoholic solution precipitates silver chloride; the mother-liquor deposits the compound  $\text{Mo}_3\text{Cl}_4(\text{NO}_3)_2 \cdot \text{EtOH}$  on keeping, but on immediate treatment of the filtrate with ether, the nitrate,  $\text{Mo}_3\text{Cl}_4(\text{NO}_3)_2$ , is obtained. The compound  $\text{Mo}_3\text{Cl}_6(\text{NH}_3)_2 \cdot 2\text{EtOH}$  is obtained by precipitating a saturated solution of the dichloride with ether and passing in dry ammonia; it is a bright yellow powder decomposing at 100°.

The compound  $\text{H}[\text{Mo}_3\text{Cl}_7 \cdot \text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}$ , already described (A., 1922, ii, 509), when heated in a stream of hydrogen chloride yields the compound  $\text{Mo}_3\text{Cl}_6 \cdot \text{H}_2\text{O}$ ; both these substances may be hydrolysed in stages, yielding compounds in which the ratio  $\text{Mo} : \text{Cl}$  is 3 : 6, 3 : 5, and 3 : 4; the complex  $[\text{Mo}_3\text{Cl}_4]$  is stable and not ionisable. The chloro-acid,  $\text{H}[\text{Mo}_3\text{Cl}_7 \cdot \text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}$ , when treated with pyridine and excess of hydrogen chloride in alcoholic solution, gives *pyridinium* salts containing alcohols, which separate as yellow, crystalline solids; the compounds  $\text{C}_5\text{H}_5\text{N} \cdot \text{H}[\text{Mo}_3\text{Cl}_7 \cdot \text{H}_2\text{O}] \cdot \text{MeOH}$  and  $\text{C}_5\text{H}_5\text{N} \cdot \text{H}[\text{Mo}_3\text{Cl}_7 \cdot \text{H}_2\text{O}] \cdot \text{EtOH}$  are described, the former being dimorphous. If the reaction is carried out in amyl alcohol, the

alcohol-free *pyridinium* salt,  $C_5H_5N.H[Mo_3Cl_7.H_2O]$ , is obtained; recrystallisation from the lower alcohols gives the alcoholate salts. Other alcohols give analogous products. From the mother-liquors, and by varying the reaction conditions, a series of compounds in the anion of which the ratio  $Mo:Cl$  varies from 3:7 to 3:9 may be obtained, but these were not more closely examined. In presence of a large excess of hydrogen chloride, the compounds  $(C_5H_5N)_3H_3Mo_3Cl_9.3MeOH$ ,  $(C_5H_5N)_3H_3MoCl_9.3EtOH$ , and  $(C_5H_5N)_3H_3MoCl_9.C_5H_5OH$  were obtained, from which on heating the compound  $C_5H_5N.H(Mo_3Cl_7)$  is formed.

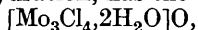
By treating solutions of the chloro-acid in the minimum quantity of hydrochloric acid with concentrated solutions of metallic chlorides, the salts  $K[Mo_3Cl_7].3H_2O$  and  $NH_4[Mo_3Cl_7].1.5H_2O$ , and their anhydrous compounds were obtained; the pyridine compound,  $C_5H_5N.H[Mo_3Cl_7]$ , readily forms alcohol-additive products, and similar compounds are obtained with aniline, carbamide, ethylenediamine, and triaminopropane.

The hydroxide,  $Mo_3Cl_4(OH)_2$ , described by Blomstrand (*J. pr. Chem.*, 1859, 77, 96) on treatment with hydrobromic acid yields an acid,  $H[Mo_3Cl_4Br_3.H_2O].3H_2O$ , which readily passes into the compound  $Mo_3Cl_4Br_2.H_2O$ . With a large excess of hydrobromic acid the compound  $H_2[Mo_3Cl_4Br_4.4H_2O].2H_2O$  is obtained. Salts of these bromine-substituted chloro-acids are obtained by the methods described above; the *pyridine* compound,



and its derivative,  $C_5H_5N.H[Mo_3Cl_4Br_3]$ , and the *potassium* salt,  $K_4Mo_{12}Cl_{25}Br_3.16H_2O$ , and the corresponding anhydrous salt are described.

Blomstrand's crystalline hydroxide (*loc. cit.*) has now been shown to have the formula  $[Mo_3Cl_4.2H_2O](OH)_2.6H_2O$ ; at  $35^\circ$ , it loses  $5H_2O$ , at  $67-100^\circ$ ,  $6H_2O$ , and at  $200-300^\circ$ ,  $7H_2O$ ; the final product, which resists further dehydration, has the composition



and is dark brown; it dissolves completely without residue in aqueous ammonia. An analogous series of amorphous hydroxides is described, which yield the same end-product on dehydration. Modified hydrolysis of the chloro-acid yields hydrated products of the compound  $Mo_3Cl_5.OH$ ; hydrolysis with very little water yields a chloride,  $[Mo_3Cl_4.2H_2O]Cl_2.2H_2O$ , which on dehydration yields  $[Mo_3Cl_4.2H_2O]Cl_2$ , in which compound two chlorine atoms are ionisable and replaceable by other anions.

Determinations were made of the molecular weight of the pyridine salt,  $C_5H_5N.H[Mo_3Cl_7.H_2O]$ , from the depression of the freezing point of nitrobenzene; the average of three readings gave 717, the formula requiring 634.  
S. I. L.

### Compounds of Tervalent Molybdenum and Tungsten.

A. ROSENHEIM and T. H. LI (*Ber.*, 1923, 56, [B], 2228-2230).—Double chlorides of tervalent molybdenum were obtained by electrolysing strongly acid solutions of molybdic acid, using a mercury cathode, adding suitable chlorides to the deep purplish-red

solution, and evaporating, the double chlorides of the general formula  $R_3MoCl_6$  separating in red needles. The following chlorides were isolated and analysed:  $K_3MoCl_6$ ;  $(NH_4)_3MoCl_6 \cdot 2 \cdot 5H_2O$ ;  $(C_5H_6N)_3MoCl_6 \cdot 2H_2O$ ; and the ethylenediammonium salt,  $(C_2H_{10}N_2)_3(MoCl_6)_2 \cdot 7H_2O$ . The crystalline aniline salt was not obtained in a pure state. The following double bromides were obtained as deep blood-red crystals by similarly electrolysing a solution of molybdic acid in hydrobromic acid:  $(NH_4)_2MoBr_5 \cdot 2H_2O$ ;  $(C_5H_6N)_3MoBr_6 \cdot 4H_2O$ . Two purplish-red double fluorides prepared analogously had the following formulæ:  $(NH_4)_3Mo_2F_9 \cdot 2H_2O$ ;  $K_3Mo_2F_9 \cdot 2H_2O$ . Compounds of tervalent tungsten are under investigation; the following compounds are noted:  $KWF_4 \cdot H_2O$ ;  $(NH_4)WF_4 \cdot H_2O$ .  
F. A. M.

**The Precipitation of Tungstic Acid.** J. A. M. VAN LIEMPT (*Rec. trav. chim.*, 1924, **43**, 30—35; cf. A., 1923, ii, 867).—A comparison was made of the rate of precipitation of tungstic acid from sodium tungstate solution by different acids, using an optical method similar to that used by Lottermoser for a similar investigation (A., 1915, ii, 267). The increasing opacity of the solution is measured by passing a beam of light from a constant source through the solution under examination to a light-sensitive cell which is connected to a galvanometer. The results obtained are influenced considerably by the method of mixing the two solutions. When the tungstate solution is added drop by drop to the acid, the rate of precipitation appears to depend on the degree of dissociation of the acid. Thus 0.25*N*-nitric, perchloric, and hydrochloric acids showed very nearly identical precipitation curves, whilst 0.25*N*-sulphuric acid showed a much more extended period of induction, before precipitation started. This last curve, however, was very similar to that given by 0.18*N*-hydrochloric acid, the dissociation of which is about equal to that of 0.25*N*-sulphuric acid. When the acid was added to the tungstate solution, the slower the addition of the acid (up to the limit of twelve minutes) the slower was the subsequent precipitation of the tungstic acid. The form of the curves indicates that the action is autocatalytic, but this deduction is probably incorrect, since the precipitate is not simply the compound  $WO_3$ , but contains water, and processes of hydration and dehydration probably occur during the precipitation.

E. H. R.

**Simultaneous Presence of Cesium and the Rare Earth [Yttrium] Metals in some Zirconium Minerals.** E. URBAIN and G. URBAIN (*Compt. rend.*, 1924, **178**, 265—266).—The atomic weights of the zirconium and of the rare earth fractions of a number of zirconium minerals have been determined. The zirconium fractions of the different minerals (purified through the oxychloride,  $ZrOCl_2 \cdot 8H_2O$ , which does not cause removal of cesium) gave atomic weights varying from 90.3 to 95.0, as determined from the conversion of sulphate into oxide. The higher atomic weights, corresponding with a higher cesium content, were obtained with

minerals of higher rare earth (yttrium metals, atomic weight 96—93) content.

E. E. T.

**The Properties of Colloidal Vanadium Pentoxide.** A. V. DUMANSKI (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 703—733).—Vanadium pentoxide sols were prepared by the method of Biltz (A., 1904, ii, 324) and their properties investigated. It is shown that the red sols so obtained contain negatively charged particles which gradually become smaller as the solution ages. The electrical conductivity at first gradually falls and reaches a certain minimum value after some days, whilst the viscosity of the solution increases; there is, however, no constant relationship between these two properties. Dilution causes a gradual rise in the conductivity, which finally assumes a constant value; this is doubtless due to the hydrolysis of the colloidal particles with the production of ions. The red colour of the sol finally changes to yellow, and yellow solutions are found to contain no colloidal particles when viewed in the ultramicroscope. The effect of temperature on the conductivity has also been studied. A rise of temperature is shown to produce an increase in conductivity; on cooling, the conductivity of the solution does not immediately regain its former value.

The sol shows the usual behaviour towards electrolytes; thus, it is readily coagulated by the addition of barium chloride, a small quantity of barium being adsorbed at the same time. On keeping for some hours in contact with excess of reagent, the amount of barium adsorbed by the colloid increases, and the composition of the solid coagulum approximates to that of barium hexavanadate,  $\text{BaH}_2\text{V}_6\text{O}_{17}$ , the conductivity of the solution rising at the same time. From the amount of barium adsorbed in the first stage, an approximate formula for the particles of the sol is deduced, namely,  $[\text{H}_2\text{V}_6\text{O}_{17}(\text{V}_2\text{O}_5)_6]'' + 2\text{H}^+$ , giving a molecular weight of 1678; cryoscopic measurements point to a similar formula. The equivalent of the particle of the sol is found to be approximately 1000.

The phenomenon of double refraction observed in vanadium pentoxide sols (Freundlich, A., 1916, ii, 442) is shown to be absent when the sol is quite clear, but is well marked when it becomes turbid or “gels”; gels therefore consist of particles arranged or oriented in a definite manner.

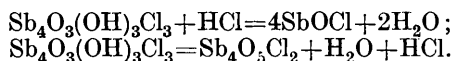
Finally, the effect of reducing agents was studied, and it was found that hydrazine produced an unstable green sol; the reduction proceeds to the  $\text{V}_2\text{O}_4$  stage or to  $\text{V}_2\text{O}_3$  if an excess of reducing agent be present.

G. A. R. K.

**Free Energy of Antimony Trioxide and the Reduction Potential of Antimony.** R. SCHUHMANN (*J. Amer. Chem. Soc.*, 1924, **46**, 52—58).—(See ii, 152).

**The System Antimonious Oxide-Hydrochloric Acid-Water.** C. LEA and J. K. WOOD (*J. Chem. Soc.*, 1924, **125**, 137—148).—The behaviour of hydrated antimonious oxide towards solutions of hydrochloric acid of varying concentrations and also the action of water on antimonious chloride are described. The transition point at which the compound  $\text{SbOCl}$  undergoes conversion into

$\text{Sb}_4\text{O}_5\text{Cl}_2$  occurs when the total concentration of chlorine is approximately  $8N$ , and this latter oxychloride only ceases to exist when the total concentration of chlorine is reduced to  $0.1N$ . These results are not in agreement with those of other observers; thus according to Le Chatelier (A., 1885, 630) the transition point of  $\text{SbOCl}$  to  $\text{Sb}_4\text{O}_5\text{Cl}_2$  occurs at a chlorine concentration of  $2.12N$ . The amorphous precipitate produced on the addition of water to antimonious chloride is not  $\text{SbOCl}$ , but has a variable composition and is probably an adsorption product formed by the adsorption of hydrochloric acid by a highly hydrated form of antimonious oxide. The adsorbed acid slowly interacts with the hydrated oxide, forming that oxychloride which most nearly approximates to its own composition. One of these metastable oxychlorides is Cooke's oxychloride,  $\text{Sb}_4\text{O}_3(\text{OH})_3\text{Cl}$ , whilst from more concentrated solutions a crystalline compound is deposited to which the formula  $\text{Sb}_4\text{O}_3(\text{OH})_3\text{Cl}_3$  is assigned. This crystalline compound can apparently change into either  $\text{SbOCl}$  or  $\text{Sb}_4\text{O}_5\text{Cl}_2$ , according to the conditions :



J. B. F.

**A New Compound of and Test for Palladium.** V. N. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 701—702).—On adding a solution of sodium nitroprusside to a solution of palladium chloride, the mixture sets to a stiff jelly; on keeping, the jelly shrinks and the solid residue, after washing and drying, consists of *palladium nitroprusside*,  $\text{PdFe}(\text{CN})_5\text{NO}$ , in the form of a greenish-grey powder. The formation of the jelly can serve as a test for palladium, but it is less sensitive than the glyoxime test.

G. A. R. K.

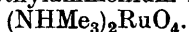
**A New Method for the Preparation of Soluble Ruthenium Compounds from Ruthenium.** F. KRAUSS and H. KUKENTHAL (*Z. anorg. Chem.*, 1924, **132**, 315—317).—Four g. of ruthenium are fused in a silver crucible with 30 g. of potassium hydroxide and 4 g. of potassium nitrate and heated until the melt is quite fluid. On cooling, the melt is extracted with 200 c.c. of water and the precipitate collected. The precipitate is then stirred with 100 c.c. of alcohol at  $40^\circ$ . The residue recovered either by decantation or filtration is washed with water and dissolved in dilute hydrochloric acid. The resulting solution is evaporated to dryness on a water-bath and the residue treated with water. To the dark brown solution potassium hydroxide or alkali carbonate is cautiously added and the ruthenium hydroxide precipitated, the liquid being still slightly acid. The precipitate is collected, washed with water until the filtrate remains clear, drained at a suction pump, and dried. The resulting black compound is free from alkali and chlorine, and is the starting material for subsequent preparations.

J. B. F.

**Alkali Ruthenates.** F. KRAUSS (*Z. anorg. Chem.*, 1924, **132**, 301—314).—Rubidium and caesium ruthenates have been prepared,



having the composition  $\text{Rb}_2\text{RuO}_4$ ,  $\text{Rb}_2\text{RuO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Cs}_2\text{RuO}_4$ , and  $\text{Cs}_2\text{RuO}_4 \cdot \text{H}_2\text{O}$ , respectively; they resemble in properties the corresponding potassium salts. Solutions of potassium and rubidium ruthenates on treatment with concentrated ammonia solution yield a salt having the composition  $(\text{NH}_4)_2\text{RuO}_4$ . In the case of the caesium salt, a product of less definite composition is obtained. From the properties of this compound it is not a true ammonium salt, but exists as "dioxy-dihydroxy-diammine-ruthenium" having the formula  $\text{RuO}_2(\text{OH})_2 \cdot 2\text{NH}_3$ . When treated with hydrochloric acid, it yields "dioxy-diaquo-diammine-ruthenon-chloride,"  $\text{Ru}_2\text{O} \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O} \cdot \text{Cl}_2$ , which is reconverted into the dihydroxy-compound on treatment with ammonia solution. On treating a solution of potassium ruthenate with a 10% solution of trimethylamine, a precipitate is obtained having a composition corresponding with trimethylammonium ruthenate,



J. B. F.

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## Analytical Chemistry.

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**Electrometric Titration. Its Methods and Application to certain Metallurgical Analyses.** G. A. SHIRES (*J. Chem. Met. Min. Soc. S. Afr.*, 1923, **24**, 129—145).—The paper contains a brief account of the theory of electrometric titrations, a description of an inexpensive apparatus for carrying out the work and examples showing the application of the method to the determination of iron in ores and of chromium, vanadium, and manganese in steels. For oxidimetric titrations, the titration cell was provided with a platinum wire electrode, connected through a moving coil mirror galvanometer to one end of the bridge wire, and a normal calomel electrode connected to the sliding contact of the wire. A 2-volt accumulator was connected across the ends of the potentiometer. The stirrer consisted of a bent glass rod supported in a greased glass tube and driven through a cork pulley and a belt of thin cord by means of a small motor at 200 revolutions per minute. In using the apparatus, the galvanometer is kept steady by moving the slider with each small change in *E.M.F.* until a small addition of solution produces a sudden big deflection in the spot of light, thus indicating the end-point. In titrating ferrous chloride solutions with dichromate, the liquid should be strongly acid with hydrochloric acid; otherwise a definite end-point is not obtained. Ferric chloride solutions may be titrated with stannous chloride with great accuracy by the use of the above apparatus as the end-point is marked by a change in the sign of the *E.M.F.* and the spot of light is violently deflected. [*Cf. B.*, 1924, 220.]

A. R. P.

**Substitution of Borchers' Metal for Platinum in Electro-analysis.** M. BLEESEN (*Z. anal. Chem.*, 1923, **63**, 209—228).—Borchers' metal is an alloy containing 65 to 60% of nickel, 30 to 35% of chromium, 2 to 5% of molybdenum, and 0.2 to 1% of silver. It becomes passive after use as an anode with low-voltage currents, but for use as a cathode it should preferably be rendered passive by treatment with strong nitric acid. The most suitable form of electrode was found to be a sand-blasted gauze or spiral. With cathodes of this material, smooth adherent deposits of copper from nitric acid and ammonia solutions, of nickel from ammonia solutions, of antimony from sodium sulphide solutions, and of tin from oxalate solutions were obtained. The deposits are readily removed by suitable treatment with acids in the cold without any serious loss in weight, although several mg. may be lost if hot acids are used. Borchers' metal cannot be used as anodes, and hence is not suitable for the deposition of lead or manganese peroxides.

A. R. P.

**Improvements in Colorimetry.** R. V. STANFORD (*Biochem. J.*, 1923, **17**, 839—843).—Details are given of various instrumental improvements in the dilution colorimeter already described by the author (*A.*, 1913, ii, 856), in which the concentration, and not the thickness of the layer examined, is altered. The improvements make for greater convenience and ease of manipulation.

J. P.

**Magnesium Perchlorate Trihydrate as a Drying Agent for Steel and Organic Combustion Analysis.** G. F. SMITH, M. BROWN, and J. F. ROSS (*Ind. Eng. Chem.*, 1924, **16**, 20—22; cf. Willard and Smith, *A.*, 1922, ii, 850).—Magnesium perchlorate may be prepared by adding magnesium oxide or carbonate to perchloric acid of 68—70% concentration. The solution is boiled until crystallisation begins, cooled, and the crystalline mass centrifuged. The hexahydrate crystals so obtained, when heated at 138—140° for fifteen to twenty hours in a good vacuum, yield the trihydrate, in which state it retains its original crystalline form and is very porous. No decomposition occurs in dehydration under these conditions. At 250°, the anhydrous salt can be prepared, but in this case slight traces of impurity cause decomposition, and the trihydrate is therefore to be preferred as a drying agent. It is a trustworthy substitute for phosphoric oxide in the analysis of steel by combustion, and it may equally well replace calcium chloride for organic combustions. It is easily handled, offers little resistance to the passage of gas, and when exhausted can be readily regenerated.

C. I.

**The Preservation of Standard Solutions of Oxalic Acid.** S. ISHIMARU (*J. Chem. Soc. Japan*, 1922, **43**, 767—772).—Decomposition of 0.1*N*-solutions of oxalic acid, when preserved in the dark, is negligible after one hundred and forty-eight days, and no greater when kept in transparent bottles. In the latter case,

contrary to Riegler (A., 1896, ii, 676), the addition of sulphuric acid increased the amount of decomposition. K. K.

**Quantitative and Qualitative Analysis with the Aid of Röntgen Rays.** D. COSTER (*Chem. Weekblad*, 1924, 21, 59—62).—The X-ray spectrum has great advantages for identification purposes, since it is purely a property of the individual atom, however combined or admixed the element examined; it is simple and characteristic, and can detect 1% of a specific element in 1 mg. of substance. It can, unfortunately, only be employed for solid elements heavier than sodium.

The use of X-rays in quantitative determinations of hafnium by addition of tantalum and comparison of the intensity of the tantalum and hafnium lines in the spectra obtained, is described. Additions of tin and antimony were also made in some determinations. The opinion is expressed that by careful elimination of present sources of error, very accurate determinations of concentrations of specific elements may be made by this method.

S. I. L.

**The Colorimetric Determination of the Hydrogen Exponent of Soil.** I. M. KOLTHOFF (*Chem. Weekblad*, 1923, 20, 675—677).—The determination of the hydrogen-ion concentration of soils by the electrometric method does not give accurate results, owing to the great resistance. Colorimetric methods are also unsatisfactory, because of the difficulty of obtaining clear, colourless solutions. The colorimetric method gives much better results if the mixture of soil and water is dialysed, using a parchment membrane, for twenty-four hours.

S. I. L.

**Application of the Mercury Electrode in the Electrometric Titration of Halides, Cyanides, Sulphides, and Thiosulphates.** I. M. KOLTHOFF and E. J. A. H. VERZYL (*Rec. trav. chim.*, 1923, 42, 1111).—Several titration curves omitted from the previous paper on this subject (A., 1923, ii, 873) are now published.

J. F. S.

**Formation of Periodate.** R. LANG.—(See ii, 165.)

**Bromometry as a Substitute for Iodometry.** W. MANCHOT and F. OBERHAUSER (*Z. anorg. Chem.*, 1923, 130, 161—167).—Bromine can be used in place of iodine in many volumetric determinations. It is best used in solution in 20—22% hydrochloric acid, such solutions being stable for many weeks, but care must be taken to avoid volatilisation losses. Arsenious acid is rapidly and accurately titrated, using indigo-carmin as indicator, and the method has the advantage over the iodine titration that it can be carried out in acid solution, hydrobromic acid not acting as a reducing agent in solutions containing less than 26% of free hydrochloric acid.

[With E. BAUER.]—Bromine oxidises thiosulphate quantitatively, forming sulphuric acid; 1 mol. of thiosulphate requires 8 atoms of bromine.

Bleaching powder may be analysed by adding it to an acidified bromide solution, and titration of the liberated bromine with arsenious acid; hypochlorite solutions and chlorine water may be analysed in the same manner. Manganese dioxide, lead dioxide, and potassium dichromate may be determined by heating with hydrochloric acid, the liberated chlorine being led either into bromide solution, with subsequent titration of the liberated bromine by means of arsenious acid, or into excess of arsenite solution, the excess being titrated with bromine solution. Permanganate may be added directly to an acidified bromide solution.

S. I. L.

**The Bromometric Determination of Ozone.** W. MANCHOT and F. OBERHAUSER (*Z. anorg. Chem.*, 1923, **130**, 168—172).—The work of Treadwell (A., 1906, ii, 123) has been repeated, and his conclusion that bromides may be used in place of iodides either in acid or in neutral solution confirmed; under suitable conditions, however, the reaction may be carried out much more quickly. The gas is introduced into a nitrometer, and shaken with 10—15 c.c. of 0.2*N*-potassium bromide in acid solution; if hydrochloric acid is used, the solution must be not weaker than *N*/1 with respect to this, whereas if sulphuric acid is used, it must be not less than 2*N*. The mixture is cooled and shaken, then washed into standard arsenite solution, and the excess of the latter determined with a standard solution of bromine in hydrochloric acid (see preceding abstract). With less acid solutions the results are too low. No hydrogen peroxide is formed with concentrations of ozone of less than 10%. The reaction is complete in ten minutes.

S. I. L.

**Determination of Dissolved Air in Small Quantities of Water.** H. G. BECKER and W. E. ABBOTT (*J. Soc. Chem. Ind.*, 1923, **42**, 484—486*T*).—The method depends on the fact that, when potassium hydroxide is dissolved in water, the dissolved air is expelled and may be collected and measured. The apparatus used consists of a graduated measuring tube, 2.5 mm. in diameter, provided at the top with a three-way, mercury-sealed tap and having at its lower end a bulb of about 30 c.c. capacity; this bulb is connected with a larger cylindrical bulb provided with a side tube and a tube at its lower end connected with a mercury reservoir. A piece of solid potassium hydroxide is introduced through the side tube; this is securely closed with a rubber stopper, the whole apparatus is filled with mercury, and the desired volume of the water (*e.g.*, 50 c.c.) is admitted through the tap. The mercury level is then lowered so that the water comes into contact with the potassium hydroxide and, when evolution of gas ceases, the volume of the bubble is measured in the graduated tube. The gas is then passed over into a small absorption vessel containing alkaline pyrogallol solution and the residual volume of nitrogen is measured subsequently. A number of other substances, such as ammonium sulphate, ammonium chloride, etc., may be used in place of the potassium hydroxide.

W. P. S.

**Volumetric Determination of Dithionic Acid in presence of Sulphurous and Thiosulphuric Acids, by Oxidation with Bromine in the Nascent State.** C. MAYR and I. SZENTPÁLY-PEYFUSS (*Z. anorg. Chem.*, 1924, **131**, 203—208).—Whilst dithionic acid is not affected by bromine in the cold, it is completely oxidised to sulphuric acid by bromates in boiling hydrochloric acid solution. A measured quantity of bromate is employed, the excess of liberated bromine being distilled over into iodide solution and determined in the usual manner. The method allows of a high order of accuracy. If sulphurous and thiosulphuric acids be present, in addition to the oxidation at the boiling point by bromine, a second oxidation with bromine in the cold is carried out (this oxidises the latter two acids only, forming sulphuric acid in each case), and an iodine oxidation in the cold, which oxidises sulphurous to sulphuric acid, and thiosulphuric to tetrathionic acid. From the quantities of halogen required in each of the three cases, the quantities of dithionic, sulphurous, and thiosulphuric acids present may be calculated.  
S. I. L.

**Method for the Rapid and Quantitative Removal of Ammonia from Solutions, Especially Applicable to the Micro-quantitative Determination of Nitrogen and Urea in Products of Living Origin.** R. V. STANFORD (*Biochem. J.*, 1923, **17**, 847—850).—An apparatus is described for the quantitative removal of ammonia from small volumes of fluid and its determination, by vacuum distillation into sulphuric acid followed by nesslerisation.  
J. P.

**Nesslerisation, and the Avoidance of Turbidity in Nesslerised Solutions.** R. V. STANFORD (*Biochem. J.*, 1923, **17**, 844—846).—Folin and Youngburg's method of "direct nesslerisation" (*A.*, 1919, ii, 304), does not give clear solutions. Turbidity may be avoided in pure solutions of ammonium salts, containing not more than 0.03 mg. of nitrogen per c.c., if the Nessler reagent be added drop by drop, with constant shaking, to the ammonia solution. Excess of alkali or of Nessler reagent, and the presence of urease produce turbidity.  
J. P.

**The Determination of Hydroxylamine with Permanganate.** A. KURTENACKER and R. NEUSSER (*Z. anorg. Chem.*, 1923, **130**, 199—204).—A comprehensive survey of the attempts described in the literature to carry out the oxidation quantitatively in acid, neutral, and alkaline solution, shows that a successful method has not been evolved. In acid solution, the results vary with the concentrations of hydroxylamine, acid, and permanganate and with time, temperature, etc., and under the most favourable conditions not more than 2.7 atomic proportions of oxygen are used. In neutral solutions all these factors, as well as the nature of the acid used for neutralisation, affect the results. Similar variations were obtained in alkaline solution, and in no case could conditions be found which would allow of quantitative determination.  
S. I. L.

**Determination of Phosphine in Acetylene.** T. E. PERKS (*Analyst*, 1924, **49**, 32—33).—Lunge and Cedercreutz's method for determining phosphine in acetylene (A., 1898, ii, 54) gives inaccurate results but is rendered satisfactory when certain modifications are introduced. [Cf. B., 1924, 161.] T. H. P.

**The Separation of Arsenic from Antimony and Tin.** W. STRECKER (*Z. anal. Chem.*, 1923, **63**, 252).—Sulphur dioxide or a sulphite is a more suitable reducing agent for quinquevalent arsenic than sodium thiosulphate as recommended by Järvinen (A., 1923, ii, 254; cf. Moser, *ibid.*, 788). Thionyl chloride is more satisfactory still, as it provides, not only the necessary reducing agent, but also the hydrochloric acid required to prevent the hydrolysis of the antimony chloride. A. R. P.

**Reduction of Arsenic Acid by Sulphurous Acid in Presence of Vanadic Acid.** V. AUGER and (MLLE.) L. ODINOT (*Compt. rend.*, 1924, **178**, 213—214).—If sulphur dioxide is passed into a boiling solution of arsenic and vanadic acids in 10% aqueous sulphuric acid, very little reduction of arsenic occurs, the result being scarcely affected by the presence or absence of vanadium (cf. Trautmann, A., 1911, ii, 544). If, as recommended by Gooch ("Methods in Chem. Anal.," 1912, 350), the solution, saturated in the cold with sulphur dioxide, is heated in a closed vessel for an hour on the water-bath, complete reduction to arsenious acid and vanadyl salt takes place. If a trace of potassium iodide is added to a warm solution containing arsenic, vanadic, and sulphuric acids, reduction by sulphur dioxide may be effected in fifteen minutes in an open vessel. After removal of sulphur dioxide by boiling, and of iodide by adding silver nitrate, the usual titration with permanganate may be carried out. E. E. T.

**The Iodometric Determination of Carbon Disulphide.** E. ANDRÉ (*Bull. Soc. chim.*, 1923, [iv], **33**, 1678—1681).—The method in general use is not trustworthy, as the reaction on which it is based is not quantitative. A series of experiments showed that the quantity of carbon disulphide which corresponds with 1 c.c. of standard iodine solution varies with the proportion of the former with respect to the amount of alcoholic potash present. Further, the time occupied in the attainment of equilibrium may introduce another source of error. H. J. E.

**The Perchlorate Method for the Determination of Potassium in Soils, Fertilisers, etc.** H. J. PAGE (*J. Agric. Sci.*, 1924, **14**, 133—138).—Samples of perchloric acid were found to contain considerable amounts of chloric acid, and as a consequence figures obtained by their use for the determination of potassium were very untrustworthy. It is also indicated that in Neubauer's method for the analysis of soil extracts, the addition of 0.1 g. of calcium carbonate (instead of the usual 0.5 g.) to soils deficient in carbonates suffices. Smaller amounts of perchloric acid may then be used in the subsequent analysis. A. G. P.

**A New Method for the Volumetric Determination of Barium.**

B. N. ANGELESCU (*Bul. Soc. Chim. România*, 1923, 5, 72—74).—A volumetric method for the determination of barium is described, based on the precipitation of barium pyroborate by the addition of a solution of sodium pyroborate to the solution of a barium salt and the subsequent hydrolysis, in dilute solutions, first to the metaborate and then to the hydroxide:  $\text{BaB}_3\text{O}_7 + 3\text{H}_2\text{O} = \text{Ba}(\text{BO}_2)_2 + 2\text{H}_3\text{BO}_3$ ;  $\text{Ba}(\text{BO}_2)_2 + 4\text{H}_2\text{O} = \text{Ba}(\text{OH})_2 + 2\text{H}_3\text{BO}_3$ . The barium solution (containing 0.20—0.25 g. of barium) is treated with 40 c.c. of alcohol and 40 c.c. of 0.1*N*-sodium pyroborate solution. A white precipitate is formed and, after fifteen minutes on the water-bath, precipitation of the barium is complete. After cooling, the solution is diluted to 100 c.c. and 25 c.c. are titrated with 0.1*N*-hydrochloric acid to determine the excess of pyroborate, dimethyl-aminoazobenzene being used as an indicator. The maximum error recorded is 0.46%.

J. W. B.

**The Accuracy of the Potentiometric Titration of Zinc with Ferrocyanoide.**

I. M. KOLTHOFF and E. J. A. H. VERZYL (*Z. anorg. Chem.*, 1924, 132, 318—320).—The accuracy of the method was tested with specially purified materials. Zinc sulphate solution containing about 1 g. of the salt in 100 c.c. of distilled water was titrated with 0.025*M*-potassium ferrocyanide solution, containing 0.1% of ferricyanide. In neutral solution at 15° and 65°, respectively, approximately 1% too little reagent was required. If 3 c.c. of 0.25*N*-sulphuric acid were added, the error at 15° was reduced to 0.7%, whilst when 3 c.c. of 0.25*N*-sulphuric acid and 3 g. of potassium sulphate were added the error was about 0.5%. For all other proportions the amount of reagent required was too small. (Cf. A., 1922, ii, 580.)

J. B. F.

**Schoenbein's Test Applied to the Micro-investigation of**

**Copper-ions.** H. IMBERT, R. IMBERT, and P. PILGRAIN (*Bull. Soc. chim.*, 1924, [iv], 35, 60—64).—The Schoenbein test for cyanides has been adapted to the detection and determination of copper in aqueous solution, at concentrations as low as five parts in ten million. The copper solution is treated with a few drops of freshly prepared guaiacum resin solution, and dilute potassium cyanide solution (0.15% for neutral and 1.5% for acid copper solutions) added, when a blue coloration appears. If excess of potassium cyanide is added, the brown coloration produced by the action of alkali on guaiacum masks the blue colour, which, similarly, does not appear in presence of an excess of acid.

The new test for copper is about twenty times as sensitive as that afforded by ammonia, ferrocyanide, or iodide, and considerably more sensitive than the electrolytic test. Electrolysis of copper solutions, followed by testing the cathode deposit (molybdic reagent), barely allows of the detection of copper at concentrations of one part in a million.

Distilled water (from a copper still), after being concentrated from 6 l. to 250 c.c., gave a positive test for copper by the new



method, which has also been applied to the detection of copper in preserved vegetables and in blood. E. E. T.

**Micro-gravimetric Determination of Copper as Copper Benzoinoxime.** R. STREBINGER (*Mikrochemie*, 1923, **1**, 72—74).—The copper solution, containing a few mg. of copper, is rendered slightly ammoniacal, heated, and treated with 1% alcoholic benzoinoxime solution. The mixture is heated in a boiling water-bath for twenty minutes, the precipitate then collected on a small filter, washed with very dilute ammonia and alcohol, dried, and weighed. The precipitate contains 22.02% of copper. W. P. S.

**Use of Hypophosphorous Acid in Gravimetric Analysis. II. Determination of Mercury, Gold, and Palladium, and a Method of Separating them from Other Metals.** L. MOSER and M. NIESSNER (*Z. anal. Chem.*, 1923, **63**, 240—252).—For the determination of mercury the solution of chloride or sulphate, free from nitric acid, is heated on the water-bath with an excess of 0.5*M*-hypophosphorous acid; 8 to 10 c.c. of concentrated hydrochloric acid are added and heating is continued until the precipitated mercury collects into a globule. This is collected on a Gooch crucible, washed free from acid with warm water, then with alcohol and finally with ether, and dried at 30°. The presence of lead, zinc, cadmium, or iron in the solution does not affect the results.

For the determination of gold, either alone or in the presence of platinum, the faintly acid solution of the chloride is treated with 2 g. of sodium chloride and heated to boiling. A 0.25*M*-solution of hypophosphorous acid is added together with a little filter-pulp, and heating is continued until the precipitate coagulates. The gold is collected on a hardened paper, washed free from chlorine with 1% acetic acid, ignited, and weighed. Any platinum in the filtrate may be separated by boiling with sodium formate.

Palladium may be determined in a similar way to that employed for gold, except that no filter pulp is necessary as the precipitated metal readily coagulates after boiling for a few minutes. If platinum is present in the solution the precipitate will be seriously contaminated with this element. Bismuth and copper are incompletely precipitated as metal by hypophosphorous acid. A. R. P.

**The Determination of Manganese. I. The Bismuthate Method.** T. R. CUNNINGHAM and R. W. COLTMAN (*Ind. Eng. Chem.*, 1924, **16**, 58—64).—It has been believed that the accurate determination of manganese by oxidation with sodium bismuthate was impracticable if the weight of manganese present exceeded 50 mg. As this limitation rendered the method unsuitable for the analysis of the metal or of alloys rich in manganese, the reactions involved in the method were examined in detail. It was found that a 60% excess of sodium bismuthate over the theoretical quantity was necessary to render oxidation complete, the quantity recommended being 2.6 g. of 80% sodium bismuthate for each 100 mg. of manganese present. A further possible source of error is the liability of the permanganic acid formed to decompose before it can be determined. An investigation of the stability of per-

manganic acid in different concentrations in contact with 11—22% nitric acid solution showed that the rate of decomposition fell with increasing dilution to a negligible amount at 0.05N. If nitric acid more dilute than 11% is used, oxidation may be incomplete. A standard time of oxidation of one minute is recommended. With such precautions, accurate and concordant analyses using up to 500 mg. of manganese were obtained. Examples, with working details, of the application of the method to metallic manganese, manganese ore, and ferro-manganese are given. C. I.

**Simplified Qualitative Analysis of the Ammonium Sulphide Group.** E. RUPP (*Ber. Deuts. pharm. Ges.*, 1923, **33**, 258—262).—The filtrate from the hydrogen sulphide treatment is boiled, oxidised with nitric acid, and treated with an excess of ammonia. The precipitate is collected and washed; a portion is tested for iron by the ferrocyanide test, a second portion is fused with sodium nitrate and carbonate on the end of a magnesia rod, when the presence of chromium is indicated by the production of a yellow stain, and the remainder of the precipitate is boiled with sodium hydroxide and hydrogen peroxide, the insoluble material filtered off and the solution acidified, then rendered ammoniacal, when any gelatinous precipitate indicates aluminium. The filtrate from the original treatment with ammonia is treated with ammonium sulphide and the washed precipitate is stirred with 5% hydrochloric acid. The insoluble material is collected and dissolved in dilute aqua regia. The solution is divided into two parts, one of which is treated with an excess of potassium nitrite, which gives a characteristic yellow precipitate of the double nitrite if cobalt is present. A drop is taken from the second portion, after addition of ammonia in slight excess, and placed on a piece of filter-paper previously soaked in a 1% alcoholic dimethylglyoxime solution; a pink spot proves the presence of nickel. Zinc is tested for in the solution of the sulphides soluble in acid, by treatment with sodium acetate and hydrogen sulphide, and manganese in the same solution by means of sodium hydroxide and by the fusion test. If phosphoric acid is present in the original sample it is removed by evaporation with nitric acid and metastannic acid; oxalic acid is removed by evaporation and ignition of the residue at 300°. A. R. P.

**The Nickel-Dimethylglyoxime Reaction by Reflected Illumination.** F. KIRSCHNER (*Mikrochemie*, 1923, **1**, 88).—The dimethylglyoxime reaction will detect the presence of nickel in a drop of solution containing 1 mg. of nickel and 300 mg. of iron per 3 litres of water. When examined by reflected light (dark ground) the crystals have an emerald-green colour, the usual red colour being seen only where the crystals are agglomerated. W. P. S.

**Critical Studies on Methods of Analysis.** I. **Nickel.** L. A. CONGDON and C. H. BELGE (*Chem. News*, 1924, **128**, 67—68). II. **Chromium.** L. A. CONGDON and R. K. GURLEY (*ibid.*, 68—70). III. **Manganese.** L. A. CONGDON and J. L. NEAL, jun. (*ibid.*, 70—71).—I. Comparative tests on a standard nickel solution showed that equally good results were obtained by the dimethyl-

glyoxime gravimetric method and the cyanide volumetric method, but that Carnot's method (A., 1918, ii, 138) gave results that were appreciably low.

II. The iodometric determination of chromium as chromate and the gravimetric determination as barium chromate in acetic acid solution appear to be the only methods in common use that yield trustworthy results. Precipitation of the chromate with mercurous nitrate gives low figures, as a small part of the chromate is reduced to chromic salt and escapes precipitation. The chromic phosphate method gives low and discordant results. Addition of an excess of ferrous salt to a chromate solution, followed by titration of the excess with permanganate, yields figures that are about 0.5% too low.

III. The determination of manganese in steel may be performed with great accuracy by the persulphate, bismuthate, or lead peroxide methods; the first-named method was found to be the most rapid.

A. R. P.

**Reactions of Chromium, Iron, and Aluminium in the Presence of Tartaric Acid and of Glycerol.** S. HAKOMORI (*J. Chem. Soc. Japan*, 1922, 43, 629—647).—The hydroxides of chromium, iron, and aluminium are not precipitated by ammonia in the presence of tartaric acid or of glycerol. The cause has been studied by the aid of the absorption spectrum of their solutions, their electrical conductivities, the ultramicroscope, and by dialysis. In the presence of a large quantity of tartaric acid, the cause is attributed to the formation of complex salts from 1 atom of the metal and 1 mol. of the acid. When the quantity of the acid is small, it is attributed mainly to the formation of colloidal solutions of the metallic hydroxide. In the case of chromium, the velocity of the formation of the complex salt is not large, but is increased by heating, *i.e.*, by increasing the concentration of the free acid. In the case of iron, the ferric salt is reduced to ferrous salt by long contact with tartaric acid. In the presence of glycerol, the cause is mainly attributed to the formation of a colloidal solution.

K. K.

**Qualitative Micro-analysis.** F. FEIGL (*Mikrochemie*, 1923, 1, 74—78).—Characteristic angular crystals are obtained when a drop of a solution of a tervalent antimony salt in dilute hydrochloric acid is treated with a small quantity of solid pyrogallol; tartaric acid may be added to prevent formation of basic antimony compounds. Copper salts yield a green, amorphous precipitate when treated with an alcoholic solution of benzoinoxime. Very small quantities of manganese may be detected by placing a drop of the solution and a drop of potassium hydroxide solution on a microscope slide, partly evaporating the mixture, and then adding a drop of a solution of benzidine in acetic acid. Blue particles or granules develop in the mixture. The sensitiveness of this test is 1 in  $5 \times 10^7$ . Benzidine may also be used for the detection of phosphoric acid, a blue coloration being obtained when a drop of phosphate solution is treated successively with molybdic acid

solution (in nitric acid), benzidine solution (in acetic acid) and ammonia.

W. P. S.

**Determination of Antimony by Means of Permanganate in Hydrochloric Acid Solution.** O. COLLENBERG and G. BAKKE (*Z. anal. Chem.*, 1923, **63**, 229—240).—For the titration of antimony with permanganate the metal is usually obtained in sulphuric acid solution and a certain amount of hydrochloric acid is added before titration. If the latter is at least 10 c.c. and not more than 19 c.c. of strong acid (*d* 1.19) per 100 c.c., the end-point is very sharp and the rose colour is persistent for at least a minute. The method gives results which agree closely with those obtained gravimetrically if the atomic weight of antimony is taken as 121.8 (cf. Knop, this vol., ii, 54). Petriccioli and Reuter's modification, in which the solution is diluted until a turbidity forms, which is discharged with a few drops of hydrochloric acid (A., 1902, ii, 177), gives low results. The addition of tartaric acid to prevent hydrolysis leads to high figures unless not more than 1 mol. of the acid is added for each atom of antimony and the concentration of tartaric acid does not exceed 0.05%. At the same time, at least 12 c.c. of hydrochloric acid per 100 c.c. must be present.

A. R. P.

**The Determination of Niobium, Tantalum, and Titanium in Minerals.** E. W. TODD (*Univ. Toronto Studies, Geol. Ser.*, 1923, No. 16, 40—45).—Metzger and Taylor's method (A., 1909, ii, 702) is the most trustworthy and the easiest to manipulate, providing the error introduced by the presence of titanium is corrected. The method, with modifications, is as follows. Five g. of the mineral are fused with potassium hydrogen sulphate, and the mass is disintegrated by boiling with 300 c.c. of water and 5 c.c. of sulphuric acid. Sulphurous acid is added until its odour is plainly perceptible, and the precipitate (which contains niobium, tantalum, silicon, and much of the titanium, contaminated with tin, zirconium, iron, aluminium, calcium, uranium, and the rare earths) is allowed to settle in the hot solution. After removal of silica with hydrofluoric acid, the residue is fused with potassium carbonate, the mass extracted with 100 c.c. of hot water, filtered, and washed. The fusion, extraction, and filtration are repeated, using less potassium carbonate. The solution, which contains niobium, tantalum, and some of the titanium and tin, is acidified with sulphuric acid, boiled for ten minutes, and treated with sulphurous acid. Ammonium sulphide is added, tin removed by washing with water, and the precipitate ignited in an atmosphere of ammonium carbonate. Its titanium content is determined colorimetrically after fusion with potassium hydrogen sulphate. In the remainder, the reduced niobium and tantalum oxides are titrated with 0.1N-potassium permanganate, according to Metzger and Taylor's method, in order to determine the niobium, a deduction being made for the reduced titanium.

CHEMICAL ABSTRACTS.

**Micro-electrolytic Determination of Gold.** K. FUCHS (*Mikrochemie*, 1923, **1**, 86—87).—Small quantities of gold (0.25 to 5.0 mg.)

may be deposited from a potassium cyanide solution, using a current of 3 volts and 3 ampères; the solution is boiled during the electrolysis, which requires ten minutes, then cooled rapidly, and the current passed through the solution for a further five minutes. The electrodes are removed before the current is interrupted, and the cathode is washed successively with water, alcohol, and ether, and dried over a flame.

W. P. S.

**Test for Palladium.** V. N. IVANOV.—(See ii, 196.)

**The Evaluation of the Purity of Various Organic Products by the Dichromate Method.** E. C. GREY (*Biochem. J.*, 1923, **17**, 768—771).—Aliphatic organic substances may be oxidised by a mixture of potassium dichromate and sulphuric acid to carbon dioxide, unless methyl groups are present, when acetic acid is also formed. By volumetric measurement of the amount of dichromate used in the oxidation, the substance oxidised may be quantitatively determined. Tables are given whereby the method may be applied to mixtures of various aliphatic alcohols and acids. Succinic acid is exceptional in that it resists oxidation by the method described.

J. P.

**Analysis of Naphthalenesulphonic Acids and Naphthalene.** W. S. CALCOTT, F. L. ENGLISH, and F. B. DOWNING (*Ind. Eng. Chem.*, 1924, **16**, 27—30).—An examination of the oxidation of naphthalenesulphonic acids by means of a solution of vanadic acid in 70% sulphuric acid shows that the conversion to phthalic or sulphophthalic acids proceeds smoothly and quantitatively, the position and number of the sulphonic acid radicals having no influence on the rate of oxidation or, of course, on the oxygen required. In the case of the mono- and di-sulphonic acids, the oxidation is quantitative within the accuracy of the methods of determination; in the case of the trisulphonic acids, the conversion is 97.5—98.0%. By titrating the vanadium reduced in the reaction with 0.1*N*-permanganate solution, the naphthalene content of a mixture of naphthalenesulphonic acids can therefore be determined and the method may be extended to the determination of the naphthalene content of crude naphthalene. The sulphonic acid content of a similar mixture may be determined by boiling with barium carbonate to remove sulphuric acid, filtering and precipitating the barium present in the filtrate as soluble sulphonate with dilute sulphuric acid. A rapid approximate method is also described for determining small proportions of moisture in refined naphthalene. [Cf. *B.*, 1924, 167.]

C. I.

**The Determination of Reducing Sugars by means of Alkaline Copper Solution.** L. MAQUENNE (*Bull. Soc. chim.*, 1923, [iv], **33**, 1681—1692).—A criticism of the work of Boutot ("Contribution à l'étude du dosage des sucres réducteurs au moyen des liqueurs cuproalcalines," Paris, 1922) and of Fleury and Boutot (*A.*, 1922, ii, 879), in which it is stated that the suggested modifications of the author's method (*A.*, 1922, i, 920) are unnecessary and have, in addition, certain disadvantages.

H. J. E.

**Application of the Iodometric Method to the Analysis of Sugar Products.** C. L. HINTON and T. MACARA (*Analyst*, 1924, 49, 2—24).—The authors have investigated the effects, on the reduction by dextrose, lactose, sucrose, and lævulose of iodine in alkaline solution, of varying the proportions of iodine and alkali used, the time and the temperature. Under suitable conditions dextrose and lactose are oxidised quantitatively to monobasic acids; sucrose and lævulose exert slight, but under definite conditions constant, reducing powers. A standard method of procedure is suggested and the corresponding iodine values are given for the different sugars. [Cf. *B.*, 1924, 189.] T. H. P.

**Iodometric Method for the Determination of Nitrogen in Osazones.** D. R. NANJI (*Biochem. J.*, 1923, 17, 761—763).—For the determination of nitrogen in osazones, 5—60 mg. are heated on the boiling water-bath with 10 c.c. of *N*-hydrochloric acid for one hour. The mixture is neutralised with 10 c.c. of *N*-sodium hydroxide, acidified with dilute acetic acid, and made alkaline with pure sodium hydrogen carbonate. The alkaline solution is added to a known excess of 0.02*N*-iodine, and after completion of the reaction with the phenylhydrazine the residual iodine is determined by titration with standard thiosulphate. A table is given from which the amount of nitrogen is read off from the volume of iodine solution used. J. P.

**A New Method for the Determination of Acetic Acid in Acetic Anhydride.** J. H. WALTON and L. L. WITHROW (*J. Amer. Chem. Soc.*, 1923, 45, 2689—2693).—Measurements are made of the inhibitory effect of from 1 to 5% of acetic acid on the catalysis, by strychnine, of the unimolecular decomposition of formic acid in the presence of acetic anhydride (cf. Schierz, A., 1923, ii, 231). The results, which are exhibited graphically, may be used as the basis of a method for determining acetic acid in acetic anhydride, when present in concentrations within the limits mentioned. Very pure acetic anhydride may be obtained from the commercial, 97% material, by treating it with sodium, first for several days at the ordinary temperature, and then for several hours at the boiling point (under reduced pressure), and finally distilling over a mixture of sodium and sodium acetate. W. S. N.

**Gold-beater's Skin Test for Tannins.** P. H. PRICE (*Analyst*, 1924, 49, 25—29).—Atkinson and Hazleton's test (*A.*, 1922, ii, 793) is modified as follows. The gold-beater's skin is successively soaked in 2% hydrochloric acid solution instead of water, washed thoroughly to eliminate the acid, treated for thirty minutes with 1 c.c. of the solution to be tested, washed for fifteen minutes, treated with 1 c.c. of 1% ferrous sulphate or chloride solution for fifteen minutes, and washed for two minutes. Staining of the skin indicates the presence of tannin. If the liquid is to be tested for phlobaphens, the gold-beater's skin, treated as above, is then left covered with 1 c.c. of 5% hydrochloric acid solution for two minutes and afterwards washed for two minutes. T. H. P.

**A Source of Error in Employing Magenta-Sulphurous Acid Solution as a Test for Formaldehyde in Ethyl Alcohol.** J. L. MAYER (*J. Amer. Pharm. Assoc.*, 1923, **12**, 698—700).—Undiluted ethyl alcohol not containing formaldehyde gives a positive colour reaction with magenta-sulphurous acid solution in the presence of sulphuric acid, but the reaction is not given with 5—10% aqueous ethyl alcohol. The test will detect 0.00005 c.c. of 37% formaldehyde in 5 c.c. of solution. The test employed by the author consists in the development of a purple colour at the surface of contact of sulphuric acid with 1 c.c. of a solution containing  $10^{-6}$  c.c. of 37% formaldehyde and five drops of 0.5% morphine sulphate solution, on gentle rotation. Dodsworth and Lyons's modification of Hepner's test (using iron, sulphuric acid, and albumin) and the morphine sulphate test are both very sensitive, detecting  $10^{-6}$  c.c. of 37% formaldehyde in 1 c.c. of solution; they are easily performed, and trustworthy. CHEMICAL ABSTRACTS.

**The Qualitative Tests for Acetone Bodies: their Significance and Value.** E. J. BIGWOOD and W. S. LADD (*J. Biol. Chem.*, 1923, **58**, 347—361).—The sodium nitroprusside colour reaction is given by both pure acetone solutions and solutions of acetoacetic acid as free as possible from acetone (cf. Harding and Ruttan, A., 1913, ii, 79). Only the acetoacetic acid solution, however, gives a colour reaction with ferric chloride. The sodium nitroprusside reaction is intensified by the presence of sodium chloride and of other electrolytes present in urine. Neither colour reaction serves as a quantitative test. E. S.

**Determination of the Iodine Value [of Fats and Oils].** S. SCHMIDT-NIELSEN and A. W. OWE (*Videnskap. Skrifter*, 1923, No. **15**, 5—77).—A systematic investigation of various methods for determining the iodine value of oils and of the conditions governing the reactions involved. Preference is given to the Hübl method since substitution of halogen does not take place as in the Wijs method; the latter method is, however, more rapid. The Waller, Hanus, and Winkler methods yield less trustworthy results.

W. P. S.

**Determination of Butter Fat and Coconut Fat in Fat Mixtures.** G. H. LEOPOLD and W. J. DE MOOY (*Rec. trav. chim.*, 1924, **43**, 103—124).—A graphic method is described for determining butter fat and coconut fat in mixtures such as margarine, containing, in addition, only neutral fats. [Cf. *B.*, 1924, 222.]

E. H. R.

**The Quantitative Preparation of Urea from Human Urine.** W. O. MOOR (*Biochem. Z.*, 1923, **143**, 423—432).—Urea may be quantitatively recovered as the oxalate from the vacuum-dried residue of urine by extraction with methyl alcohol, and the addition of oxalic acid to the extract dissolved in amyl alcohol. The urea may be determined by Kjeldahl's method either directly on the oxalate, or in the solution obtained by treating the oxalate with calcium carbonate. Comparing the results obtained by this

method with those given by the Mörner-Sjöquist method, the latter is found to give high results which run parallel with the capacity of the alcoholic extract to decolorise permanganate.

J. P.

**Iodometric Determination of Thiosinamine : Comparison with Other Methods, and Applications.** MORVILLEZ and R. MEESEMACKER (*J. Pharm. Chim.*, 1923, [vii], 28, 442—445).—To 10 c.c. of the thiosinamine solution, acidified with sulphuric acid, are added *A* c.c. (excess) of 0.1*N*-iodine. After keeping in the dark for fifteen minutes, the unchanged iodine is titrated back with 0.05*N*-sodium thiosulphate, in the presence of starch and 10 c.c. of chloroform. The titre of the thiosinamine solution is given by  $(A - n/2)0.0058 \times 10$ , where *n*=no. of c.c. of 0.05*N*-thiosulphate required. The method, which gives results in close agreement with those found by the methods of Volhard and of Denigès, is applicable to the estimation of allylthiocarbimide in oil of mustard.

W. T. K. B.

**Volumetric Method for the Determination of the Alkaloids.** A. IONESCU and (MLLE.) E. SPIRESCU (*Bul. Soc. Chim. România*, 1923, 5, 74—80).—The authors have extended their "mercurimetric" method previously described for acetone (A., 1923, ii, 666) to the determination of several alkaloids. The procedure is as previously described, 1—10 c.c. of the solution of the alkaloid (containing 0.01—0.03 g.) being employed, the final dilution with water before the addition of the sodium nitroprusside solution being with 200 c.c. of water. Each c.c. of 0.1*N*-sodium chloride solution is equivalent to the following quantities of alkaloids: quinine, 0.0066 g.; strychnine, 0.014 g.; morphine, 0.0083 g.; codeine, 0.01 g.; cocaine, 0.009 g. The corresponding theoretical figures for the precipitate ( $\text{HgI}_2$ )<sub>3</sub>.(Alk.HI)<sub>2</sub> are: quinine, 0.0127 g.; strychnine, 0.011 g.; morphine, 0.0102 g.; codeine, 0.0107 g.; cocaine, 0.0102 g.

J. W. B.

**Beckurts' Method for Determining the Alkaloids in Cinchona Extract.** G. RECORDATI (*Boll. Chim. Farm.*, 1923, 62, 707).—When 5 c.c. of liquid cinchona bark extract are extracted with chloroform, the residue from the chloroform solution should be dissolved in 100 c.c. of 0.01*N*-hydrochloric acid and the excess of the latter determined by titration with sodium hydroxide solution. [Cf. B., 1924, 150.]

T. H. P.

**Preparation and Determination of Arginine.** A. KOSSEL and R. E. GROSS (*Sitzungsber. Heidelberg Akad. Wiss.*, [B], 1923, 1—6; from *Chem. Zentr.*, 1923, iii, 1151—1152).—Protein is hydrolysed with hydrochloric acid and the products, after removal of the excess of acid and neutralisation with sodium carbonate, are treated with "Naphthol-yellow-S" or 2:3-dinitro-1-naphthol-7-sulphonic acid (m. p. 150—151°). From the arginine salt thus obtained, the dye acid may be liberated by boiling with 33% sulphuric acid, and serves as a means of determining the arginine. Data are given for the solubilities of the arginine, histidine, lysine,



guanidine, and ammonium salts. The arginine salt has m. p. above  $260^{\circ}$ ; histidine salt,  $224-226^{\circ}$  (decomp.); lysine salt,  $213^{\circ}$  (decomp.); guanidine salt, m. p.  $274^{\circ}$  (decomp.); the salts contain equimolecular proportions of base and acid, except in the case of the ammonium salt which contains two molecules of base to one of acid. The dye acid also gives crystalline precipitates with agmatine, methylguanidine, creatinine, tetramethylenediamine, and purine derivatives. With carbamide, a crystalline salt of the composition  $\text{CO}(\text{NH}_2)_2 \cdot \text{C}_{10}\text{H}_6\text{O}_2\text{N}_2\text{S}$  is obtained. G. W. R.

**The Determination of Fibrinogen. II.** W. STARLINGER (*Biochem. Z.*, 1923, **143**, 179—185).—A further survey of the methods available for the determination of fibrinogen (cf. A., 1923, ii, 890). The addition of sodium citrate, either as solid or in solution, to native plasma has a purely additive effect on the refractive index. The following readily applicable method for the determination of fibrinogen by differential refractometry is given. The native plasma (*NP*) obtained by centrifuging 4 c.c. of blood is collected in paraffined vessels. A known volume of this—approximately 1 c.c.—is treated with citrate and the refractive index of the native salt plasma (*NSP*) so obtained is measured. The residue of the *NP* is allowed to coagulate spontaneously, and the native serum (*NS*) from this compared in the refractometer with the salt serum obtained by heating the *NSP* at  $55^{\circ}$  for five minutes. The differences between the *NP* (obtained by a formula from *NSP*) and *NS*, and between the *NSP* and salt serum give respectively the native fibrinogen and the salt fibrinogen. J. P.

**A Substitute for Acid Hæmatin as the Standard in Sahli's Hæmoglobinometer.** L. D. FELTON (*Bull. Johns Hopkins Hosp.*, 1923, **34**, 357—359).—Sufficient 40% sodium hydroxide solution is added to a 10% solution of pyrogallol in 75% ethyl alcohol to yield a solution containing 10% of sodium hydroxide. The mixture is oxidised by bubbling air through it over-night, or as long as a precipitate is formed. The supernatant liquid is decanted, and the tarry residue dissolved in water. Precipitation with 75% alcohol and re-dissolution are continued until the product is no longer strongly alkaline. After being washed with 95% alcohol, the precipitate is left in the air until the odour of alcohol has disappeared, and is then dried in a desiccator over sulphuric acid. The standard liquid, prepared by dissolving the powder in a Sørensen phosphate buffer mixture of  $p_{\text{H}}$  6, matches acid hæmatin very closely down to a value representing 60%.

CHEMICAL ABSTRACTS.

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## General and Physical Chemistry.

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**Spectroscopic Confirmation with Cæsium of Bohr's Distribution Numbers.** E. FUES (*Z. Physik*, 1924, **21**, 265—280).—A development of previous work (A., 1923, ii, 1, 103, 353), in which it was shown how the potential gradient inside the atom could be computed from the spectral terms. The mathematical treatment has been extended from the point of view of relativity. The underlying assumption that a single value for the potential gradient can be employed for all possible orbits is only approximately correct, so that the numerical results can agree only to a few units per cent. Within these limits, it is possible to calculate a potential gradient within the cæsium atom giving orbits which correspond in their energy values on the one hand with the terms of the cæsium spectrum and on the other with the requirements of the quantum theory. From this are deduced the dimensions of the atom shells and further, by the introduction of Bohr's distribution numbers, those of the individual groups of orbits. This gives a "model" from which, together with very probable assumptions as to the distribution of the electrons, a second computation of the potential gradient within the atom is made. This is in good agreement with the first, which is considered to be a confirmation of Bohr's distribution numbers. The atomic field of magnesium has also been examined.

L. J. H.

**Interpretation of the Quantum Theory.** R. MECKE (*Z. Physik*, 1924, **21**, 26—37).—A discussion of the quantum theory in the light of the principles of relativity.

J. S. G. T.

**Theory of Radiation Transformation.** G. KORNFELD (*Z. physikal. Chem.*, 1924, **108**, 118—120).—An experiment designed to test Weigert's theory of the transformation of radiation in chemical reactions (A., 1923, ii, 3, 813) is described. According to this hypothesis, in a mixture of ozone and chlorine the decomposition of ozone by light is effected by radiation absorbed by the chlorine and re-emitted in a form which is absorbed by the ozone. To test this, the author has examined the formation of carbon dioxide in the presence of carbonyl chloride. It is known that carbon monoxide and oxygen combine under the influence of light in the presence of carbonyl chloride to form carbon dioxide. A quartz tube containing carbonyl chloride, carbon monoxide, and oxygen was surrounded by a second tube with quartz ends containing carbonyl chloride and submitted to light. It was found that no combination of oxygen and carbon monoxide occurred in the inner tube, thus demonstrating an error in the assumptions made in Weigert's hypothesis and furnishing further proof of the sensitisation of the reaction between oxygen and carbon monoxide by kinetic means.

J. F. S.

**Behaviour of the Many-lined Spectrum of Hydrogen at Low Temperatures.** L. CITRON (*Ann. Physik*, 1924, [iv], **73**, 470—476).—The intensities of the lines in the spectrum of hydrogen, cooled in liquid air, were compared with those at the ordinary temperature, errors due to impurities which might be condensed, or to the change in density on cooling being eliminated as far as possible. The greater number of the lines in the spectrum exhibited no change in intensity, but others showed variations ranging from  $-65\%$  to  $+140\%$ . It was not found possible, as a result of these experiments, to distinguish groups of related lines. M. S. B.

**Origin of certain Spectral Lines hitherto attributed to Oxygen.** W. JEVONS (*Phil. Mag.*, 1924, [vi], **47**, 586—590).—A re-examination of the  $O_1$  lines of Schniederjost (*Z. wiss. Phot.*, 1904, **2**, 283) shows that of the twenty-five lines of this series, twenty-one are not due to oxygen but may be ascribed to carbon impurity since they are successfully identified with Deslandre's carbon band-heads (A., 1888, 637; *Compt. rend.*, 1903, **137**, 460). The line  $2883.93 \text{ \AA}$ . is confirmed as a genuine oxygen line, although it is possibly an enhanced  $O_2$  rather than an  $O_1$  line. The remaining three,  $2895.37$ ,  $2858.81$ , and  $2708.18 \text{ \AA}$ ., may still be regarded as oxygen lines, pending further investigation of the bands. A. E. M.

**Spectrum of Manganese.** S. GOUDSMIT (*Nature*, 1924, **113**, 238).—With reference to Catalán's work (A., 1922, ii, 726) the values of some of the multiple terms are calculated. A. A. E.

**New Rays in the Arc Spectrum of Scandium in Air between 3200 and 2200  $\text{\AA}$ .** S. PIÑA DE RUBIES (*Anal. Fís. Quím.*, 1924, **22**, 49—55).—Scandium oxide was prepared from the oxalate by way of the acetylacetone salt. Using this material, a series of arc and spark spectrographs were obtained. The data are tabulated. G. W. R.

**Extreme Ultra-violet Spectra.** R. A. MILLIKAN and I. S. BOWEN (*Physical Rev.*, 1924, **23**, 1—34).—By the measurement and comparison of thirty plates obtained by the use of the vacuum apparatus and explosive spark previously described, numerous lines between  $136 \text{ \AA}$ . and  $1862 \text{ \AA}$ . have been identified as belonging to one or other of the elements, hydrogen, helium, lithium, beryllium, sodium, boron, carbon, nitrogen, oxygen, fluorine, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, chromium, and copper, the results being tabulated. A progression of spectra with atomic number in this region is revealed which is similar to that observed by Moseley for hard X-rays. The method is capable of revealing the full  $M$ -spectra of all the elements up to copper (atomic number 29); with a few omissions above 20, these have been observed. In the case of copper, this spectrum extends to about  $155 \text{ \AA}$ . Interpretation of the results in terms of Bohr's theory gives values of constants of the  $L$  and  $M$  levels of the atoms as follows: for sodium,  $L(I)$ ,  $\nu/R=2.826$ ; for magnesium,  $L(I)$ ,  $4.298$ ,  $L(II)$ ,  $3.402$ ,  $L(III)$ ,  $3.381$ ; for aluminium,

$L(I)$ , 6.045;  $L(II)$ ,  $L(III)$ , 5.008; for calcium,  $M(II)$ ,  $\nu/R=1.839$ ,  $M(III)$ , 1.810. There is evidence that in some cases the strongest lines are emitted by atoms from which all the valency electrons have been stripped.

A. A. E.

**Measurements of the Intensity and Direction of the Penetrating Radiation [occurring in the Earth's Atmosphere].**

W. KOHLHÖRSTER (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1923, **34**, 366—377).—The intensity of the penetrating radiation increases with the height above sea-level; at 3000, 4000, and 5000 metres, it liberates 4, 9, and 17 ions  $\text{cm}^{-3} \text{sec}^{-1}$ , respectively. The radiation is shown to be  $\gamma$ -rays with an absorption coefficient,  $\mu_{\text{H}_2\text{O}}=2.5 \times 10^{-3} \text{ cm}^{-1}$  as compared with that of  $\gamma$ -rays from Th- $D$ ,  $\mu_{\text{H}_2\text{O}}=3.3 \times 10^{-2} \text{ cm}^{-1}$ . It is thus harder than the  $\gamma$ -radiation from any known radioactive element. From measurements made in a glacier on the Jungfrau at 3550 metres, it is shown that the maximum intensity occurs between the hours 8 and 9 in the morning and evening when the milky way passes through the zenith. It is concluded that the radiation is emitted from the red stars of the milky way, and is due to the disintegration of radioactive elements unknown on the earth. There is no evidence supporting the view that either the sun or the earth is the source of this radiation.

W. E. G.

**Soft X-Rays from Carbon.** P. I. LUKIRSKY (*Phil. Mag.*, 1924, vi, **47**, 466—470).—A contribution to the study of the gap between "optical" and "X-ray" spectra. The photoelectric effect has generally been utilised for the detection of radiation in this difficult range. A variant of the usual method is here developed, in which the wave-length of the radiation is deduced from the velocity of the secondary electrons it releases from a target. These velocities are determined by an electrostatic method. The method is applied to the spectrum of carbon, and a value 48.9 Å. ( $\pm 1\%$ ) is obtained for the  $K$  line.

S. B.

**Soft X-Rays from Tungsten.** C. B. BOZZANI and C. T. CHU (*J. Franklin Inst.*, 1924, **197**, 183—197).—An analysis of the production of X-radiation from the point of view of the Bohr theory, calling attention to the fact that, when the energy contents of successive orbits are plotted against atomic numbers, these curves cross one another in the region of soft X-rays, indicating that for any particular atomic number either of two exterior orbits is equally probable. With the apparatus of Richardson and Bozzani (*A.*, 1922, ii, 14), a critical impact of 356 volts, identified with the  $M_3$  line, has been confirmed for molybdenum. With tungsten, critical values have been obtained at 33.6, 34.6, 39.2, 36.6, and 71 volt impacts ( $\pm 1 \text{ v.}$ ) and these figures are identified with the  $N_1$ ,  $N_2$ ,  $O_{3-4}$ , and  $O_5$  levels, respectively, and are in substantial agreement with the figures of Bohr and Coster (*A.*, 1923, ii, 110) and of Hjalmar (*A.*, 1923, ii, 448). Thus the five-quantum levels  $O_5$  and  $O_{3-4}$  have greater negative energies than the four-quantum levels  $N_1$  and  $N_2$ , which is in accordance with the Bohr theory.

A. E. M.

**Spectral Series in the Soft X-Ray Region.** G. K. ROLLEFSON (*Physical Rev.*, 1924, **23**, 35—45).—In the range 40—175 volts, nine critical radiation potentials (of the  $M$  series) were observed photoelectrically for iron, values for  $\nu/R$  being 3.46, 6.03, 7.05, 8.21, 9.63, 10.40, 10.88, 11.33, and 11.83, respectively. Corresponding values in the range 600—700 volts, for the  $L$  series, were 45.5, 47.0, and 51.5. All but the first and third of the first series of points fall on a straight line when plotted against  $1/N^2$  ( $N=7$ ); the convergence limit of the  $M_5$  series is found to be 13.1. For the  $L$  series,  $L_1(\nu/R)=59.0$ . The critical potentials are considered to correspond with emission lines of wave-length 264, 151, 129.6, 111.0, 94.6, 87.8, 83.9, 80.5, and 77.0 Å., respectively, and (for the  $L$  potentials) with 20.0, 19.4, and 17.7 Å. A. A. E.

**The N-Series of X-Ray Spectra.** V. DOLEJŠEK (*Z. Physik*, 1924, **21**, 111—119).—The identification and classification of lines in the  $N$  series of X-ray spectra of elements of atomic numbers ranging from 46 to 92 are critically discussed by means of the Bohr-Coster scheme of classification and the Moseley diagram, and the results compared with those found by Hjalmar (A., 1923, ii, 448). J. S. G. T.

**Röntgenographic-chemical Investigations. III. Quantitative Chemical Analysis by means of Röntgen Radiation.** H. STINTZING (*Z. physikal. Chem.*, 1924, **108**, 51—69; cf. this vol., ii, 83).—The possibilities of using X-ray spectrum analysis as an aid to chemical analysis are discussed. It is shown that with a sufficiently long exposure of the photographic film, X-ray spectrum analysis is capable of detecting even smaller quantities of elements than optical spectrum analysis. A method is put forward, the principle of which has been experimentally tested, which is capable of quantitatively determining the amount of a given element in a mixture. This method, which is not applicable to the lighter elements, hydrogen to sodium, consists in embedding the substance to be analysed together with a comparison substance in suitable quantity and state of subdivision in an indifferent substance. The quantitative relationships are deduced from the ratio of the intensities of the lines of the substance to be analysed and the comparison substance. The indifferent substance used was graphite and this mixed with powdered material was compressed with water-glass into pastilles. The method will only give usable results when a very efficient mercury vapour pump is used in the system. It is shown that the lighter elements may also be examined by the use of mixed crystals of suitable superposed space lattices, whereby, in vacuum, interference occurs between wave-lengths of double the normal value. This increase in the value of the lattice constant is sufficient to make it possible to obtain the X-ray spectra of the elements lighter than sodium and so determine them. J. F. S.

**Röntgenographic-chemical Investigations. IV. Measuring Instruments for High Vacua.** H. STINTZING (*Z. physikal. Chem.*, 1924, **108**, 70—81; cf. preceding abstract).—Two methods of

measuring the pressure in high vacua are described. The method of compressing the gas has been modified so that it may be used to measure pressures down to  $10^{-6}$  mm. of mercury. By combining this method with the discharge method, it is possible to measure pressures down to  $10^{-10}$  mm. of mercury. J. F. S.

**Variation of the Band Spectrum of Nitrogen produced by the Rare Gases.** W. STEUBING and M. TOUSSAINT (*Z. Physik*, 1924, 21, 128—137).—Very marked variations in the respective intensities of the various series of bands in the nitrogen spectrum are produced by the presence of large proportions of ionised argon (*Z. Physik*, 1923, 19, 271). The authors find that a similar effect, less marked both qualitatively and quantitatively, is produced by the presence of strongly ionised neon. The effect is not attributable to a variation of temperature of the discharge and is not produced by the presence of other electronegative or electropositive elements of high or low atomic weights. It is suggested that the effect produced by the ionised rare gases is attributable to an alteration in their respective electronic configurations occurring due to ionisation, and that the effect on the nitrogen band spectrum is produced in the case of argon when this gas becomes singly ionised, whilst multiple ionisation is necessary in order that the effect may be produced by neon. J. S. G. T.

**Continuous Spectrum of Hydrogen.** O. W. RICHARDSON and T. TANAKA (*Nature*, 1924, 113, 192—193).—Using as a source of electrons a filament either of tungsten, or of platinum coated with barium oxide about 2 cm. from a flat, circular nickel anode of 2.5 cm. diameter, provided with a central rectangular slit, the whole being enclosed in an evacuated silica tube, observations have been made of electron discharges in hydrogen which appear to supplement those described by Lemon (this vol., ii, 133). Over the range examined, except at the lowest pressures, there are two stable types of luminous discharge; at pressures from 0.05 to 0.1 mm., on a higher range of voltage, a third type is observed. The continuous spectrum is observed in the case of the low-voltage type. Details of the work are promised in a subsequent communication. A. A. E.

**Continuous Spectrum of Hydrogen.** F. HORTON and A. C. DAVIES (*Nature*, 1924, 113, 273—274; cf. A., 1923, ii, 820).—In view of the results previously obtained by the authors, it is probable that the change from a line spectrum to the continuous spectrum, which Lemon (this vol., ii, 133) found to occur on increasing the electron emission from the filament, was due to an accompanying decrease in the electric intensity between the filament and the part of the luminous discharge under observation. A. A. E.

**Properties of Dyed Materials.** H. WALES (*J. Amer. Chem. Soc.*, 1923, 45, 2420—2430).—The position of the maximum in the absorption spectrum of a solution of a dye determines the general

colour, but not the particular shade, both of the solution and of wool dyeings produced from it. A logical method of comparing dyes is to map the reflection spectrum of a dyed fabric. This has been done by a method similar to that of Meek and Watson (*Chem. Soc. Trans.*, 1916, **109**, 544), using wool coloured by means of a series of xanthene dyes having absorption maxima between 4875 and 5550 Å. The spectrophotometric curves from wool dyeings are much broader than those from aqueous or alcoholic solutions. Dyeings made on filter-paper have reflection curves identical with those of the dyed wool. The reflection spectra of thin gelatin films containing Eosin BN and erythrosin are the same as those of the wool dyeings, and the transmission spectra of these films correspond with those of the aqueous solutions. These results indicate that the dyes are actually dissolved in the wool. A discussion follows of the "simple solution" theory of dyeing. W. S. N.

**Variations in the Specific Refraction of Gases with Pressure below one Atmosphere.** V. POSEJPAL (*J. Phys. Radium*, 1923, [vi], **4**, 451—460).—Measurements of the variations in the refractive index of oxygen and hydrogen with pressure have been made at pressures below 760 mm. Using data for the refractive indices and the compressibilities of the gases, the change in their specific refraction is calculated over a wider pressure range. The specific refraction of oxygen (as of air and carbon dioxide) increases rapidly with pressure up to two or three atmospheres, above which it is nearly constant, whilst the values for hydrogen diminish at first with rise of pressure, becoming nearly constant above one atmosphere. A qualitative explanation of the behaviour of these gases is given, based on the Bohr theory. S. B.

**Formula for Rotation-dispersion.** F. BÜRKE (*Helv. Chim. Acta*, 1924, **7**, 163—167).—From the formula  $[\alpha] = k/\lambda^2 - \lambda_0^2$ , it is shown that the relation between wave-length and rotation for optically active substances is given by  $[\alpha] = C/\lambda_2 \cdot e^{\beta/\lambda^2}$ , where  $C$  and  $\beta$  are constants. This may be regarded as a generalised form of Boltzmann's formula,  $[\alpha] = A/\lambda^2 + B/\lambda^4$ . The formula may also be written  $\log \lambda^2[\alpha] = \log C + \beta\nu^2$ , where  $\nu$  is the frequency;  $\log \lambda^2[\alpha]$  is a linear function of the square of the frequency. This graphic relation is found to hold in the examples tested. E. H. R.

**Harmonic Frequency Relations in the Infra-red Absorption Spectra of Liquids and Solids.** J. W. ELLIS (*J. Opt. Soc. Amer.*, 1924, **8**, 1—9).—A determination of the respective frequencies of the bands in the infra-red absorption spectra of various substances, including cottonseed oil, a petroleum distillate, lard oil, kerosene, mesitylene, pentane, heptane, and water, suggests that a pair of chemically combined atoms, e.g., carbon and hydrogen, or oxygen and hydrogen, responds not only to an incident electromagnetic wave of a certain frequency, but also to waves the frequencies of which are whole multiples or approximately whole multiples of the fundamental frequency. J. S. G. T.

**Near Infra-red Absorption Spectra of some Organic Liquids.** J. W. ELLIS (*Physical Rev.*, 1924, **23**, 48—62).—Observations with a self-recording prism spectrograph were made in the following cases: methyl, ethyl, propyl, butyl, methylene, and ethylene halides, butyl nitrite, benzene, toluene, pentane, hexane, heptane, octane, mesitylene, *p*-xylene, chloroform, and bromoform. The wave-lengths of the absorption maxima, accurate to about  $0.01 \mu$ , are tabulated up to  $2.4 \mu$ . Visual observations were also made in the case of chloroform, benzene, toluene, acetone, methyl iodide, pentane, hexane, heptane, ethyl bromide, and ethyl ether. Besides common bands at about  $1.17$ ,  $1.38$ , and  $1.7 \mu$ , bands near  $0.9$  and  $1.0 \mu$  appear in many of the compounds; their presence is ascribed to the carbon-hydrogen linking, since they are not observed with carbon disulphide or carbon tetrachloride, or with compounds containing hydrogen without carbon. Shifts (up to  $\pm 0.03 \mu$ ) in the positions of the bands, for different liquids, may be due to a change in the relative intensity of the two components of the band.

A. A. E.

**Absorption of Potassium Vapour at High Temperatures, and Satellites accompanying the Members of the Principal Series.** A. L. NARAYAN and D. GUNNAYYA (*Physical Rev.*, 1924, **23**, 46—47).—The existence of the lines  $5340$ ,  $5300$ ,  $5205$ ,  $5100$ ,  $4970$ , and  $4831 \text{ \AA}$ . is confirmed. Fifteen satellites observed in the absorption spectrum are tabulated.

A. A. E.

**Absorption Spectra of some Derivatives of Phenol and other Substances.** J. E. PURVIS (*J. Chem. Soc.*, 1924, **125**, 406—418).—A continuation of previous work (*Chem. Soc. Trans.*, 1923, **123**, 2515). Absorption spectra of solutions (in some cases vapours) of many phenolic substances have been investigated. None of the substances exhibited any of the narrow vapour bands characteristic of phenol or of its simpler derivatives. The type, position, and intensity of absorption in the ultra-violet regions are regulated by the nature of the unsaturated elements or groups of elements acting as oscillatory centres. With increasing complexity, the vapour bands, and eventually the solution bands also, disappear. It is probable that completely saturated substances do not exhibit specific absorption in the ultra-violet. The general absorption depends on the translatory motion of the molecule, and this will be controlled by the weight (cf. A., 1913, ii, 363).

S. K. T.

**Fluorescence Spectra. II. Phenol and Phenolic Ether Vapours.** J. K. MARSH (*J. Chem. Soc.*, 1924, **125**, 418—423).—All the substances examined in continuation of previous work (*Chem. Soc. Trans.*, 1923, **123**, 3315) had similar spectra beginning with wave-lengths of about  $2750 \text{ \AA}$ ., attaining a maximum at about  $2900 \text{ \AA}$ ., and dying out at about  $3700 \text{ \AA}$ . Some substances (veratrole, methyl salicylate, benzyl alcohol, etc.), show a second spectrum in the blue region and phenyl mercaptan shows this spectrum alone. The weight of the side chain, the residual affinity in the side chain,



and ortho-substitution may influence the production of this second region. In the case of cresols, the fluorescence increases in the order ortho, meta, para. Phenol and anisole show a number of fine fluorescence bands, and *p*-cresol and its methyl ether each show a few.

S. K. T.

### Sensitised Fluorescence of Lead and Bismuth Vapours.

H. KOPFERMANN (*Z. Physik*, 1924, **21**, 316—325).—The method of sensitising fluorescence in vapours by the action of light absorbed by mercury vapour, used by Cario and Franck (*A.*, 1922, ii, 809), is applied to lead and bismuth vapours at 950°. Lead gave the lines: 4057·93, 3683·60, 3639·71, 2873·40, and 2833·17 Å. which agree with the series scheme of Grotrian (*A.*, 1923, ii, 710). Those of bismuth, 4722·72 and 3067·81 Å., suggest further regularities in the arc spectra of this element.

L. J. H.

### Fluorescence of some Organic Compounds. E. BAYLE and

R. FABRE (*Compt. rend.*, 1924, **178**, 632—635).—The dominant wave-length of the fluorescence spectra of a number of organic compounds has been measured, using, as source of excitation, the Hg<sub>3650</sub> line. The intensities of fluorescence are compared with that of sodium salicylate, which possesses a high fluorescence under these conditions. Novocaine shows an intense fluorescence, which permits of its ready detection in mixtures also containing cocaine and stovaine. These substances exhibit no fluorescence.

E. E. T.

### Polarised Light of Fluorescence. A. CARRELLI (*Atti R.*

*Accad. Lincei*, 1924, [v], **33**, i, 21—23).—The author confirms the results obtained by Weigert (*Physikal. Z.*, 1922, **23**, 232) and by Schmidt (*ibid.*, 233) with reference to the influence of the solvent on the polarisation of the fluorescent light emitted by a solution. It is also shown that the emission is polarised when it leaves the particles, so that the polarisation depends neither on dichroism of the solution nor on a phenomenon of luminous diffusion.

T. H. P.

### Phosphorescence of Fused Transparent Silica. D. L.

CHAPMAN and L. J. DAVIES (*Nature*, 1924, **113**, 309).—When oxygen or hydrogen is driven into fused quartz by the electric discharge, the quartz acquires the property of phosphorescing. After the glow has ceased, the quartz can again be made to phosphoresce by heating it; the phosphorescence caused by heating can be observed with no apparent diminution in intensity 24 hours after the stimulating discharge has been stopped.

A. A. E.

### Phosphorescence of Fused Transparent Silica. E. B.

LUDLAM and W. WEST (*Nature*, 1924, **113**, 389).—The observation of Chapman and Davies (preceding abstract) is confirmed. The phosphorescence exhibited by fused silica after exposure to the light from an aluminium spark has already been attributed to the fact that silica begins to absorb strongly in the neighbourhood of lines at 1860 and 1760 Å. The colour of the phosphorescence differs with the specimen of silica, and is probably due to impurity. A strong line at 2060 Å. is observed in the case of iodine.

A. A. E.

**Method of Determining Radiating and Ionisation Potentials not necessitating Low Pressures.** W. J. CLARK (*Proc. Durham Phil. Soc.*, 1922—23, 6, 312—322).—A stream of electrons from a cathode coated with lime passes through an adjacent gauze screen which can be charged positively to give varying accelerating potentials. The stream then traverses the gas and falls on an insulated conductor connected to an electroscope. Working with air at pressures of the order of 1 mm. of mercury, the author has determined the form of the curves showing the variation of the potential of the conductor and the current to it with varying accelerating potentials. The potential curves are influenced considerably by perturbing secondary effects, but the current curves, under suitable conditions, exhibit discontinuities from which approximate values of the radiating potentials of nitrogen and oxygen and of the ionisation potential of oxygen have been derived. S. S.

**Statistical Equilibrium and Mechanism of Ionisation by Electronic Impacts.** R. H. FOWLER (*Phil. Mag.*, 1924, [vi], 47, 257—277).—A discussion of the mechanism of the equilibrium between ions, electrons, and atoms in a dissociating gas, with special reference to the relative importance of collision and radiative processes. Klein and Rosseland's theory of non-radiative collisions has been amplified, and extended to ionisation by electronic impact. It is deduced that radiationless (collision) processes are negligible in the reversing layer of the sun ( $10^{-4}$  atm.) but are of greater importance than radiative captures at a pressure of 1 atm. Other astrophysical applications are mentioned. S. B.

**Theory of the Electron Current in Ionisation by Collision.** L. HEIS (*Physikal. Z.*, 1924, 25, 25—41).—The theory of Townsend on the ionisation of gases by collision (London, Constable, 1910) is not in good agreement with experiment for the rare gases and breaks down completely under the experimental conditions of Franck (*Physikal. Z.*, 1921, 22, 358). The author extends this theory and deduces relationships which are in agreement with the experimental work of both Townsend and Franck. A. E. M.

**Ionisation by Collision in Helium.** J. S. TOWNSEND and T. L. R. AYRES (*Phil. Mag.*, 1924, [vi], 47, 401—415; cf. A., 1923, ii, 366, 721).—Measurements were made of the currents passing between electrodes in helium with variation of gas pressures, potential differences, and electrode distances. From these it is deduced that the energy necessary to ionise a helium atom does not exceed that of a 10-volt electron, but that the energy of the electrons must be twice this value for appreciable ionisation to occur. Previous work on ionisation and resonance potentials is criticised in the light of these results, which, it is claimed, show that electrons moving with velocities corresponding with resonance potentials rarely lose their energy by molecular collisions. S. B.

**Motions of Electrons in Neon.** V. A. BAILEY (*Phil. Mag.*, 1924, [vi], 47, 379—384; cf. A., 1923, ii, 721, and preceding abstract).—Measurements have been made of the velocity and energy of

agitation of electrons in neon under the influence of an electric field. The values deduced for the mean free paths of the electrons in neon and in other gases are in disagreement with those obtained from viscosity determinations. S. B.

**Re-combination of Gaseous Ions, Chemical Combination of Gases, and Monomolecular Reactions.** J. J. THOMSON (*Phil. Mag.*, 1924, [vi], 47, 337—378).—The first section of this paper is devoted to the theory of the rate of re-combination of positive and negative ions, the rate of formation of complex ions, and kindred subjects. In the second section, the results are applied to problems of chemical combination. With the assumption that complex formation must precede true chemical combination, it is deduced that charged ions or “polar” molecules can accelerate reactions (a) by promoting the formation of additive compounds, (b) by assisting atomic rearrangements within the molecule. An expression resembling Arrhenius’ empirical equation is obtained for the rate of dissociation of gaseous compounds, on the hypothesis that the decomposition is due to molecular collisions, and the usual objections to this view are discussed. Finally, an expression is developed for the rate of unimolecular reactions in solids, such as sublimation, on the assumption that the “critical energy increments” are supplied by pulses running through the space lattice of the solid. The influence of the walls of the containing vessel on reaction velocities is considered in the light of this theory. S. B.

**Potential Gradient in the Sodium-Potassium Vapour Arc Lamp.** F. H. NEWMAN (*Phil. Mag.*, 1924, [vi], 47, 603—608).—The fall of potential along the arc of a vapour lamp with each electrode of sodium-potassium alloy (2 parts Na to 1 part K) has been investigated by means of a probe electrode for currents of 1—2 amp. The potential gradient along the arc column is uniform. The potential drop at the cathode is greater than that at the anode, but both are small compared with the results for other metal electrodes. Application of Poisson’s law shows no preponderance of ions of either sign. The small potential difference between the terminals of the lamp when working is explained by the photo-electric effect exhibited by the alloy. A. E. M.

**Calculation of the Normal Cathode Drop of Potential in Mixtures of Gases.** A. GÜNTHER-SCHULZE (*Z. Physik*, 1924, 21, 50—59).—An expression for the normal cathode drop of potential,  $V_m$ , in a mixture of gases is derived in the form  $V_m^2 = [(\lambda_2/\lambda_1) + (1-x)\beta_2 V_{i\alpha_2}/x\beta_1 V_{i\alpha_1}]/[(\lambda_2/\lambda_1 V_1^2) + (1-x)\beta_2 V_{i\alpha_2}/x\beta_1 V_{i\alpha_1} V_2^2]$ , where  $V_{i\alpha_1}$  and  $V_{i\alpha_2}$  are the ionisation potentials of the respective gases,  $V_1$  and  $V_2$  the respective normal cathode falls,  $\lambda_1$  and  $\lambda_2$  the values of the mean free atomic paths in the gases at N.T.P.,  $\beta_1$  and  $\beta_2$  the respective mean number of ions produced by an electronic impact,  $\alpha_1$  and  $\alpha_2$  are coefficients relating to the increase of the cathode fall due to inelastic impacts, and  $x$  and  $1-x$  the respective proportions in which the gases 1

and 2 are present in the mixture. The formula is shown to be in close agreement with experimental results for mixtures of monatomic gases, *e.g.*, mixtures of argon and mercury vapour. In the case of mixtures containing a diatomic or other multi-atomic gas or vapour, the measured values of the normal cathode drop of potential are in all cases greater than the calculated values throughout the greater part of the range of mixtures employed. This discrepancy between experimental and calculated values is attributed to the removal, by a process of chemical combination, of cations produced in the glow by the primary electrons. The discrepancy is exhibited to a slight extent by mixtures of argon and oxygen, and to a considerably more marked degree by mixtures of helium and oxygen, and the author concludes that in both these cases, in consequence of ionisation, compounds of the respective gases, argon and helium, with oxygen are formed. J. S. G. T.

**Theory of Emission of Positive Ions and Electrons from Glowing Metals.** M. VON LAUE (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1923, **32**, 334—348).—A theoretical paper in which the thermodynamic equilibrium between a metal and its ionised vapour is employed as a basis for the deduction of expressions for the positive and negative saturation currents from the surface of the metal. It is deduced that the saturation currents at the melting points of the metals will be the same for the liquid and solid phases. This is in agreement with the experiments of Goetz (*Physikal. Z.*, 1923, **24**, 377) at the melting points of iron, copper, and manganese.

A. E. M.

**Law and Mechanism of the Emission of Electrons from Hot Bodies.** S. C. ROY (*Phil. Mag.*, 1924, [vi], **47**, 561—569).—Assuming that the electrons within a metal form ideal Born-Kármán space lattices, and utilising a quantum theoretical value for their energy content, and identifying the thermally emitted electrons with photo-electrons, an expression is deduced giving electron emission as a function of temperature. This is essentially of the same form as that of Dushman (*Physical Rev.*, 1922, **20**, 109). Intrinsic potentials for alkali and alkaline-earth vapours are calculated from thermionic and from photoelectric data, and are in fair agreement with thermionic observations. Comparison of intrinsic potential with observed resonance potential suggests that the mechanism of emission is a resonance process.

A. E. M.

**Normal and Selective Photoelectric Effects associated with the Alkali Metals.** K. FARWIG (*Z. Physik*, 1924, **21**, 38—45).—Measurements of the photoelectric effects exhibited by sodium, potassium, and rubidium, illuminated by radiation between 2000 and 6000 Å., indicate that the photoelectric effect on the long wave-length side of the selective region characterising these metals is continuous with the normal effect exhibited on the short wave-length side of this region. The curve representing the selective photoelectric effect is superposed on the continuous curve representing the normal effect, as suggested by Pohl and Pringsheim

(*Verh. d. D. Phys. Ges.*, 1910, **12**, 682, and A., 1910, ii, 922). Franck's interpretation of the maximum selective effect (*Z. Physik*, 1923, **13**, 241) is shown to be untenable. J. S. G. T.

**Photoelectric Effects in Rock Salt Crystals.** J. BINGEL (*Z. Physik*, 1924, **21**, 229—241).—Several rock-salt crystals, natural and artificially coloured (by exposure to X-rays), were exposed to monochromatic illumination of intensities  $5 \times 10^{-5}$ — $5 \times 10^{-3}$  cal./sec. cm.<sup>2</sup>, and the photoelectric currents measured. There is a linear relationship between current and applied voltage and no evidence of saturation up to field strengths of 50,000 volt/cm. The quantum relationship between the energy absorbed and output tends to show that the phenomenon is that of photoelectric conduction rather than of dielectric polarisation. The displacement of the crystal lattice can be of only molecular dimensions.

A. E. M.

**Electrical Conductivity associated with the Excitation of, and Emission of Light from [various] Phosphors.** B. GUDDEN and R. POHL (*Z. Physik*, 1924, **21**, 1—8).—In continuation of previous work (cf. A., 1922, ii, 680), the authors have correlated the photo-excitation of various phosphors, e.g., crystals of Zn-S- $\alpha$ Cu, Zn-S-Mn, Zn-S- $\gamma$ Cu, and the emission of light accompanying the excitation with the phenomena of the primary and secondary photoelectric currents in the crystals. Employing a string electrometer, the authors were able to detect transport of electricity within the excited crystal independently of whether the returning electron caused emission of light or not. The conditions under which the quantum equivalence law holds for the absorption and emission processes are briefly discussed.

J. S. G. T.

**Change in the Temperature Coefficient [of Electrical Conductivity] of pure Platinum by Mechanical Treatment.** O. FEUSSNER (*Z. Physik*, 1924, **21**, 163—167).—A number of experiments are described in which the resistance of a thin, pure platinum wire (0.1 mm. diam.) is compared with that of a similar wire which is subjected to the pull of various weights from 0 to 130 g. The measurements were made at 0° and 100°. In most cases, the change in the temperature coefficient scarcely falls outside the experimental error.

J. F. S.

**Pyro-electricity of Two Derivatives of Camphor.** M. R. LUCAS (*J. Phys. Radium*, 1923, [vi], **4**, 491—492).—Pyro-electric phenomena have been observed with *p*-dimethylaminobenzylidene-camphor and dibenzylcamphor. When crystals of these substances are suspended by fibres and heated at 100°, they are attracted or repelled by charged bodies. The direction of polarisation is perpendicular to the long axis of the crystals, whereas tourmaline is polarised in the direction of this axis.

S. B.

**Hall Effect and Specific Resistance of Cathodically Deposited Films of Gold.** S. S. MACKBOWN (*Physical Rev.*, 1924, **23**, 85—93).—The Hall coefficient for sputtered films of gold is the

same as for bulk metal, namely,  $643 \times 10^{-6} (\pm 1\%)$ . The results of experiments on the resistance and change of resistance of such films are in agreement with work already published, and are expressed in graphical form.

A. A. E.

**Magneto-chemical Investigations.** E. WEDEKIND (*Z. angew. Chem.*, 1924, **37**, 87—89).—Whilst the compounds of iron, with the exception of the oxide  $\text{Fe}_3\text{O}_4$ , are much less strongly magnetic than the metal itself, the reverse is true of manganese. In the latter case, the magnetic effect is a maximum when the metal is present in the tervalent state (*e.g.*, in the boride, arsenide, etc.), and is considerably less in the bivalent state (*e.g.*, the sulphide). Chromium is feebly magnetic, but yields two strongly magnetic oxides,  $\text{Cr}_4\text{O}_9$  and  $\text{Cr}_5\text{O}_9$ , which may be regarded as derived from the tri- and sesqui-oxide and are thus analogues of  $\text{Fe}_3\text{O}_4$ . Vanadium also exhibits latent magnetism, the monoxide,  $\text{VO}$ , having the highest susceptibility, and the other oxides,  $\text{V}_2\text{O}_3$ ,  $\text{VO}_2$ , and  $\text{V}_2\text{O}_5$ , following in order of diminishing susceptibility; for the sulphides, however, this order is reversed. The susceptibility of titanium compounds is still less than that of vanadium compounds, the maximum being found here, as in the chromium series, in the salt-like oxide,  $\text{Ti}_3\text{O}_5$ . Whilst the susceptibility decreases in passing down the series iron, manganese, chromium, vanadium, titanium, the effect of the second component (*e.g.*, oxygen, sulphur) varies. In general, the susceptibility of the oxides decreases with increasing oxygen content, with the exception of the mixed, salt-like oxides (*e.g.*,  $\text{Fe}_3\text{O}_4$ ). Copper, itself feebly diamagnetic, is magnetic in many cupric compounds, but generally diamagnetic in cuprous compounds. Attention is directed to the periodic nature of the susceptibility, and the relation between the latter and colour, in the case of the rare earths.

W. T. K. B.

**Mass Spectra of Chemical Elements. V. Accelerated Anode Rays.** F. W. ASTON (*Phil. Mag.*, 1924, [vi], **47**, 385—400).—The extension of mass-spectrum analysis has been hampered by difficulties in the production of the mass rays of many metallic elements. Unsuccessful attempts to produce them by drawing out the ions from a vacuum arc are described. Details are given of a method using the anode rays from a composite anode of graphite and metallic salts, which has proved of very general application. With this apparatus, the principal isotopes of lithium, beryllium, magnesium, and calcium are found to have atomic weights closely approximating to whole numbers (*cf.* A., 1923, ii, 748).

S. B.

**Capture and Loss of Electrons by  $\alpha$ -Particles.** E. RUTHERFORD (*Phil. Mag.*, 1924, [vi], **47**, 277—303).—The frequency of the capture and loss of electrons by  $\alpha$ -particles is discussed, from observations on the number of singly charged and neutral helium atoms present in a pencil of  $\alpha$ -rays. The experimental procedure is to observe the magnetic deflection in a high vacuum of  $\alpha$ -rays from radium-*B* and radium-*C*, counting the particles by the scintillation method. The neutral atoms remain undeflected and the singly

charged atoms are deflected half as much as the doubly-charged atoms. The velocity of the  $\alpha$ -particles is varied by placing mica screens before the source. With decreasing velocities, the number of particles which have captured electrons becomes relatively larger. It is found that the number of singly charged and neutral atoms falls off almost exponentially with increase of the gas pressure in the apparatus. The mean free paths of a particle for capture and loss of an electron are deduced from this effect of the presence of gas. For example, with  $\alpha$ -particles of velocity  $0.85 \times 10^9$  cm./sec., the mean free path for loss is 0.005 mm., and for capture 0.037 mm. in air at N.T.P. The ratio of the mean free path for capture to that for loss varies as  $V^{46}$ , where  $V$  is the velocity of the  $\alpha$ -particles.

The theoretical difficulties involved in the capture of electrons by high-speed  $\alpha$ -rays are considered, and it is concluded that the process is intimately connected with that taking place in the ionisation of a gas by the rays. S. B.

**Application of the Law of Probability to the Radioactive Emission of Polonium.** W. KUTZNER (*Z. Physik*, 1924, **21**, 281—298).—The  $\alpha$ -ray emission of polonium was investigated to see whether it conformed to Bateman's law (A., 1910, ii, 917) and was found to show sub-normal dispersion, that is, the proportion of the time fractions during which approximately the average number of particles was emitted was found greater than theory requires. The cause is discussed and it is suggested that the atoms are influenced by emissions from other atoms. L. J. H.

**Precision Measurement of Radium Emanation.** A. BECKER (*Z. Physik*, 1924, **21**, 304—315).—An instrument for the comparative measurement of radium emanation and a method of calibrating it are described. L. J. H.

**Experiments with a Glow Lamp as a Counting Chamber [for the Detection of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -Rays, etc.].** O. v. BAEYER and W. KUTZNER (*Z. Physik*, 1924, **21**, 46—49).—When a direct-current voltage of from 150 to 200 volts is applied to a circuit comprising a high resistance in series with an electric glow (microphone) lamp shunted with a suitable capacity, the lamp glows intermittently. With suitable choice of the applied voltage, the intermittent glow disappears, but may be restored by bringing near the lamp a source of  $\alpha$ -,  $\beta$ -, or  $\gamma$ -radiation, each lighting-up of the lamp indicating the incidence of an  $\alpha$ -,  $\beta$ -, or  $\gamma$ -ray. The phenomenon may also be produced by the incidence of light of shorter wave-length than about 3800 Å. on the iron anode employed in the lamp, or as the result of electrostatic effects produced in the neighbourhood of the lamp. The frequency of the intermittence appears to be proportional to the intensity of the incident light. J. S. G. T.

**Number of  $\alpha$ -Particles expelled by Radium. I. Counting of Scintillations.** H. GEIGER and A. WERNER (*Z. Physik*, 1924, **21**, 187—203).—The number of  $\alpha$ -particles emitted by 1 g. of radium

(without disintegration products) per sec. has been determined by counting the scintillations produced in a zinc sulphide screen, and the value  $3.40 \times 10^{10}$  obtained. The method used was designed to eliminate the more obvious causes of error, such as fatigue of the eye and imperfections of the screen. This value is compared with Rutherford and Geiger's value of  $3.57 \times 10^{10}$  and Hess and Lawson's value  $3.72 \times 10^{10}$ , and the reasons for the discrepancy are discussed. Making use of the above figure and of Millikan's value of the elementary quantum, the half period of radium is calculated to 1730 years and the evolution of helium to 159 cu. mm. per year per gram of radium in equilibrium with emanation, radium-A, and radium-C'. The heat evolution of 1 g. of radium (free from disintegration products) is calculated to 22.25 cal./hour per gram of radium. Comparing this value with the experimental values of Rutherford and Hess, namely, 25.2 and 25.1 cal./hour, it appears likely that in the radioactive changes of the radium atom, in addition to the kinetic energy of the  $\alpha$ -particles and the recoil atoms, other quantities of energy must be set free in consequence of the changes in the atomic nucleus.

J. F. S.

**Employment of Normal Radium and Uranium Solutions for Emanation Measurements.** II. P. LUDEWIG and E. LORENSER (*Z. Physik*, 1924, **21**, 258—263).—Using the apparatus previously described (A., 1923, ii, 453), further measurements have been made with normal radium solutions from the Physikalisch-Technische Reichsanstalt and with several uranium solutions of the Freiberg Radium Institute. The influence of the pressure in the ionisation chamber on the ionisation effects of  $\gamma$ - and  $\alpha$ -rays has been investigated between 400 and 1000 mm. The  $\gamma$ -ray ionisation is a linear function of pressure, and  $\alpha$ -ray ionisation is a maximum at 715—735 mm. The extension of the measurements over a further year and the application of the pressure corrections has served to prove the constancy of the solutions and to substantiate further the use of the method as a standard.

A. E. M.

**Artificial Disintegration of Atoms.** G. KIRSCH and H. PETTERSSON (*Phil. Mag.*, 1924, [vi], **47**, 500—512).—A detailed account of previous work (A., 1923, ii, 675, 819).

A. E. M.

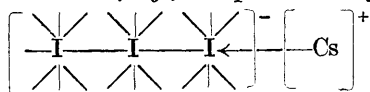
**Electronic Theory of Valency.** B. FLÜRSCHHEIM (*Phil. Mag.*, 1924, [vi], **47**, 569—576; *Trans. Faraday Soc.*, 1923, **19**, 531—535).—A reply to criticisms by Lowry (A., 1923, ii, 848) of conceptions advanced by the author.

A. E. M.

**Secondary Valency in the Light of Recent Researches.** II. **Alkali Polyhalides.** G. L. CLARK (*Amer. J. Sci.*, 1924, **7**, 109—120; cf. A., 1923, ii, 856).—A detailed consideration of the facts which must be taken into account by any constitutional formula for alkali polyhalides, leads to the conclusion that there is only one possible mechanical formulation for these substances which is in agreement with experimental facts. This is the constitutional



formula suggested by Knorr (*Z. anorg. Chem.*, 1923, **129**, 109) according to which caesium iodide, *e.g.*, is represented by

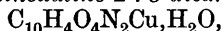


This represents the halogen atoms in a line as a singly acting unit, with two atoms sharing a single electron which describes an eccentric orbit around them. Each iodine atom is surrounded by the rare gas configuration of eight electrons. The arrow shows that a valency electron has been removed from the caesium atom with a resultant polar linking between the halogen group and the metal ion. Consequently, the halogen atom next to the metal will invariably be the strongest halogen, accounting for the fact that in changes brought about by increased temperature the strongest halogen remains bound to the metal. J. F. S.

**Specific Subsidiary Valency Linkings. Internally Complex Salts of Bivalent Iron.** H. LEY, C. SCHWARTE, and O. MÜNNICH (*Ber.*, 1924, **57**, [B], 349—356).—Although glycine and its homologues,  $\alpha$ - and  $\beta$ -aminopropionic acids, piperidinoacetic acid, and aromatic amino-acids such as anthranilic acid, do not give characteristically coloured ferrous salts, this is not the case with compounds obtained from acids containing the group,  $\text{C}:\text{N}\cdot\text{CO}_2\text{H}$ , in which the  $\text{C}:\text{N}$ -group is a component of a cyclic system; these vary in colour from reddish-yellow to dark violet, and are regarded as internally complex salts having the group,  $\left[ \cdot\text{Fe} \begin{array}{c} \text{N}\cdot\text{C} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{array} \right]$ , which is analogous to the

ferronitric oxide complex,  $\left[ \text{Fe} \begin{array}{c} \text{NO} \\ \diagup \quad \diagdown \\ (\text{OH}_2)_n \end{array} \right]$  (cf. Manchot, A., 1914, ii, 557, 567). They show the ultra-violet absorption spectrum of the acid from which they are derived, but possess a characteristic band in the neighbourhood of  $1/\lambda = 2000$  which is considered to be characteristic of the attachment of ferrous iron to nitrogen by a subsidiary valency. The tendency of the acids to form complex copper and ferrous salts does not appear to be parallel.

The following new salts have been prepared: *Ferrous pyridine-2-carboxylate*,  $(\text{C}_6\text{H}_4\text{O}_2\text{N})_2\text{Fe}\cdot 4\text{H}_2\text{O}$ , brown crystals, which, in aqueous solution in the absence of air and light, passes into *basic ferric pyridine-2-carboxylate*,  $(\text{C}_6\text{H}_4\text{O}_2\text{N})_2\text{FeOH}$ , a microcrystalline, yellow substance; *ferrous pyridine-2:3-dicarboxylate* (+  $\text{H}_2\text{O}$ ), brownish-black, lustrous crystals, and the *salt*,  $\text{C}_7\text{H}_3\text{O}_4\text{NFe}\cdot 2\text{H}_2\text{O}$ , yellow crystals; *ferrous pyrazine-2:3-dicarboxylate*,  $\text{C}_6\text{H}_2\text{O}_4\text{N}_2\text{Fe}\cdot 2\text{H}_2\text{O}$ , small prisms; *copper quinoxaline-2:3-dicarboxylate*,



a pale green substance; *ferrous quinoxaline-2:3-dicarboxylate*,  $\text{C}_{10}\text{H}_4\text{O}_4\text{N}_2\text{Fe}\cdot 3\text{H}_2\text{O}$ , dark prisms.

A neutral solution of quinoxaline-2:3-dicarboxylic acid is a sensitive reagent for ferrous iron, with which it gives a violet coloration; in the presence of salts of ferric iron, nickel, cobalt, or copper the quinoxaline-2:3-dicarboxylates of these metals are first

precipitated, after which the coloration appears. The sensitiveness is of the same order of magnitude as that of Turnbull's blue reaction.  
H. W.

**Structure of Phosphorus.** H. COLLINS (*Chem. News*, 1924, 128, 145—147).—The author's views, (a) that the atom of phosphorus has the constitution expressed by the formula  $\text{Na}-\text{H}-\text{H}_3-\text{H}-\text{H}_3$ , and (b) that the heat of formation of an element is proportional to the product of the atomic weight and the change of volume, are developed.  
A. A. E.

**Constitution and Structure of an Atom of Sodium.** H. COLLINS (*Chem. News*, 1924, 128, 161—163).—Various numerical values are considered to support the author's view that an atom of sodium has been formed by the union of an atom of carbon with one of boron.  
A. A. E.

**Chemical Nature of the Purple of Cassius.** A. HUBER (*Physikal. Z.*, 1924, 25, 45—47).—An X-ray analysis of a sample of purple of Cassius by the Debye-Scherrer powder method gave thirteen interference lines, for eleven of which the corresponding lattice constant is that of gold. The remaining two are also given by a preparation of colloidal stannic acid and correspond with the strongest reflections from crystalline stannic oxide. It is concluded therefore that the gold is not chemically combined, but that the substance is merely a mixture of colloidal gold and colloidal stannic acid.  
A. E. M.

**Structure of Vanadium.** H. COLLINS (*Chem. News*, 1924, 128, 100—102).—Evidence, based on the relative volumes and the heats of formation of their compounds, is adduced in an attempt to prove that vanadium has been formed by the union of an atom of magnesium with an atom of aluminium.  
A. R. P.

**Solid Solutions and Inter-atomic Relationships.** A. L. NORBURY (*Nature*, 1924, 113, 271).—Polemical with Rosenhain (*ibid.*, 1923, 112, 832). Experimental data show that there is no connexion between the sizes of the solute atoms and their effects in increasing the electrical resistivity of a metallic solvent. The diminution of conductivity of metals with increasing temperature is probably due to the effect of heat on the electrons, and not on the atoms.  
A. A. E.

**Solid Solutions and Inter-atomic Relationships.** W. ROSENHAIN (*Nature*, 1924, 113, 271—272; cf. Norbury, preceding abstract).—Polemical and explanatory. The effect of the contraction or expansion of a lattice on the electrical properties of a metallic system is discussed.  
A. A. E.

**Crystal Structure of Hydrogen Chloride.** F. SIMON and C. VON SIMSON (*Z. Physik*, 1924, 21, 168—177).—An apparatus is described whereby the crystal structure of condensed gas may be determined, using the X-ray method. By means of this apparatus, the structure of the two modifications of hydrogen chloride has been

examined. The variety stable above  $98^\circ$  abs. has a cubic face-centred lattice with a lattice constant of  $5.50 \pm 0.05 \text{ \AA}$ . Accurate measurements could not be made with the second variety, which is stable below  $98^\circ$  abs., but sufficient information was obtained to show that it possesses a smaller symmetry than the other variety. Hydrogen chloride is shown to possess a molecular lattice. The density of both modifications of hydrogen chloride has been determined; for the variety stable above  $98^\circ_{\text{abs}}$ ,  $d_{107} = 1.469$ , for that stable below  $98^\circ_{\text{abs}}$ ,  $d_{31} = 1.507$ . Using the first of these values the lattice constant of the variety stable above  $98^\circ$  abs. is calculated to  $5.47 \text{ \AA}$ . The density of hydrogen chloride at the melting point is  $1.277$ . It contracts therefore  $15\%$  on freezing and  $2.5\%$  on transition at  $98^\circ$  abs. J. F. S.

**Halogen Hydrides.** H. BELL (*Phil. Mag.*, 1924, [vi], 47, 549—560).—The energy formula of Born and Hückel is used in a theoretical analysis of the infra-red absorption data of hydrogen fluoride, chloride, and bromide. Evaluation of the constants in the formula has rendered possible the determination of the variation, with distance, of the force acting on the hydrogen nucleus as it vibrates along the nuclear line. The relative range of vibration of hydrogen fluoride is larger than those of the other two compounds, owing to the larger relative size of its quantum. The restoring forces for HF, HCl, and HBr are in the proportion  $1.84 : 1 : 0.80$ , and the corresponding relative variation with distance is  $1.33 : 1 : 0.98$ . It is deduced that the halogen atoms have all increased in radius by a constant quantity at the expense of other atoms. The radius of Cl-ions has been increased from  $1.05 \text{ \AA}$ . to  $1.72 \text{ \AA}$ ., which value is in agreement with those of Bragg, James, and Bosanquet (A., 1922, ii, 703) and of Davey (A., 1923, ii, 17). It is concluded that the hydrogen nucleus is well within the halogen shell and is buried to the same depth in all three, and from the argon electron "economy" of Kramers (*Naturwiss.*, 1923, 27, 550) it is deduced that the oscillations of the hydrogen nucleus are always well outside the stable configuration of the neon shell. A. E. M.

**Difference between the Specific Heats of Liquid and Vapour at Constant Volume.** A. BRANDT (*Ann. Physik*, 1924, [iv], 73, 412—414).—On applying to carbon dioxide Planck's formula for  $c_1 - c_2$ , where  $c_1$  is the specific heat of the liquid at constant volume, and  $c_2$  that of the saturated vapour at the same temperature, it is found that, at  $-5^\circ$ ,  $+10^\circ$ , and  $+25^\circ$ ,  $c_1 - c_2 = 0$ . Similar results are obtained with the so-called normal substances, pentane, isopentane, etc. It must not be inferred from this that the specific heat at constant volume depends only on temperature and not on volume. There is, in fact, a considerable amount of experimental evidence which points to the contrary. The approximate equality of  $c_1$  and  $c_2$  for substances which undergo dissociation with rise of temperature can be explained by the assumption that the influence of temperature on the degree of dissociation is the same for both liquid and saturated vapour. M. S. B.

**Specific Heat of Graphitic Carbon and Coke.** P. SCHLÄPFER and P. DEBRUNNER (*Helv. Chim. Acta*, 1924, 7, 31—58).—The specific heat of carbon in the form of (a) Ceylon graphite, containing 0.35% of ash; (b) retort graphite, practically free from ash; (c) carefully purified beech charcoal; (d) a number of samples of gas coke, was determined over the temperature range 20—1200° by making use of a mixing calorimeter the details of which are described and illustrated. It is found that all these varieties of carbon have the same specific heat over the temperature range examined. The mean specific heat between 0° and  $t^\circ$  is given by the formula  $c_{0,t} = 0.1517 + 3.9043 \cdot 10^{-4}t - 2.1908 \cdot 10^{-7}t^2 + 0.596 \cdot 10^{-11}t^3 + 2.8850 \cdot 10^{-14}t^4$ . The specific heats of gold and cast quartz were also determined, since containers made of these substances were used for holding the samples in the calorimeter. The mean specific heat of gold between 20° and  $t^\circ$  is  $0.0308 + 3.481 \cdot 10^{-6}(t - 20)$  and of cast quartz, between 0° and  $t^\circ$ ,  $0.18324 + 0.10321 \cdot 10^{-3}t - 0.13210 \cdot 10^{-7}t^2 - 0.99987 \cdot 10^{-11}t^3 - 0.889275 \cdot 10^{-14}t^4$ . E. H. R.

**Proposed Empirical Equation of State for Fluids.** S. LEES (*Phil. Mag.*, 1924, [vi], 47, 431—446).—A new empirical equation of state is derived, of the form  $(p + ap^{1/3}/TV^{5/3})(\bar{V} - b) = RT$ , the correction term for  $p$  being made a function of three variables. It is claimed that the agreement with experiment on certain points is closer than with previously proposed formulæ. S. B.

**Simple Derivation of van der Waals' Vapour Pressure Equation with a Note on Molecular Diameters.** S. P. OWEN (*Proc. Durham Phil. Soc.*, 1922—23, 6, 308—311).—The van der Waals vapour pressure equation,  $\log p_c/p = B/R \times (\theta_c - \theta)/\theta_c$  (in which  $B$  is a constant,  $p$  the vapour pressure at temperature  $\theta$ ,  $p_c$  the critical pressure, and  $\theta_c$  the critical temperature) is deduced from kinetic considerations, using the Maxwell law of distribution of velocities. It is assumed that all the molecules striking the surface of the liquid are absorbed, whilst the only molecules which escape from the liquid are those which have a kinetic energy greater than a critical value  $\frac{1}{2}mu_1^2$  which is assumed to be proportional to  $\theta_c - \theta$ .

If the critical kinetic energy is taken to be equal to the cross-sectional area of the molecule multiplied by the surface tension, then by the aid of the Eötvös equation for the variation of molecular surface energy with temperature, it is shown that the diameter of the molecule is given by  $d = \sqrt{fR(Mv)^{2/3}/0.4343\pi k}$ , where  $f = B/R \log_{10}e$  and  $k = 2.12$  is the temperature coefficient of molecular surface energy. The molecular diameters for seven substances calculated from this formula are in substantial agreement with the values deduced from viscosity, limiting density, etc. S. S.

**Critical Constants of Various Gases.** S. F. PICKERING (*J. Physical Chem.*, 1924, 28, 97—124).—An account is given of the methods used by different investigators in determining the critical constants of a large number of gases, including oxygen, ozone, air, nitrogen, nitric and nitrous oxides, ammonia, hydrogen, carbon

monoxide and dioxide, the inert gases, chlorine, the halogen hydrides, saturated and unsaturated hydrocarbons of low molecular weight, methyl and ethyl chlorides, carbonyl chloride, sulphur dioxide, and hydrogen sulphide. A selected list of these constants has been compiled and reasons are given for the choice. Those values about which there is still considerable uncertainty are indicated.

M. S. B.

**Degradation of the Ideal Gaseous State and the [Mean] Free Path.** E. SCHÖDINGER (*Physikal. Z.*, 1924, **25**, 41—45).—In the theories of the degradation of a gas from the ideal gaseous state (which occurs for a perfect gas in the neighbourhood of the absolute zero), the characteristic temperature  $\Theta$  at which the gas begins to depart from the gas laws is given by the relation  $\Theta = h^2/8\pi m l^2 k$ , where  $h$  is the Planck constant and  $m$  the mass of the molecule;  $l$  has the dimensions of length and in the different theories has different meanings. These theories lead to values of  $\Theta$  in the neighbourhood of  $1^\circ K$ , which conflict with the experimental equation of state. The author develops a theory in which the distance  $l$  is taken as the mean free path of the molecule  $\lambda$ . It is shown that  $\Theta$  for a gas under normal conditions is of the order of  $1/10,000^\circ K$ . This does not conflict with the experimental data for the equations of state and the thermal behaviour of gases. For the electrons within a metal, on the other hand,  $\Theta$  has a value between  $4500$  and  $18,000^\circ K$ . Thus, at a moderate temperature, the electrons in a metal will be degraded from the ideal gaseous state. W. E. G.

**Connexion between van der Waals' Equation and Trouton's Rule.** A. BRANDT (*Ann. Physik*, 1924, [iv], **73**, 403—405).—The author deduces a value for the ratio of the molecular heat of vaporisation to the absolute boiling point, using van der Waals' equation and Guldberg's relationship  $T/T_c = 0.6$ , where  $T$  and  $T_c$  are the boiling point and critical temperature, respectively. The value found, however, is only half that given by Trouton's rule.

M. S. B.

**Cohesion Pressure.** A. BRANDT (*Ann. Physik*, 1924, [iv], **73**, 415—425).—Van der Waals' equation is discussed with reference to the view, first put forward by E. and U. Dühring in 1886, that all substances, liquid and gaseous, exhibit association, the extent of which depends on the pressure, temperature, and volume, and may become zero. The negative value found by Amagat for the cohesion pressure of hydrogen is explained as being due to the increased association of the molecules which results when the volume is increased at high pressures.

M. S. B.

**Latent Heat of Evaporation and Pressure of Saturated Vapour at very low Temperatures.** A. BRANDT (*Ann. Physik*, 1924, [iv], **73**, 406—408).—A criticism of two papers by Ariès (*Compt. rend.*, 1917, **164**, 343; A., 1917, ii, 192).

M. S. B.

**Molecular Association of Liquids and Highly Compressed Gases. III. Molecular Association of Liquids.** E. E. WALKER (*Phil. Mag.*, 1924, [vi], **47**, 513—525).—A discussion of the

theory of corresponding states leads to the conclusion that only those substances the molecules of which have the same mean collision area are truly corresponding substances. The modified law is applied to associated liquids after making the corrections indicated by the author (cf. this vol., ii, 144) for the effect of molecular association on the critical constants. The association factors of twenty-four substances at the boiling point have been determined from selected experimental data. The results show no anomalies, and calculations based on temperature-vapour pressure relationships agree substantially with those calculated from reduced volumes and apparent reduced temperatures. Normal paraffins are used as comparison substances, since they show the least (if any) evidence of association. The data for isomeric esters indicate that the acetates are more highly associated than the formates, propionates, or butyrates, and it is suggested that the methyl group exerts a specific influence. The degree of association is in all cases greater at the boiling point than at the critical point.

A. E. M.

**Relation between the Fluidity and the Temperature of Liquids.** H. J. M. CREIGHTON (*Proc. Nova Scotian Inst. Sci.*, 1918—22, 15, 165—168).—The author finds that the absolute temperatures at which two liquids, e.g., methyl alcohol and water or octane and benzene, have the same fluidity (reciprocal of viscosity) are connected by an equation which is similar to the isobaric temperature formula of Ramsay and Young for substances which are not closely related (*Phil. Mag.*, 1885, 20, 515; 1886, 21, 33). This relation may be expressed in the form  $R' = R + c(t' - t)$ , where  $R'$  is the ratio of the absolute temperatures corresponding with two values of the fluidity for one of the two liquids, and  $R$  is the corresponding ratio for the second liquid. The term  $(t' - t)$  is the temperature difference for one of the liquids concerned.

J. S. G. T.

**Viscosities of Liquids experimentally correlated to Pendulum Dampings.** E. H. BARTON and H. M. BROWNING (*Phil. Mag.*, 1924, [vi], 47, 495—500).—The appearance of some of the exponentially-damped vibrations obtained with a lathe and bob pendulum (*Phil. Mag.*, 1923, 46, 399—406) suggested that these damping effects might be utilised for comparative measurements of the viscosities of liquids. A method has been devised for the determination in which the pendulum carries a pair of planes dipping into the liquid under examination, and moving parallel to, and at measured distances from, the inner side of the containing vessel. Mixtures of glycerol and water were used in standardising the apparatus, which may be modified so as to be suitable for oils or for liquids with viscosities as low as that of water.

A. E. M.

**Binary and Ternary Molybdenum Alloys.** DREIBHOLZ (*Z. physikal. Chem.*, 1924, 108, 1—50).—Binary systems of molybdenum with copper, silver, gold, platinum, nickel, and cobalt, respectively, and the ternary systems, copper-nickel-molybdenum and copper-cobalt-molybdenum have been investigated. Copper,

silver, and gold form no alloys with molybdenum. Platinum is capable of forming alloys with molybdenum and in the neighbourhood of its melting point takes up at least 16% Mo into solid solution. On lowering the temperature, however, the molybdenum separates from the solid solution. Baar's diagram for molybdenum-nickel (A., 1911, ii, 611) is confirmed and has been amplified in some respects. The Brinell hardness of a series of mixed crystals of molybdenum and nickel increases with increasing molybdenum content. The miscibility gap in the system molybdenum-copper is closed by the addition of nickel at the composition 35.5% Cu, 15.5% Mo, 49% Ni. Copper-nickel alloys are not improved in their electrical properties by the addition of molybdenum. Numerous phase diagrams and photographs of sections of the alloys are included in the paper. J. F. S.

**Piezochemical Studies. XXIV. Experimental Determination of the Fictitious Volume Change in Solution Equilibria.** II. E. COHEN, W. A. T. DE MEESTER, and A. L. T. MOESVELD (*Z. physikal. Chem.*, 1924, **108**, 103—117; cf. A., 1923, ii, 746).—Making use of methods previously published (*loc. cit.*), the authors have determined experimentally the fictitious volume change in solution equilibria for several systems. The following values are recorded: for naphthalene-tetrachloroethane,  $\Delta v = 0.1313$  c.c./g.; benzene-naphthalene, 0.128 c.c./g.; ethyl alcohol-*p*-nitrotoluene, 0.089 c.c./g.; ethyl acetate-resorcinol, 0.011 c.c./g. The influence of constitution on the value of  $\Delta v$  is discussed (cf. Bridgeman, *Phys. Rev.*, 1915, **6**, 94; Block, A., 1912, ii, 128). J. F. S.

**Fractional Distillation of Small Quantities.** G. WIDMER (*Helv. Chim. Acta*, 1924, **7**, 59—61).—A fractionating column for small quantities of liquid (about 20 c.c.) consists of three concentric tubes. The vapours pass upwards between the outside and middle tubes, then downwards between the middle and inside tubes, and finally up the middle tube, which contains a glass rod on which is wound a glass spiral. From the top of this tube the vapours pass to the side tube. All the tubes return condensed liquid to the flask. The whole is surrounded by a wide glass tube to protect it from temperature fluctuations. At the ordinary pressure, the apparatus can be used up to 170°, and at low pressures up to 190°. A mixture containing 10 c.c. of ethylaniline (b. p. 204°) and 10 c.c. of diethylaniline (b. p. 213°) was separated with this apparatus in 2½ hours into 8.6 c.c. of ethylaniline, 2.0 c.c. of a middle fraction, and the rest diethylaniline. For still smaller quantities of liquid, use is made of an apparatus fitted only with the inner tube, the glass rod, and the spiral. E. H. R.

**Electrical Resistance of Phenol-Water Systems near the Critical Solution Temperature.** M. H. FISCHER (*Kolloid-Z.*, 1924, **34**, 97—99).—As a preliminary to work on soap solutions, measurements have been made of the electrical resistance of mixtures of phenol and water above and below the critical solution temperature. S. B.

**The Equilibrium Hydrogen-ion-Methyl Alcohol-Water.** H. GOLDSCHMIDT and P. DAHL (Z. physikal. Chem., 1924, 108, 121—127).—The electrical conductivity of hydrogen chloride in absolute methyl alcohol and aqueous methyl alcohol containing 0.01 to 3 moles of water per litre has been determined at 25°. The equivalent conductivity in absolute methyl alcohol at infinite dilution at 25° is found to be 204.2. The conductivity decreases with increasing concentration of water, reaching the value 108.4 in 3*N*-solution. The equivalent conductivity in solutions up to 0.5 mole per litre is given by the formula  $\Delta_n = 204.2 - 98.9n(r + n)$ , where  $n$  is the number of moles of water per litre and  $r$  is the constant for the equilibrium between hydrogen-ion, methyl alcohol, and water. The value of  $r$  is 0.235; this value is in satisfactory agreement with the value 0.21 determined from esterification experiments. J. F. S.

**Determination of the Equilibria involving Calcium-, Hydrogen-, Carbonate-, Bicarbonate-, and Primary, Secondary, and Tertiary Phosphate-ions.** I. N. KUGELMASS and A. T. SHOHL (J. Biol. Chem., 1924, 58, 649—666).—In connexion with the physiology of bone calcification and of nervous irritability, determinations have been made of a number of constants which are characteristic for the conditions of ionic equilibrium in the blood at 38°. For the calcium-carbonate-bicarbonate equilibrium, both in presence and in absence of sodium bicarbonate,  $[\text{Ca}^{++}][\text{HCO}_3']^2/[\text{H}_2\text{CO}_3] = 4.14 \pm 0.14 \times 10^{-5}$  and  $[\text{Ca}^{++}][\text{HCO}_3']/[\text{H}^+] = 133 \pm 3$ ; for the equilibria in which phosphate plays a part, the carbon dioxide pressure being variable,  $[\text{Ca}^{++}][\text{HPO}_4''] = 67 \pm 7 \times 10^{-8}$ ,  $[\text{Ca}^{++}]^2[\text{HCO}_3']^2[\text{HPO}_4'']/[\text{H}^+][\text{H}_2\text{PO}_4'] = 4.0 \pm 0.4 \times 10^{-3}$  and  $[\text{Ca}^{++}]^2[\text{HCO}_3'][\text{HPO}_4'']/[\text{H}^+] = 7.6 \pm 0.6 \times 10^{-5}$ . These and other derived equilibrium constants are compared with previously determined data. G. M. B.

**Physico-chemical Basis of Vital Permeability. IV. Capillary Activity of Oxygen and of Carbon Dioxide at the Interface Light Petroleum-Water.** R. BRINKMAN and A. VON SZENT-GYÖRGYI (Biochem. Z., 1924, 144, 47—51).—The interfacial tension between light petroleum and water is lowered by oxygen, carbon dioxide, or ammonia, although oxygen and ammonia have no effect on the surface tension at the interface water-air. Importance is attached to this observation in its bearing on the selective permeability of the cell membrane. J. P.

**Surface Tension of Gelatin Solutions.** C. E. DAVIS, H. M. SALISBURY, and M. T. HARVEY (Ind. Eng. Chem., 1924, 16, 161—163).—The variation of the surface tension of gelatin solutions with concentration, temperature, hydrogen-ion concentration, and age of solution has been studied by Morgan's drop weight method. The concentration of the solutions could be raised to nearly 10% if the temperature was kept above 38°. Further evidence of a transition point at this temperature was found by these measurements, the drop weight-temperature curves showing a marked



change of slope at this point. Increasing concentration causes a decrease in the drop weight. In the more concentrated solutions the drop weight increases with rise of temperature, but a maximum is reached, and then the drop weight falls as the temperature approaches the transition point. Above this temperature, the drop weight remains nearly constant. As the  $p_H$  value increases, gelatin solutions of all concentrations afford evidence of a minimum value of the drop weight at the neutral point. The drop weight changes slightly with the age of the solution. H. C. R.

**Surface Tension of Soap Solutions.** L. LASCARY (*Kolloid-Z.*, 1924, **34**, 73—83).—The surface tension of solutions of sodium salts of thirteen of the fatty acid series between formic and cerotic acids has been determined by the drop number method. The undissociated salt and fatty acid molecules have considerable influence in diminishing the surface tension of the solution, whilst the colloids present only affect it secondarily through adsorption of ions and molecules. The surface tension-concentration curves for the salts ranging from sodium caprate to laurate show a break or inflexion at the concentration at which the solution becomes turbid. This is correlated with a corresponding break in the concentration of fatty acid molecules in solution. The effect of these salts on surface tension increases with molecular weight to sodium myristate, above which it decreases. S. B.

**Theory of Colloid Phenomena.** U. R. EVANS and L. L. BIRCUMSHAW (*Kolloid-Z.*, 1924, **34**, 65—72).—A discussion of the forces determining colloid phenomena. In addition to surface tension, there must be forces which act at right angles to the surface of the colloidal particles. These are treated as being electrical in nature. The idea of the selective adsorption of ions is used to explain coagulation, peptisation, etc. S. B.

**Formation of Colloids by the Electrolysis of Dilute Solutions.** P. N. PAVLOV (*Kolloid-Z.*, 1924, **34**, 100—102).—Observations have been made on the formation of colloidal particles by electrode disintegration during the electrolysis of water and dilute salt solutions with *E.M.F.*'s ranging from 2 to 16 volts. Both electrodes were observed to emit streams of particles which showed electrophoresis phenomena.

The particles from the cathode are metallic, those from the anode are composed of the oxide of the metal. Experiments were made with electrodes of silver, iron, gold, bismuth, and copper. The cathodic disintegration investigated in these experiments appears to be of the same character as that which occurs in the production of colloids by the arc discharge under water. S. B.

**Viscosimetric Investigations on Lyophilic Colloids.** W. R. HESS (*Rec. trav. chim.*, 1923, **42**, 1097—1103).—A reply to de Jong's criticisms (*A.*, 1923, ii, 132) of the author's work on the viscosity of lyophilic colloids, particularly of blood. It is shown that de Jong has misunderstood the nature of the author's work and has mis-

interpreted the results. A short *résumé* is given of the essential points of the work, which deals mainly with the influence of pressure on viscosity.  
J. F. S.

**Colloidal Nickel Hydroxide.** O. F. TOWER (*J. Physical Chem.*, 1924, 28, 176—178; cf. Tower and Cooke, A., 1922, ii, 853).—The most favourable conditions for obtaining nickel hydroxide gel by the action of *N*/1 alcoholic solution of potassium hydroxide on a glycerol solution of nickel acetate have been studied in detail. Additional proof was obtained that the peptisation of nickel hydroxide in the formation of a colloidal solution is due to the presence of traces of potassium chloride in the solution. Experiments were also carried out to determine whether nickel hydroxide, as it is ordinarily precipitated from solution, is really  $\text{Ni}(\text{OH})_2$  or  $\text{NiO}$  with adsorbed water. Samples of the precipitate from both hot and cold solutions were air-dried, pulverised, and left in a vacuum desiccator over sulphuric acid of increasing concentration until the weight became constant. The percentage of nickel was determined electrolytically and indicated that the final stable product was  $\text{Ni}(\text{OH})_2$ , and not the oxide or any intermediate hydroxide.  
M. S. B.

**Colloidal Silica.** F. DIÉNERT and F. WANDENBULCKE.—(See ii, 253.)

**Effect of the Concentration of Colloidal Clay upon its Hydrogen-ion Concentration.** R. BRADFIELD (*J. Physical Chem.*, 1924, 28, 170—175).—The colloidal clay separated from soils has an acid reaction whilst the non-colloidal portion is neutral. If the former is extracted, diluted to different concentrations with water, and the hydrogen-ion concentration determined by the hydrogen electrode, the  $p_H$  value is found to vary with concentration in a similar manner to acetic acid. This is regarded as confirming the opinion that the acidity of soils is due to a true acid and not to the preferential adsorption of  $\text{OH}$  ions by soil colloids. [Cf. B., 1924, 269.]  
M. S. B.

**Technique of Ultra-filtration.** C. WHA.—(See i, 458.)

**Preparation of Membranes with Uniform Distribution of Pores.** F. E. BARTELL and M. VAN LOO (*J. Physical Chem.*, 1924, 28, 161—165; cf. Bartell and Carpenter, A., 1923, ii, 221, 298).—During the drying and setting of collodion membranes containing volatile and non-volatile constituents, and also visible particles in suspension, the cooling of the surface by evaporation of the volatile portion gives rise to vortex action; at first there is a large number of small vortices of varying strengths, but later a more uniform arrangement of a small number of more powerful ones of similar strength is reached. By the mutual thrust of these on one another a condition of closest packing results, *i.e.*, each one is in contact with six others and the surface appears to be made up of hexagonal cells. The centre of each vortex or cell forms a pore, at first con-

taining liquid with a high concentration of volatile matter. By adding water after a certain interval of time, the volatile constituent is removed and an opening or pore is left. The size of the pore, and therefore also the permeability of the membrane, depends on the amount of volatile matter left when the water is added, and hence on the time the vortex action is allowed to continue. The longer the time the smaller is the pore. M. S. B.

**Adsorption.** G. C. SCHMIDT and F. DURAU (*Z. physikal. Chem.*, 1924, **108**, 128—150).—Experiments have been made on the adsorptive properties of sheet glass and glass powders with the object of determining whether the adsorbed substances form a single layer or a series of superposed layers. The solubility of glass, both massive and powdered, in a solution of sodium hydroxide  $N/2$  and sodium carbonate  $N$  was determined and the surface of the glass powder was measured by the Wartenberg-Wolff method (*Z. angew. Chem.*, 1922, **35**, 138). It is shown that the amount of glass dissolved, whether massive or powdered, is independent of the rate of stirring the solution and the concentration of the solvent; it increases with the time and also with the temperature, at first slowly and then rapidly. The similarity of the dissolution processes is indicated by the validity of the equation  $a/o = b/x$ , where  $a$  is the loss of weight of a sheet of glass,  $o$  its surface,  $b$  the loss of weight of a powdered glass, and  $x$  its surface. If the dyes examined have a cubic molecular structure, the results of the experiments indicate that two adsorption layers are formed, but if the molecule has a parallelepiped structure and if the narrower face lies on the glass, there is only one adsorption layer. J. F. S.

**Adsorption as a Preliminary to Chemical Combination, and Adsorption Measurements on Zirconium Oxide Gels.**—E. WEDEKIND and H. WILKE (*Kolloid-Z.*, 1924, **34**, 83—96).—The adsorption of arsenious acid by zirconium oxide gels is normal and reversible, equilibrium being attained in a few hours; the amount of arsenic acid removed from solution continues to increase for some days, and only part of the acid can be recovered from the gel by washing. It is suggested that the zirconium oxide and the adsorbed arsenic acid undergo slow chemical combination, and a formula,  $Zr(HAsO_4)_2$ , is ascribed to the compound. S. B.

**Rôle of Adsorption in the Determination of Residual Nitrogen.** J. H. CASCÃO DE ANCIACO.—(See ii, 273.)

**Hydration of Natural and Artificial Glasses.** G. SCHOTT and G. LINCK (*Kolloid-Z.*, 1924, **34**, 113—116).—Measurements have been made of the rate at which obsidian, pitchstone, and artificial glasses take up water when the finely powdered substances are heated with water at about  $250^\circ$  and 35 atm. pressure. A Jena borosilicate glass, for example, absorbed more than 7% of water in 3 weeks. The results suggest that the process of taking up water is not usually one of chemical combination, but of imbibition by a

gel. The view that the obsidians contain chemically combined water is supported by observations on the dehydration of these substances. S. B.

**Rhythmic Banding of Precipitates (Liesegang's Rings).** H. McGUIGAN and G. A. BROUGH (*J. Biol. Chem.*, 1923, **58**, 415—423).—Mainly a reiteration of McGuigan's theory of the Liesegang phenomenon (A., 1922, ii, 38). Experiments, most of which are taken from the literature, are adduced to show that ring formation occurs in the absence of a gel provided that the factors which produce turbulence or assist diffusion are reduced to a minimum. A gel, when it is the medium in which precipitation takes place, further fixes the precipitate at the position of formation. E. S.

**Rhythmic Crystallisation of Undecoic Acid.** W. E. GARNER and F. C. RANDALL (*J. Chem. Soc.*, 1924, **125**, 369—372).—The rhythmic crystallisation of thin films of undecoic acid has been examined microscopically, by means of ordinary and polarised light. The troughs and crests of the wave forms are permanent and the distance between the crests varies with the thickness of the film. Rhythmic forms of the same kind are obtained when the glass surface of the microscope slide is replaced by a silver plate or by the crystal faces of selenite, calcite, or quartz.

The velocity of crystallisation diminishes with rise of temperature, and observations near the melting point showed that a solid skin, possessing a greater area than the glass surface, is produced on the surface of the acid which is still in the liquid condition. This skin wrinkles after the passage of the wave of crystallisation and gives rise thereby to the rhythmic structure. The formation of the solid skin is attributed to differences between the solidification temperatures of the acid at the liquid-air and liquid-glass interfaces.

Other acids, *e.g.*, myristic, lauric, decoic, etc., exhibit the phenomenon. S. K. T.

**Absorption of Gases by Colloidal Oxides, and the Mode of Action of Electric Accumulators.** P. BARY (*Rev. Gén. Coll.*, 1924, **2**, 33—37).—The mechanism involved in the production of current by lead storage batteries and by accumulators of the Edison and the Lalande-Chaperon types is considered to be analogous to that of the gas cells described by Cailletet and Collardeau (*Compt. rend.*, 1894, **119**, 830). J. S. G. T.

**Calorific Action of Radiation on Metals immersed in Solutions of their Salts.** G. ATHANASIU (*Compt. rend.*, 1924, **178**, 561—563).—The author has investigated the effect of illuminating, by means of a quartz mercury arc, one of two metal plates, immersed in a solution of a salt of the metal. With mercury, lead, and platinum, the *E.M.F.* generated between the two surfaces may be entirely ascribed to the heating effect of the radiation, whilst with silver, copper, cadmium, and zinc, a secondary effect, due to chemical alteration of the illuminated surface, is observed. E. E. T.

**Measurement of Small Quantities of Heat. Use of the Compensating Microcalorimeter.** A. TIAN (*Compt. rend.*, 1924, 178, 705—707).—An apparatus is described which the author has designed for the measurement of the relatively small heat changes which are associated with enzyme and similar reactions. It consists of a thermally insulated vessel serving as the calorimeter immersed in a constant-temperature bath. The two vessels are connected by a thermopile and a galvanometer which serve to detect and measure the variation in temperature difference between the two. Further details are given, for which the original should be consulted.  
E. E. T.

**Constitution and Heat of Combustion.** F. KIRCHHOFF (*Chem.-Ztg.*, 1924, 48, 113—114).—For saturated hydrocarbons from hexane onwards, the heat of combustion is expressed by the formula  $H=53,000(2n+2)+50,500(n-1)$ , the value 53,000 corresponding with the C·H linking and the value 50,500 with the C·C linking. For the lower members, the values are somewhat higher, in conformity with their gaseous condition. Using these values for the unsaturated series, the C:C bond has values varying from 2·0 to 2·3 times the value of the single bond, the C:C linking values from 3·3 to 4·0 times this value. For cyclic hydrocarbons, the single C·C linking has the value 63,000 cal. for *cyclopropane*, falling to 51,160 for *cyclohexane*. In the benzene series, taking the number of C·C linkings in benzene itself as 9, the value for this is 51,660 cal., and in the polycyclic benzene compounds, counting the number of linkings in the same way, the value remains approximately constant. From a consideration of the heats of combustion of the hydrogenated benzenes, the prism formula of Ladenburg is favoured, reduction to *cyclohexadiene* and *cyclohexene* leading to formation of *cyclobutane* and *cyclopentane* rings, respectively. Incomplete combustion of benzene yields amorphous carbon, which should therefore possess the same type of C·C linking; since the molecule of the latter contains about 1000 atoms, the number of C·C linkings may be taken as double the number of atoms, and as the heat of combustion per g. atom of amorphous carbon is 96,960, the value for a C·C linking is 48,480 cal., which is considered as a limiting value for benzene derivatives in the solid state of aggregation.

S. I. L.

**Thermodynamic Surface of Water.** A. BRANDT (*Ann. Physik*, 1924, [iv], 73, 409—411).—Diagrams are given to show the relationship between pressure, temperature, and volume in the equilibria which characterise the behaviour of water as a one-component system.  
M. S. B.

**Theory of the Velocity of Chemical Reactions.** N. BJERRUM (*Z. physikal. Chem.*, 1924, 108, 82—100).—The author discusses Brönsted's formula (A., 1922, ii, 699) for the influence of salts on the velocity of chemical change. In a new method of deducing Brönsted's formula the assumption is made that the velocity is proportional to the concentration of a complex intermediate sub-

stance formed by collision between the molecules of the reactants. The conclusion is drawn that the concentrations of the reacting substances cannot be replaced by either their osmotic pressures or their activities.

J. F. S.

[Theory of the Assimilation of Carbon Dioxide.] O. WARBURG and E. NEGELEIN (*Z. physikal. Chem.*, 1924, **108**, 101—102).—A criticism of the interpretation given to the authors' work by Weigert (A., 1923, ii, 1271) in the development of a theory relating to the assimilation of carbon dioxide.

J. F. S.

**Gas Kinetics.** C. S. LIND (*J. Physical Chem.*, 1924, **28**, 55—58).—The reaction of hydrogen with bromine is photosensitive at 250°. The reaction velocity under arc lamp illumination is twelve times that under the dark thermal conditions employed by Bodenstein and Lind (A., 1907, ii, 76), and the experiment affords quantitative confirmation of the results obtained by Kastle and Beatty (A., 1898, ii, 214). Calculation shows that the observed reaction velocity does not exceed the value required by photochemical equivalence and also that the Nernst hypothesis (A., 1919, ii, 208) is not violated by the reaction. Discussion of the mechanism of this reaction and of that of hydrogen and chlorine affords support for the view of Nernst and Noddack (A., 1923, ii, 526) that photochemical partial reactions are not amenable to thermodynamic treatment. The multicyclical theory of Nernst seems to offer the most reasonable explanation. In view of the results of Bodenstein and Dux (A., 1913, ii, 1039) it is held that the negative results of Amato (Kastle and Beatty, *loc. cit.*) for the reaction of hydrogen with chlorine at —12° may be due to the presence of oxygen or some other inhibitor. It is suggested that inhibitors for thermal and photochemical reactions are identical in nature, and that the mechanism is the same in both cases. Attempts to arrest the propagation of explosion in mixtures of hydrogen and oxygen, by means of an electric field, gave negative results.

A. E. M.

**Velocity of Oxidation of Nitric Oxide and its Importance in Nitrogen Fixation.** G. W. TODD (*Proc. Durham Phil. Soc.*, 1922—23, **6**, 291—307).—The equations derived by the author (A., 1918, ii, 102, 190) are discussed with reference to the experimental data obtained by Lunge and Berl (A., 1907, ii, 863) for the reactions  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$  and  $2\text{NO} + \text{O}_2 = \text{N}_2\text{O}_4$ . It is shown that these data give sensibly constant values for the velocity coefficient at 20° when pure oxygen is added to nitric oxide, but with air as oxidising agent higher values of the coefficient are found in the earlier stages of the reaction. This is ascribed to the time required for mixing the gases, and a mean value for the velocity coefficient is calculated from the data for later stages in the reaction. This value is used to derive the optimum conditions for the chemical change in question in the ammonia oxidation and arc processes for the fixation of nitrogen.

S. S.

**Starch-Iodine Reaction.** N. R. DHAR (*J. Physical Chem.*, 1924, 28, 125—130).—The nature of the starch-iodine reaction has been explained, on the one hand, by assuming the formation of a definite chemical compound, to which thirteen different formulæ have been ascribed, and, on the other, by the assumption that the blue colour is due to the adsorption of iodine by colloidal starch. The author considers that adsorption plays an important part in the formation of the blue substance. When an alcoholic iodine solution is added to an aqueous starch solution, the electrical conductivity of the resulting solution is definitely greater than the sum of the conductivities of the separate constituents. It is suggested that a colloidal adsorption product is formed which conducts by means of micellar ions. It behaves rather like an unstable iodide, and is readily destroyed by oxidising agents. The blue colour is immediately developed on the addition of freshly prepared alcoholic iodine solution to starch paste or colloidal starch, and in these circumstances the iodide ion can only be formed by hydrolysis of iodine, which reaction, being non-ionic, is probably slow. The effect of added electrolytes appears to consist in the intensification of the blue colour in consequence of the coagulation of the colloid.

M. S. B.

**Simplicity of Mechanism of Reaction as One of the Factors Conditioning Catalysis.** E. R. BULLOCK (*J. Physical Chem.*, 1924, 28, 179—181).—The reaction between silver in gelatin and a solution containing potassium dichromate and a bromide, slightly acidified with acetic acid, only occurs in presence of potassium ferricyanide or copper sulphate, which appear to act as catalysts. The author accounts for the action of the catalyst by the greater simplicity of the initial ionic reaction  $\text{Fe}(\text{CN})_6''' + \text{Ag} = \text{Ag}^* + \text{Fe}(\text{CN})_6''''$  or  $\text{Ag} + \text{Cu}'' = \text{Ag}^* + \text{Cu}^*$  as compared with  $3\text{Ag} + \text{Cr}'''' = 3\text{Ag}^* + \text{Cr}'''$  which involves four ions instead of two. Experiment also showed that 0.0001*N*-ferric sulphate increases by ten times the rate of "bleaching" of a silver image by 0.05*N*-bromic acid, and simplification of the mechanism is again suggested as the explanation.

The only other known instance of a catalysed reaction of this type is afforded by the reaction between zinc and a dilute solution of potassium permanganate and sulphuric acid in presence of a trace of pure nitric acid. This may be explained by the relative simplicity of the reaction  $\text{Zn} + \text{N}'''' = \text{Zn}'' + \text{N}'''$ . It is admitted, however, that further instances should be sought before the principle is accepted as valid.

M. S. B.

**Negative Catalysis.** J. A. CHRISTIANSEN (*J. Physical Chem.*, 1924, 28, 145—148).—The author is of opinion that Taylor's explanation (*A.*, 1923, ii, 399) of negative catalysis in homogeneous systems, namely, that the formation of molecular compounds with the negative catalyst leads to a reduction in the number of the reactive molecules, cannot be true in all cases, for the proportion of such non-reactive compounds must be very small where the number of molecules of catalyst necessary is only a small fraction

of the total number of molecules of reacting gases. The molecules of the reaction products possess, immediately after the reaction, an amount of available energy which is greatly in excess of the mean energy at the temperature considered, since not only do they contain the critical energy necessary for the reaction to occur, but often also the kinetic or potential energy which is represented by the heat evolved in the reaction. These molecules are able to activate more molecules of the reactants by collision, and these in turn produce fresh activators as in the so-called "chain reactions" (Bodenstein, *Z. physikal. Chem.*, 1913, **85**, 346; A., 1916, ii, 422). The author suggests that in such cases the negative catalyst acts by taking up the energy from the active molecules and thus breaking the chain (Göhring, A., 1922, ii, 9). This theory indicates a method by which chain reactions may be detected. They are reactions which can be inhibited by a small quantity of a foreign substance.

There are other instances of negative catalysis where the mechanism must be different. For example, the decomposition of oxalic acid by sulphuric acid is retarded by the presence of small quantities of water, probably in consequence of the displacement of the equilibrium  $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{O} + \text{SO}_3$ , since addition of small quantities of  $\text{SO}_3$  greatly increases the rate of reaction.

M. S. B.

**Catalytic Hydrogenation of Organic Compounds with Common Metals at the Temperature of the Laboratory. VI. Influence of Oxygen on Nickel Catalysts. Influence of Water on Nickel Catalysts at Elevated Temperatures, Temperature of Reduction, and Activity.** C. KELBER (*Ber.*, 1924, **57**, [B], 136—141).—It has been shown previously (Kelber, A., 1921, ii, 630) that, contrary to the statement of Willstätter and Waldschmidt-Leitz (A., 1921, ii, 187), the presence of oxygen is not necessary for hydrogenation in the presence of metallic nickel. A comparison of the behaviour of the pure metal with that of the metal deposited on a carrier shows that the latter catalyst recovers its activity more rapidly than the pure metal when, after inactivation has been induced by relatively short contact with oxygen, the two forms are placed in hydrogen. After prolonged contact with oxygen at 20°, both types of catalyst regain activity more slowly in the presence of hydrogen and do not become fully active after many hours. Catalytic activity seems to be destroyed permanently by exposure of the catalysts to oxygen at 60—70°.

The nickel catalyst deposited on a carrier suffers a marked loss in activity when its suspension in water is heated in an atmosphere of hydrogen, whereby it is caused to react with the water, yielding hydrogen and, apparently, nickelous oxide, which forms a coating over the unchanged metal. Under similar conditions, the pure nickel catalyst does not become oxidised or suffer loss in catalytic activity.

In contrast with the pure nickel catalyst (cf. Kelber, A., 1916, ii, 309), the metal deposited on a carrier exhibits an optimum



activity when prepared at 350°, but is not completely inactive when reduction is effected at 1000°. On the other hand, pure nickel, prepared at 550°, is practically inactive. H. W.

**Catalytic Hydrogenation of Organic Compounds with Common Metals at the Temperature of the Laboratory. VII. Hydrogenations with Elementary Nickel in the Absence of Oxygen.** C. KELBER (*Ber.*, 1924, 57, [B], 142—143).—The possibility of effecting catalytic hydrogenation with the aid of nickel in the absence of oxygen (cf. Kelber, A., 1921, ii, 630; Willstätter and Waldschmidt-Leitz, A., 1921, ii, 187; Willstätter and Seitz, A., 1923, i, 771) is established by the observations that diphenyldiacetylene and azobenzene dissolved in hexane are very readily reduced in the presence of nickel prepared from nickel cyanide. The activity of the catalyst thus obtained resembles that of the product derived from nickel carbonate, since the optimum results are secured when reduction is effected at about 300° and less active specimens are formed at higher temperatures. Support is thus afforded for the author's view that loss in activity is due to surface changes in the metal. H. W.

**Photolysis and the Law of the Photochemical Equivalent.** VOLMAR (*Compt. rend.*, 1924, 178, 697—700).—The wave-lengths of the radiant energy which is responsible for the photolysis of ketones, aldehydes, and aliphatic acids have been calculated from the law of photochemical equivalence, in the form  $Q\lambda = 3 \times 10^4$  (where  $Q$  is the energy in cal. required to effect photolysis). Indirect methods were used to calculate  $Q$ . It is found that  $\lambda = 0.27\mu$  for ketones,  $0.28\mu$  for aldehydes, and  $0.21\mu$  for aliphatic monocarboxylic acids, these values being in good agreement with experiment. It is further shown that the active wave-length is the same for different compounds which contain the same group, and that this wave-length corresponds with the position of maximum absorption.

E. E. T.

**Photographic Action of Canal Rays.** M. JAKOBSON (*Ann. Physik*, 1924, [iv], 73, 326—338; cf. Königsberger and Kutschewski, *Physikal. Z.*, 1910, 11, 666).—By observation of the blackened traces produced on photographic plates by the action of canal rays which have passed through a combined magnetic and electric field, a gas mixture can be analysed qualitatively. The author thought it might be possible, by measuring the degree of blackness produced, to make a quantitative analysis also. To do this, it was first necessary to determine under what conditions such measurements might be regarded as trustworthy. Perutz silver chloride-bromide diapositive plates were found to be most satisfactory. The light was found to produce only a small proportion of the blackening from a short exposure, but its relative importance increases with length of exposure. When both act together, however, the canal rays apparently reduce the effect of the light rays still further. Three stages have been observed as the length of exposure is gradually increased. (1) A blackening is obtained which increases

to a limiting value. This effect is not fundamentally different from that due to the action of light, and it is from this that it should be possible to make quantitative determinations. (2) A white circular patch appears in the centre of the black spot, comparable with the effect obtained by over-exposure to light. (3) Black islets appear in the white patch, and these are probably crystals of silver surrounded by gelatin. For the last two stages, an explanation is suggested which depends on the disintegration of the gelatin and its subsequent re-hardening under the prolonged bombardment by the canal rays. M. S. B.

**Influence of Gum Arabic on the Hydrolysis of Methyl Acetate.** J. N. PEARCE and J. V. O'LEARY (*J. Physical Chem.*, 1924, 28, 51—54).—Gum arabic solutions absorb infra-red radiation, and if it is capable of emitting infra-red radiation which is absorbable by methyl acetate, then according to the radiation hypothesis gum arabic might be expected to accelerate the hydrolysis of methyl acetate. Measurements of the rate of hydrolysis of methyl acetate in presence of hydrochloric acid at 25° have shown that the velocity of the reaction is diminished in the presence of gum arabic. The decreased velocity is shown to be due to a diminution in the hydrogen-ion concentration brought about by the adsorption of the hydrochloric acid by the gum. The fall in the hydrogen-ion concentration increases with the amount of gum arabic present in the solution. J. F. S.

**Accurate Calibration of Capillary Tubes.** K. J. ISAAC and I. MASSON (*J. Physical Chem.*, 1924, 28, 166—169).—The tube, closed at the top, is mounted vertically in a jacket at constant temperature and the calibration is made with mercury. Horizontal calibration is untrustworthy, since the meniscus sags and its volume cannot be determined. The weights of successive 2 cm. mercury threads are determined; a second calibration with intervals overlapping those of the first set is then made, and, finally, as a check, a single "overall" determination. Corrections for the mercury meniscus, which should always be a rising one, are made by the aid of Schalkwijk's data [*Comm. Phys. Lab. Leiden*, No. 67 (1901); *Verslag. Kon. Akad. Wet. Amst.*, 1900, 462: 1901, 512]. The mean calibration curve, showing mean cross-section or volume per linear cm., is plotted. The aggregate volume of the tube is calculated and compared with the "overall" determination. The difference, which is not usually more than 1 in 6000, is distributed proportionally over the length of the tube as being probably due to a cumulative error in the meniscus correction. The accuracy of the calibration is 1 part in several thousand parts. M. S. B.

**[Substitute for Ground Joints in Vacuum Technique.]** G. LANDESEN (*Ber.*, 1924, 57, [B], 183).—A claim for priority against von Antropoff (*A.*, 1923, ii, 850). H. W.

**Apparatus for Drying Gases.** V. T. JACKSON (*Ind. Eng. Chem.*, 1924, 16, 163).—A glass tube 45 cm. × 5 cm. is fitted with a gas inlet at the lower end and an outlet near the top. In the

bottom is placed a layer of glass wool 1 cm. thick, and on this glass beads to a depth of 10 cm. The tube is filled to this depth with concentrated sulphuric acid. Openings are also provided for filling and emptying. If charged with 50% potassium hydroxide solution, the apparatus serves for removing carbon dioxide from air.

C. I.

**Constant-level Regulator for Water Distillation.** L. JEND-RASSIK (*Biochem. Z.*, 1924, **144**, 285—286).—A simple constant-level apparatus for continuous water distillation is described. The principle consists in passing the condenser water through a constant-level vessel from which a siphon tube, terminating in a capillary, reaches to the bottom of the still.

J. P.

**Prevention of "Bumping" during Vacuum Distillation.** H. G. BECKER (*J. Chem. Soc.*, 1924, **125**, 460—461).—"Bumping" is prevented by the use of a flask, inclined at 45°, which is rotated rapidly about its axis (150—200 revs. per min. for small flasks) and is connected with the rest of the apparatus by means of a well-greased ground joint.

S. K. T.

**Device for Gas-heated Thermostats.** W. MURRAY (*J. Chem. Soc.*, 1924, **125**, 461—462).—A device for obviating the sticking of mercury in a thermo-regulator is described. Two calcium chloride towers are arranged in U-tube form by connecting the lower tubulures, and are partly filled with water. The upper end of one of these towers is closed by a cork, through which pass the gas supply tube and the exit tube leading to the regulator. The ball-shaped head of a glass float fits into the supply tube, and when the pressure exceeds the normal, the water in the tower is driven down and the float closes the entry tube. When the excess of gas thus trapped is used up, the water rises and the process is repeated. The flame of the regulator pulsates in step with the float (adjusted, by the quantity of water, to 30 or 40 pulsations per minute) and the mercury surface in the regulator is in constant but almost imperceptible motion.

S. K. T.

**Automatic Pressure Regulator.** L. E. DAWSON (*Ind. Eng. Chem.*, 1924, **16**, 160—161).—The device described, which is capable of maintaining for days a constant difference of pressure between a partly exhausted system and the atmosphere, consists of a trap connected on the one hand to the system under suction, and, on the other, by two vertical tubes of different diameters, to a mercury reservoir open to the atmosphere and placed below the trap. The narrower of the two connecting tubes dips less deeply into the reservoir than the wider one. Should the pressure in the trap fall, mercury is drawn up into it, uncovering the end of the narrower tube and permitting air to be momentarily sucked up, restoring equilibrium. The lengths of the two tubes are adjusted to the pressure difference which is to be maintained, and their diameters to the capacity of the air-pump used. The apparatus can readily be modified to work with a pressure greater than atmospheric.

C. I.

**Soxhlet Extraction Apparatus.** P. H. PRAUSNITZ (*Z. angew. Chem.*, 1924, **37**, 50).—The usual paper extraction thimble is replaced by a filter-plate made of porous glass (cf. following abstract), which is fused into the extraction vessel and is preferably concave upwards. The rest of the apparatus is as usual, except that an extra tube, connecting the parts of the apparatus above and below the filter-plate, is necessary for equalising the pressure or removing displaced air. The apparatus can be used for extracting with such solvents as acetic acid or 20% hydrochloric acid. W. T. K. B.

**Use of Filter-plates made of Sintered Glass.** G. F. HÜTTIG (*Z. angew. Chem.*, 1924, **37**, 48—50).—Glass filter-plates of various degrees of porosity, prepared by sintering finely powdered and sieved glass, are sealed into glass crucibles, filter funnels, etc. Crucibles fitted with such plates are found to be preferable to Gooch crucibles for quantitative analytical work, in that they filter more quickly, dry more readily, show less variation in weight when left exposed to the atmosphere, and do not require packing with asbestos. They cannot, of course, be heated to redness, nor are they resistant to strong alkalis. W. T. K. B.

**Rapid Analysis of Sugars. Purification and Concentration of Enzyme Solution.** F. W. REYNOLDS.—(See i, 464.)

**Apparatus for the Determination of Colour in Terms of Dominant Wave-length, Purity, and Brightness.** I. G. PRIEST (*J. Opt. Soc. Amer.*, 1924, **8**, 173—200).—The author describes a monochromatic colorimeter and accessory apparatus for the determination of the dominant wave-length in heterogeneous light, for the investigation of the purity of white light, and the changes produced by transmission and reflection under specified conditions.

**Transport Apparatus.** A. JANEK (*Kolloid-Z.*, 1924, **34**, 103—104).—An apparatus is described suitable for the rapid determination of the sign of the charge on a dispersoid. The colloidal solution is placed in a U-tube the ends of which are closed by colloidal membranes, and the electrodes are supported above the membranes in wider tubes which are attached to the limbs of the U-tube. The movement of the particles towards one film and away from the other is observed either visually or by analysis of the solution. S. B.

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### Inorganic Chemistry.

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**Halogen Hydrides.** H. BELL.—(See ii, 230.)

**Crystal Structure of Hydrogen Chloride.** F. SIMON and C. VON SIMSON.—(See ii, 229.)

**Determination of the Boiling Point of Bromine.** A. BOUZAT and G. LELUAN (*Compt. rend.*, 1924, 178, 635—637).—The b. p. of  
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pure bromine is found to be  $58.80^{\circ}/760$  mm. (referred to the hydrogen scale). The result is thought to be correct to less than  $0.1^{\circ}$  (cf. Ramsay and Young, T., 1886, 49, 453). E. E. T.

**Vapour-pressure Measurements for Pure Ozone.** E. H. RIESENFELD and M. BEJA (*Z. anorg. Chem.*, 1923, 132, 179—200).—The vapour pressures of pure ozone between  $-169^{\circ}$  (4.8 mm. mercury) and  $-108.5^{\circ}$  (840.8 mm.) have been determined with an accuracy estimated to be within about 1%. From the results, the Nernst equation for ozone is found to be  $\log p = -742.4/T + 1.75 \log T - 0.01169T + 5.4769$ ,  $T$  being the absolute temperature and  $p$  mm. of mercury. The heat of vaporisation at absolute zero is calculated as 3500 cal. per mol., and values are given for each  $10^{\circ}$  rise from  $111^{\circ}$  to  $165^{\circ}$  Abs. The chemical constant  $c$ , calculated from the relation observed by Nernst with the van der Waal constant  $a$ , namely,  $c = 1.1a$ , using the average value of  $a$  for ozone at about half an atmosphere pressure, is 2.90; employing this and the value 3500 for the heat of vaporisation at absolute zero, the Nernst equation becomes  $\log p = -765.7/T + 1.75 \log T - 0.01268T + 5.783$ , which also agrees well with the observed vapour pressures. The b. p. calculated from this equation is  $-110.7^{\circ}$ , the actual value previously observed by Riesenfeld and Schwab (A., 1922, ii, 761) being  $-112.3^{\circ}$ ; the true temperature may therefore be assumed on present knowledge to be  $-111.5^{\circ} \pm 0.5^{\circ}$ . The molecular heat of liquid ozone is calculated to be about 18. S. I. L.

**Thiosulphates.** F. FOERSTER and E. T. MOMMSEN (*Ber.*, 1924, 57, [B], 258—263).—The reaction between sulphurous acid and hydrogen sulphide can be represented by the equilibrium  $\text{H}_2\text{S} + \text{H}_2\text{SO}_3 \rightleftharpoons \text{H}_2\text{S}_2\text{O}_2 + \text{H}_2\text{O}$  (cf. Foerster and Hornig, A., 1923, ii, 23); the intermediate product is converted by an excess of sulphurous acid into sulphylic acid, which becomes polymerised to thiosulphuric acid:  $\text{H}_2\text{S}_2\text{O}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow 3\text{H}_2\text{SO}_2$  and  $2\text{H}_2\text{SO}_2 \rightarrow \text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$ . The production of thiosulphuric acid may therefore be expected to be the end-point of the changes if the reaction can be conducted under conditions such that the hydrogen-ion concentration is insufficient to affect the stability of the thiosulphate anion. These conditions are realised experimentally when aqueous solutions of sodium hydrogen sulphide and sodium hydrogen sulphite in the molecular proportion 1 : 2 are mixed, whereby sodium thiosulphate is obtained readily and in a high degree of purity:  $2\text{NaHS} + 4\text{NaHSO}_3 \rightarrow 3\text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$ . The preparation of sodium thiosulphate from sodium sulphide and sulphur dioxide or from sodium sulphite and hydrogen sulphide occurs very smoothly and almost without separation of sulphur when alkali hydroxide is added initially to the solution in such amount as to lead ultimately to the presence of sodium hydrogen sulphide and sodium hydrogen sulphite in the correct proportion. H. W.

**Maxted's Synthesis of Ammonia at High Temperatures.** W. MOLDENHAUER (*Chem.-Ztg.*, 1924, 48, 73—74).—Haber and Nernst have shown that ammonia is an exothermic compound and

that the quantity in equilibrium with its constituent gases at temperatures above  $1000^{\circ}$  is vanishingly small. Maxted (A., 1918, ii, 165), however, has synthesised ammonia by injecting nitrogen and hydrogen into an oxy-hydrogen flame, and the equilibrium constant of the reaction calculated from his figures is shown to increase with the temperature, suggesting that the reaction is endothermic. Haber's results show a maximum heat of formation at  $1100^{\circ}$  and a zero value above  $2000^{\circ}$ . It is suggested that at the temperature of the flame nitric oxide is formed, and on cooling the gases (which contain a large amount of unburnt hydrogen) this is reduced to ammonia.

A. R. P.

**Influence of Temperature on the Decomposition of Ammonia by Ultra-violet Light.** W. KUHN (*Compt. rend.*, 1924, 178, 708—709; cf. A., 1923, ii, 815).—The rate of photochemical decomposition of ammonia ( $20$ — $500^{\circ}$ ) is independent of the pressure, between 30 and 300 mm. It rises with increase of temperature, but to a less extent than for most chemical changes. The rate falls off as decomposition proceeds, is decreased in presence of hydrogen, but is unaffected by the presence of nitrogen. This is due to the fact that molecular hydrogen, but not molecular nitrogen, is capable of reacting with activated ammonia molecules. E. E. T.

**Catalysts for the Oxidation of Ammonia. II. Sand Iron Briquette as a Catalyst. III. Effect of Impurities in the Catalyst.** K. INABA (*Rikwagaku Kenkyujo Ihô*, 1923, 2, 426—431, 431—434; cf. *ibid.*, 2, 222).—II. Grains of "sand iron briquette" (Yamaguchi, *J. Chem. Soc. Japan*, 42, 317) were used as a catalyst for the oxidation of ammonia. The briquette, when reduced by the cyanide process, immersed in nitric acid containing bismuth nitrate, and heated at red heat, gave a 72.23% yield (9.51% concentration of ammonia). When thorium nitrate was added to a solution of nitric acid and bismuth nitrate, about 72% yields were obtained (10% concentration of ammonia). A gap in the yield-curve was observed at about 7% ammonia, which may be attributed to the presence of titanium (5%) in the briquette.

III. The addition of 1% of calcium oxide to the iron-bismuth-thorium catalyst described above gives about 3% increase of the yield. Titanium oxide has practically no effect, but a break in the yield curve was observed at about 7% concentration of ammonia. With 1% of zinc or magnesium oxide decreases of 17—18% and 7—8% respectively were observed in the yield of ammonia.

K. K.

**Oxidation of Hydroxylamine.** A. KURTENACKER and R. NEUSSER (*Z. anorg. Chem.*, 1923, 131, 27—47).—The oxidation of hydroxylamine by excess of permanganate, bromate, or ferric salt is greatly influenced by the acidity or alkalinity of the solutions and to a much smaller extent by the concentrations. With permanganate in acid or strongly alkaline solutions, the products of oxidation are nitrous oxide and nitric acid or nitrite; in slightly alkaline solutions the oxidation products also contain nitrogen. With

bromate, the oxidation takes place only in neutral or acid solutions, and occurs in two stages: (1) a slow oxidation by the bromate itself yielding nitrogen only, followed by (2) the liberation of free bromine with rapid oxidation to nitrous oxide and nitric acid, the proportion of the latter increasing with the acidity. Reaction (2) is greatly accelerated by acids, and in strongly acid solution the sole oxidation product is nitric acid. With ferric salt in acid solution, the sole oxidation product is nitrous oxide, but the action is not complete unless the ferric salt is in considerable excess. In neutral solution, a little nitrogen is produced, but in alkaline solution the ferrous hydroxide formed is itself oxidised by the hydroxylamine.

These results are discussed and accounted for by the following scheme of reactions: (1)  $\text{NH}_2\cdot\text{OH} + \text{O} = \text{NOH} + \text{H}_2\text{O}$ , (2)  $2\text{NOH} = \text{H}_2\text{N}_2\text{O}_2 = \text{N}_2\text{O} + \text{H}_2\text{O}$ , (3)  $\text{NOH} + \text{O}_2(\text{O}) = \text{HNO}_3(\text{HNO}_2)$ , (4)  $\text{NOH} + \text{NH}_2\cdot\text{OH} = \text{N}_2 + 2\text{H}_2\text{O}$ . Reaction (1) is greatly accelerated by acids, and reaction (4) cannot take place in acid solution. W. H.-R.

**Peculiar Catalytic Decomposition of Hydroxylamine.** A. KURTENACKER and R. NEUSSER (*Z. anorg. Chem.*, 1923, **131**, 310—320).—The decomposition of hydroxylamine in presence of a vanadate in acid solution yields nitrogen and nitrous oxide, the proportion of the latter first decreasing and then increasing with decreasing acidity. Simultaneous reduction of the vanadate takes place. In neutral solution, nitrous oxide only is produced, but in alkaline solution catalytic decomposition to nitric and nitrous oxides and nitrogen takes place, the proportions of the first two decreasing with increasing alkalinity. The oxygen in these gases must be derived from the hydroxylamine, and the reduction of the latter to ammonia was proved, 100 mols. of hydroxylamine giving 48.8 mols. of ammonia in weakly alkaline solutions and 2—3 mols. in acid solutions.

When the vanadate is replaced by ammonium molybdate, nitric oxide, nitrogen, and nitrous oxide are produced, the first-named decreasing in amount as the solution passes from acid to alkaline. The gas evolution corresponds with about half the hydroxylamine used; the molybdate behaves like the vanadate in strongly alkaline solutions. S. K. T.

**Velocity of Oxidation of Nitric Oxide and its Importance in Nitrogen Fixation.** G. W. TODD.—(See ii, 241.)

**Structure of Phosphorus.** H. COLLINS.—(See ii, 229.)

**Relation between the Glow of Phosphorus and the Formation of Ozone.** W. E. DOWNEY (*J. Chem. Soc.*, 1924, **125**, 347—357).—Pure dry oxygen was passed over purified phosphorus in non-actinic light, the oxides of phosphorus was afterwards frozen out, and the ozone absorbed in 2% potassium iodide solution, the iodine liberated being determined colorimetrically. The amount of ozone formed was proportional to the intensity of the glow, although a perfectly fresh phosphorus surface did not show this until it had become "acclimatised." The action of the glow on a stream of oxygen through windows of quartz or fluorite 2 mm.



thick caused the formation of ozone, similar stains being produced on potassium iodide-starch paper in 10 minutes with a window of quartz and 1 minute with one of fluorite. The use of phosphorus trioxide in place of phosphorus gave similar results, but of a much lower degree of intensity, *e.g.*, an hour elapsed before ozone was detected in the second experiment (fluorite window). The glow was shown to be capable of ionising air and hence (Hughes, *Proc. Camb. Phil. Soc.*, 1910, **15**, 483) its spectrum extends into the region  $\lambda$  1200—1800 Å., which supports the idea that the ozone is formed by the glow of the phosphorus. S. K. T.

**Unimolecular Decomposition of Phosphine.** C. N. HINSHELWOOD and B. TOPLEY (*J. Chem. Soc.*, 1924, **125**, 393—406).—The rate of thermal decomposition of pure phosphine in a silica bulb was investigated under varying conditions. The bulb seemed to exert some activating influence which, after a time, decreased to a constant minimum; porcelain was no less active than silica. The addition of powdered fused silica of an approximately known surface area caused a velocity increase corresponding with the increased surface; the reaction was thus shown to be heterogeneous ("wall-reaction" as distinct from gas-reaction) up to 1044° Abs. at least, in contradiction to the results of Trautz and Bhandarkar (*A.*, 1919, ii, 277). The decomposition is unimolecular over the pressure range 37.5—707 mm. The heat of activation determined from the experimental results was approximately constant between 40,000 and 50,000 cals., the average calculated value for a homogeneous (gas-) reaction between 940° and 956° being 86,719 cals. Thus no evidence is afforded that the wall-reaction changes its nature at higher temperatures. S. K. T.

**Dissociation Constants of Phosphoric Acid.** E. B. R. PRIDEAUX and A. T. WARD (*J. Chem. Soc.*, 1924, **125**, 423—426).—From the various published dissociation constants of phosphoric acid, it is shown that the most probable values of  $k_2$  and  $k_3$  are about  $6 \times 10^{-8}$  and  $1.1 \times 10^{-12}$ , respectively. S. K. T.

**Preparation of Metallic Arsenides by the Action of Arsenic Hydride on Metallic Salt Solutions.** A. BRUKL (*Z. anorg. Chem.*, 1923, **131**, 236—246).—Arsenides of the heavy metals are prepared by dropping an aqueous solution of a salt of the appropriate metal into an atmosphere of arsenic hydride in the complete absence of air, the reaction vessel being frequently shaken; precipitation by the usual method is accompanied, in the cases of copper, mercury, lead, gold, and silver, by a secondary reaction with the excess metallic ions in the solution,  $M_3As + 3M^+ + 3H_2O = 6M + 3H^+ + As(OH)_3$ , and in the cases of metals of higher valency by the production of the lowest oxides of these metals. With metals of the iron group, alcoholic solutions of the salts were required, aqueous solutions giving a product contaminated with arsenic.

The heavy metal arsenides are black, readily oxidisable substances. On keeping in air they are converted into the metal and arsenious acid, whilst in the dry state they ignite spontaneously.

At higher temperatures, in the absence of air, the arsenides of the noble metals lose nearly all their arsenic, the other heavy metal arsenides being converted to lower arsenides. Metallic arsenides and phosphides (cf. A., 1922, ii, 393) are of similar structure, the former being the more stable.

Arsenides of the following metals were prepared : copper ( $\text{Cu}_3\text{As}$ ), lead ( $\text{Pb}_3\text{As}_2$ ), mercury ( $\text{Hg}_3\text{As}$ ), gold ( $\text{AuAs}$ ), silver ( $\text{Ag}_3\text{As}$ ), bismuth ( $\text{BiAs}$ ), cadmium ( $\text{Cd}_3\text{As}_2$ ), iron ( $\text{Fe}_3\text{As}_2$ ), and nickel ( $\text{Ni}_3\text{As}_2$ ). Cobalt arsenide could not be prepared free from elementary arsenic. Of the above arsenides, those of lead and cadmium give arsenic hydride with cold dilute acids and those of copper, gold, and bismuth are stable towards dilute acids and alkalis. Strong nitric acid decomposes gold arsenide, yielding spongy gold, whilst hot water and alkalis decompose lead arsenide, yielding spongy lead. Zinc and manganese arsenides are readily hydrolysed, and so could not be prepared by the above method. S. K. T.

**Formation of Arsenate Jellies.** H. B. WEISER and A. P. BLOXSOM (*J. Physical Chem.*, 1924, 28, 26—40).—A typical inorganic jelly is made up of a network of minute particles that adsorb liquid strongly; hence jellies may be prepared by coagulating a colloidal solution of a highly hydrated substance in the absence of an electrolyte that possesses an appreciable solvent action. The effect of salts on the formation of jellies is determined in large measure by the precipitating and stabilising action of the ions. A relatively slow rate of precipitation is essential such as may be realised in the immediate vicinity of the precipitation concentration of an electrolyte. A little below this value no precipitation or only a slight precipitation occurs, whilst above it coagulation is usually so rapid that a gelatinous precipitate is formed instead of a jelly. The formation of jellies by dialysis of a colloidal solution of a hydrated substance is a special case of coagulation of a colloid by decreasing the adsorption of the stabilising ion below a critical value. Colloidal ferric arsenate and aluminium arsenate have been prepared which owe their stability to adsorbed hydrogen ions. Jellies result by reducing the concentration of the stabilising ions by dialysis. Similar results have been obtained by coagulating the colloids with various electrolytes having strongly adsorbed cations, such as citric, sulphuric, phosphoric, and oxalic acids, ammonia, sodium sulphate and acetate. Since jellies are formed by coagulation of the colloid by acids, it is evident that the neutralisation of the adsorbed hydrogen ion and not the hydrogen-ion concentration in the solution is important. Jellies may be formed by mixing quite dilute solutions that react to form a hydrated precipitate, provided the precipitation can be delayed until the interacting solutions are thoroughly mixed and then can be made to proceed at a suitable rate. These conditions have been realised with the arsenates of manganese, cobalt, ferrous iron, cadmium, and zinc by mixing solutions of their salts of strong acids with potassium dihydrogen arsenate in the cold and keeping them at the ordinary temperature or warming to a suitable temperature. J. F. S.

**Colloidal Silica.** F. DIÉNERT and F. WANDENBULCKE (*Compt. rend.*, 1924, 178, 564—566).—The conversion, in aqueous solution, of colloidal into non-colloidal silica is effected by dissolved salts, and is accelerated by rise of temperature. Alkali carbonates are more active catalysts than neutral salts, whilst salts with an acid reaction (*e.g.*, aluminium sulphate) hinder the conversion. The change is so much more rapid in quartz than in platinum vessels that in the former case it proceeds in a short time in the absence of salts, under which conditions no change occurs in platinum vessels. The dialysis of a solution obtained by mixing sodium silicate and hydrochloric acid solutions has been followed by the molybdate method (A., 1923, ii, 507).

A solution of sodium (or potassium) silicate was kept in a glass vessel for several months. On then submitting it to the action of a current of carbon dioxide, it showed an increased silica content (as determined by the molybdate method), the original silica content being observed, however, a day later, when the carbon dioxide had disappeared.

E. E. T.

**Hydration of Natural and Artificial Glasses.** G. SCHOTT and G. LINCK.—(See ii, 238.)

**Soft X-Rays from Carbon.** P. I. LUKIRSKY.—(See ii, 215.)

**Fusibility of Carbon in the Heat of the Electric Arc.** A. THIEL and F. RITTER (*Z. anorg. Chem.*, 1923, 132, 153—158).—The presence of apparently solidified drops of graphite in the crater of the carbon electrode allowed to cool after forming the arc, is confirmed by photomicrographs, but from a study of the arc in being it is definitely concluded that the spherical formation is not a result of fusion. When no chemical action takes place in the vicinity of the arc, a cloud of carbon dust is formed, which settles partly on the electrodes, especially on the anode, forming crystalline, dendritic structures which glow brightly and disappear by sublimation. It is intended to obtain cinematographic pictures of the arc in being in order to decide if momentary fusion occurs.

S. I. L.

**Determination of the Vapour Pressure of Carbon.** A. THIEL and F. RITTER (*Z. anorg. Chem.*, 1923, 132, 125—152).—Two methods which might be expected to indicate temperatures corresponding with definite vapour pressures have been examined. In the first, a filament of 0.4 mm. diameter, purified to contain only 0.02% of ash by a preliminary heating for 2 minutes at 1700—1800° in a high vacuum, was heated for short periods to definite temperatures in an atmosphere of pure helium at definite pressures, the rate of loss of weight at each temperature and pressure being recorded (*cf.* Ruff and Bergdahl, A., 1919, ii, 265). The rate of loss-temperature curve for 2.0 mm. pressure showed no sudden break, but a rapid change in direction; that for 0.03 mm. was not very definite, although a very sharp break was indicated. The curve for 0.08 mm. was very well defined, and showed a sudden break at 2415° Abs., which is accepted as the temperature at which the vapour pressure

of the carbon filament became equal to the external pressure of the argon atmosphere.

In the second method, a cylindrical length of pure carbon was heated under constant pressures of pure argon by means of increasing electric currents; measurements were made at 100, 10, and  $1.0 \pm 0.1$  mm. of mercury, and curves constructed for each pressure to show the relation of temperatures to electric power. These showed no definite maximum temperatures, but that for 1 mm. indicated approach to a maximum at a temperature estimated to be about  $2400^{\circ}$  Abs.; experimental difficulties prevented the completion of the curves.

Measurements of the absolute temperature of the positive crater of a pure carbon arc under various pressures of air and argon were also made, but the former were some  $500^{\circ}$  lower than those given by Kohn (A., 1921, ii, 302); in argon at a pressure of 1 mm. the observed temperature was  $2300^{\circ}$  Abs. It is doubtful if the arc system really corresponds with a vaporisation equilibrium, although it is recognised that the results obtained by the other two methods cannot be regarded as final.

S. I. L.

**Graphite as a Metallic Modification of Carbon.** E. RYSCHEWITSCH (*Chem.-Ztg.*, 1924, 48, 101).—The atomic configuration of graphite is characterised, like that of the metals, by the presence of free electrons which make it a good conductor of heat and electricity and confer on it its metallic lustre. It is a better conductor of electricity than mercury, and a better conductor of heat at high temperatures than many of the pure metals. It resembles metals in not being soluble without change in any solvents except liquid metals, and it yields the positive  $C^{+++}$  ion in sufficient concentration to be electromotively active.

A. R. P.

**[Oxidation of] Carbon Monoxide.** G. FESTER and G. BRUDE (*Brennstoff-Chem.*, 1924, 5, 49—53; cf. this vol., ii, 173).—Carbon monoxide is oxidised to carbon dioxide by oxygen, even at the atmospheric temperature, in the presence of a palladium catalyst. The latter does not bring about preferential oxidation of carbon monoxide in admixture with hydrogen, but, given a sufficient partial pressure of carbon monoxide, such preferential oxidation occurs with vanadic acid as catalyst. Carbon monoxide is also slowly oxidised at the atmospheric temperature by an acid solution of vanadium pentoxide (5 g. in 50 c.c. of concentrated sulphuric acid containing 0.1 g. of mercury).

W. T. K. B.

**Absorption Spectrum of Potassium Vapour at High Temperatures.** A. L. NARAYAN and D. GUNNAYYA.—(See ii, 219.)

**Constitution and Structure of an Atom of Sodium.** H. COLLINS.—(See ii, 229.)

**Determination of Molecular Weights of Sodium Salts by Cryoscopy in Fused, Hydrated Sodium Thiosulphate.** A. BOUTARIC, E. CHAUVENET, and (MLLE.) Y. NABOT (*Compt. rend.*, 1924, 178, 571—572; cf. A., 1911, ii, 1060, etc.).—Sodium thio-

sulphate pentahydrate, used as a cryoscopic solvent, gives normal values for the molecular weights of most sodium salts (chloride, bromide, iodide, carbonate, nitrate, nitrite, phosphate, acetate, and arsenate). Sodium sulphate (anhydrous) had  $M=303$ , a value attributed to polymerisation, whilst borax had  $M=140$  (anhydrous salt), no doubt owing to hydrolysis. No experimental details are given.

E. E. T.

**Thermal Analysis of the System, Sodium Thiosulphate-Water.** M. PICON (*Compt. rend.*, 1924, **178**, 566—568).—By studying the re-heating curves of sodium thiosulphate-water systems obtained by spontaneous crystallisation (in nuclei-free closed vessels), two new hydrates (10 and 12 [ $\frac{1}{2}$ ]H<sub>2</sub>O) of sodium thiosulphate have been detected. The *decahydrate* is isolable at low temperatures, the *dodecahydrate*, however, undergoing transformation during attempts to isolate it. A third new hydrate is suggested, but not proved, by the results obtained. The author concludes that the hydrates of sodium thiosulphate do not exist in solution.

E. E. T.

**Hydrates of Sodium Thiosulphate.** M. PICON (*Compt. rend.*, 1924, **178**, 700—703; cf. previous abstract).—A continuation of previous work, the concentration of the salt being now carried to the limit (for 1 atm. pressure) of 23 mols. per 100 mols. of water. The existence of tertiary, quaternary, and quinary hydrates (described by Young and Burke) could not be confirmed above 13 mols. of salt to 100 mols. of water. All hydrates are either primary or secondary.

E. E. T.

**Explosibility of Ammonium Nitrate.** R. AUFSCHLÄGER (*Z. ges. Schiess- u. Sprengstoffw.*, 1923, **18**, 117—120).—Determinations of the heat of explosion of ammonium nitrate at constant volume and the estimated temperature of explosion are tabulated. The rate of detonation as measured by Dautriche's method under various conditions of confinement and diameter of cartridge was found to lie between 1270 and 2400 m. per sec. There is no doubt that this compound must be looked upon as a high explosive, although of a very insensitive nature. Like other explosives, it is more difficult to detonate in the free than in the confined state, but even in the free state it can be repeatedly detonated if sufficient initial impulse is given.

H. C. R.

**Properties of Ammonium Nitrate. VII. The Reciprocal Salt Pair Ammonium Nitrate and Sodium Sulphate.** E. P. PERMAN and W. R. HARRISON (*J. Chem. Soc.*, 1924, **125**, 364—369; cf., T., 1923, **123**, 2128).—This system exhibits two ternary points; the main one is at 118°, at which sodium nitrate, sodium sulphate, and mixed crystals of ammonium nitrate and ammonium sulphate are in equilibrium. The other is at 117° and consists of sodium nitrate, mixed crystals (as above), and ammonium nitrate. The latter is represented by a very small area on the equilibrium diagram, due, apparently, to the conversion of ammonium nitrate into the  $\delta$ -form.

S. K. T.

**Susceptibility of Silver Bromide to Reduction.** A. REYCHLER (*Bull. Soc. chim. Belg.*, 1923, **32**, 404—407).—Silver bromide can be reduced by alkaline quinol, in absence of gelatin, not only when exposed to light, but also in darkness. The initiation of the action depends on the presence of quinol, but is complicated in photographic developers by the fact that the sodium sulphite present also plays a part in the reduction. The author interprets his results as showing that, in the presence of sodium carbonate, quinol reacts with 2 mols. of silver bromide, but on addition of sodium sulphite the latter is activated by the quinol, and if present in sufficient quantity the two substances together react with 4 mols. of silver bromide. Any excess of sulphite is inactive, as also is sulphite in absence of quinol. Suggested equations representing the oxidation of quinol are given. H. J. E.

**Solubility of Silver Bromate in Solutions of other Salts and the Corresponding Activity Relations.** R. H. DALTON, R. POMEROY, and L. E. WEYMOUTH (*J. Amer. Chem. Soc.*, 1924, **46**, 60—64).—Determinations of the solubility of silver bromate at 25° show that different salts of the same valency type (namely, potassium nitrate and perchlorate, potassium and sodium sulphates, magnesium and barium nitrates) have effects on the activity coefficient product of silver bromate that differ by amounts (3 or 10% at 0.5*N*) which indicate specific effects of the separate ions that are pronounced enough to merit recognition as important secondary factors. The salts of different valency types have, on the average, in conformity with the rule of Lewis and Randall, nearly equal activating effects when  $\Sigma(cv^2)$  has the same value, where *c* is the molecular concentration and *v* the valency of the ions. J. F. S.

**Constitution of Bleaching Powder.** S. OCHI (*J. Chem. Ind. Japan*, 1923, **26**, 1—14).—The curve of the heat of solution of bleaching powder indicated the existence of a monohydrate,  $\text{OCl}\cdot\text{CaCl}_2\cdot\text{H}_2\text{O}$ , the heat of solution of which is 7530 cal., whilst that of  $\text{OCl}\cdot\text{CaCl}_2$  is 9830 cal., giving the heat of hydration, 2300 cal. The vapour pressure of the water in bleaching powder containing 0.82 mol. of water for 1 mol. of  $\text{OCl}\cdot\text{CaCl}_2$  (determined by passing pure dry air through it) was found to be 7.99 mm. at 30°, 3.93 mm. at 20°, and 1.80 mm. at 10°, and the heat of hydration calculated from these data is 2260 cal. (from 10° and 20°) or 2000 cal. (from 20° and 30°). Bleaching powder moistened with tetrachloroethane exhibits double refraction, which is most distinct when the material contains a quantity of water corresponding with the formula  $\text{OCl}\cdot\text{CaCl}_2\cdot\text{H}_2\text{O}$  and vanishes when the substance is dried or moistened with water; some amorphous masses are considered to be unchanged calcium hydroxide. The author concludes that bleaching powder consists essentially of the compound  $\text{OCl}\cdot\text{CaCl}_2\cdot\text{H}_2\text{O}$ , mixed with calcium hydroxide or oxide. K. K.

**High-temperature Researches. XVI. Synthesis and Decomposition of Calcium Carbide.** O. RUFF and E. FOERSTER (*Z. anorg. Chem.*, 1923, **131**, 321—347; cf. A., 1922, ii, 818).—Attempts were made to prepare pure calcium carbide. A 92.3%

product resulted by softening commercial carbide (74.9%  $\text{CaC}_2$ ) in hydrogen at 2000–2100° and squeezing out with a carbon rod, the process being repeated on the expressed material. Very pure calcium carbide was also obtained by heating at above 1000° powdered carbon or soot (0.2–1.2% ash) with metallic calcium (97.5% Ca) in either open or closed crucibles of carbon or iron and in an atmosphere of hydrogen or argon. In this way, carbide of 90–93% purity was prepared. The product obtained in an open crucible is always of a loose nature and very sensitive to moisture, but by careful remelting in argon at 780 mm. it is obtained as a greyish-black, crystalline mass, in which form it was used in the experiments described below. In a closed iron crucible, carbides of 90% purity were obtained (in one case 94%).

No evidence was found to support the supposed existence of a carbide,  $\text{CaC}$ .

Vaporisation of calcium carbide in nitrogen at 1100° (cf. A., 1919, ii, 265) yields calcium cyanamide, which vaporises with partial decomposition at about 1300°. In hydrogen, traces of acetylene are formed above 2200°, and in carbon monoxide, calcium oxide and carbon at 1700°. From the curves representing these processes and also for the dissociation in argon, the dissociation pressure of calcium carbide was found to be 1 atm. at  $2500^\circ \pm 50^\circ$ , i.e., 1 mm. at  $1825^\circ \pm 50^\circ$ . By comparing the theoretical weight of the residue in the argon experiment with the weight observed, it was shown that the vapour is mostly that of calcium, 4.5% being the maximum amount of carbide vapour at 1 atm.

The "softening temperature" of mixtures of calcium carbide and calcium oxide decreases with increasing calcium oxide content up to about 30%  $\text{CaO}$ , after which it increases again. Extrapolation of the "softening temperature"—composition curve showed that pure calcium carbide melts at about 2300°.

The equilibrium of the reaction  $\text{CaO (liquid)} + 3\text{C} \rightleftharpoons \text{CaC}_2 \text{ (liquid)} + \text{CO}$  depends on the partial pressure of the carbon monoxide as well as on the ratio  $[\text{CaC}_2]/[\text{CaO}]$ . In an atmosphere of carbon monoxide, when the eutectic solidifies, this reaction is rapidly and completely reversed. It should be possible on theoretical grounds to prepare pure carbide from calcium oxide and carbon below 2300° for a certain carbon monoxide pressure. This was not realised experimentally.

S. K. T.

**Chemical Effects with Crystals. VI. Etching and Solution Phenomena of Aragonite.** F. RINNE and W. KRÜGER (*Ber. Sächs. Ges. Wiss., Math.-Phys. Kl.*, 1923, **74**, 253–268; from *Chem. Zentr.*, 1924, i, 154).—Etching and solution experiments with aragonite, using hydrochloric acid of *d* 1.12, showed that the resultant form was rhombic bipyramidal.

G. W. R.

**The Dolomite System.** H. L. J. BÄCKSTRÖM (*J. Chem. Soc.*, 1924, **125**, 430–434).—Mitchell's figures (T., 1923, **123**, 1055) do not give the true dissociation pressures of calcite, magnesite, and dolomite, the agreement with the Nernst approximation formula in the case of calcite being limited to a very restricted range.

Mitchell's conclusion that dolomite dissociates in one step is based on the continuity of the pressure-temperature curve; it is now pointed out that stepwise dissociation only makes itself apparent in the pressure-composition curve and dolomite dissociates in two steps (cf. A., 1913, ii, 516). Moreover, the method used for determining the specific heats of magnesite etc. is liable to a 10% error on the final result. Mitchell's thermochemical equations lead to the conclusion that calcium carbonate and magnesium oxide can form a compound with a heat of formation from its constituents of about 17 Cals. Objections are also raised to the method used for finding the heat of solution of dolomite.

S. K. T.

**Position of Beryllium and Magnesium in the Periodic System of the Elements.** P. PFEIFFER (*Z. angew. Chem.*, 1924, **37**, 41).—The author, whilst agreeing with the long-period classification of Paneth (*ibid.*, 1923, **36**, 407), prefers to place beryllium and magnesium in the zinc-cadmium group. The alkaline-earth metals form salt-like hydrides,  $\text{XH}_2$ , and metal-ammonia compounds,  $\text{X}(\text{NH}_3)_6$ , and (in their salts) give a characteristic coloration to the Bunsen flame, but none of these properties is shown by beryllium or magnesium. On the other hand, the halides and oxalates of the latter, like those of zinc and cadmium, show a tendency to form double halides and double oxalates which is not possessed by the corresponding alkaline-earth salts. The former also give hexammine salts, whereas the halides of the calcium group form octammine salts. The relationship of beryllium and magnesium with zinc and cadmium is particularly clearly seen from their hydrated sulphates, some of which are isomorphous, as well as from their ability to form double sulphates, which also show isomorphism; these characteristics are not shown by calcium, strontium, and barium.

W. T. K. B.

**Equilibrium between Metals and Salts in the Molten State. I. The System Lead, Cadmium, Lead Chloride, Cadmium Chloride.** R. LORENZ, W. FRAENKEL, and J. SILBERSTEIN (*Z. anorg. Chem.*, 1923, **131**, 247—265).—Equilibrium according to the equation  $\text{Cd} + \text{PbCl}_2 \rightleftharpoons \text{CdCl}_2 + \text{Pb}$  is attained in ten minutes when lead, cadmium, lead chloride, and cadmium chloride are fused together at 600—700°. The system consists of three phases, and with each salt phase of given composition there corresponds a whole series of metal phases. The composition of the equilibrium mixture was independent of the absolute quantities of the phases present and of the direction of the reaction according to the above equation, and nearly independent of the temperature over the interval 600—700°.

The value of  $[\text{Pb}]/[\text{Cd}] \cdot [\text{CdCl}_2]/[\text{PbCl}_2]$  at constant temperature decreased steadily as the cadmium content decreased. Addition of lithium chloride and of mixtures of sodium and potassium chlorides favour the forward reaction in the above equation. Bismuth has no influence on the equilibrium, but antimony favours the reaction from right to left in the equation above. Explanations are attempted on the basis of the formation of compounds in both



salt and metal phases and on the variation of surface tension at the metal-salt boundary. S. K. T.

**Fluorescence of Lead and Bismuth Vapours.** H. KOPFERMANN.—(See ii, 220.)

**Lead Tetrachloride.** E. KRAUSE (*Ber.*, 1924, **57**, [B], 318).—Lead tetrachloride which has been purified by distillation in a high vacuum gives intensely brownish-red solutions in benzene and its homologues; the colour is discharged by the addition of carbon tetrachloride, chloroform, dibromoethane, glacial acetic acid, or ether without conversion of the lead tetrachloride into the dichloride. Cold dilute solutions may be preserved unchanged in the dark during several hours, after which gradual decomposition occurs with separation of lead dichloride. Concentrated solutions decompose after some time with explosive violence without any apparent cause. H. W.

**Colloidal Lead Arsenate.** F. J. BRINLEY (*J. Agric. Res.*, 1923, **36**, 373—374).—A mixture of 311.96 g. of disodium arsenate and 17.35 g. of gelatin is dissolved in a small quantity of hot water and diluted to 10 litres, and a solution of 331.4 g. of lead nitrate in 10 litres of water is added slowly, with constant stirring, avoiding excess of lead. The resulting lead arsenate is colloidal and does not separate for several days. Stronger solutions than 0.1M yield a curdy precipitate, and in 0.01M solutions there is a tendency to form fine, needle-shaped crystals. A. G. P.

**Thallic Sulphates and Thallic Selenates.** J. MEYER and H. WILK (*Z. anorg. Chem.*, 1923, **132**, 239—259).—Thallium is readily dissolved in the thallic condition by the action of bromine in hydrobromic acid solution, but not by the action of chlorine in hydrochloric acid solution. The solution is freed from halogen and the hydroxide precipitated by means of ammonia; the washed hydroxide is converted into thallic oxide by long boiling under water. For analysis, the hydroxide is precipitated by means of ammonia, converted into oxide in the same way, and weighed; titration with permanganate after reduction also gives very accurate results. The system, thallic oxide, sulphur trioxide, water yields two compounds,  $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{OH} \cdot \text{TlSO}_4 \cdot 2\text{H}_2\text{O}$ , which are stable only in strongly acid solutions, and are readily hydrolysed by water; the transition at 30° with a concentration of 30%  $\text{H}_2\text{SO}_4$  requires many days, and both compounds adsorb sulphuric acid. The transition temperature rises from 20° at 42% acid to 90° at about 60% acid. The basic salt exists at 25° in concentrations from 10 to 40% sulphuric acid, and the acid salt in concentrations from 42 to 75%; in acid stronger than this the oxide does not dissolve. No other salts could be observed; the normal heptahydrate of Crookes and of Strecker is thought to have been a molecular mixture of these two. The transition temperatures in acid of varying concentrations were determined as a result of eighty-nine analyses of the equilibrium systems.

Analogous thallic selenates,  $\text{HTl}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{OH} \cdot \text{TlSeO}_4 \cdot \text{H}_2\text{O}$ ,

have been found to be the only selenates capable of separate existence. They are likewise very sensitive to water, hydrolysing even in moist air; the solubility relations are almost exactly expressed by the diagrams for the sulphates.

Thallic hydroxide dissolves in a saturated solution of ammonium sulphate, forming a solution from which addition of ammonia and alcohol at 0° precipitates a compound,  $\text{Ti}_2(\text{SO}_4)_3 \cdot 12\text{NH}_3 \cdot 12\text{H}_2\text{O}$ , stable only in an atmosphere of ammonia; the constitutions  $[\text{Ti}(\text{H}_2\text{O})_6(\text{NH}_3)_6]_2(\text{SO}_4)_3$  and  $[\text{Ti}(\text{H}_2\text{O})_6(\text{NH}_3)_6]_2(\text{SeO}_4)_3$  are suggested for this and the analogous selenate compound.

A thallo-thallic selenate,  $\text{Ti}_2\text{SeO}_4 \cdot \text{Ti}_2(\text{SeO}_4)_3$ , which is colourless, and a yellow double salt,  $5\text{Ti}_2\text{SeO}_4 \cdot \text{Ti}_2(\text{SeO}_4)_3$ , exactly analogous to the known double sulphates, have been obtained, and a salt of the composition  $\text{Ti}^{\text{III}}\text{Ti}^{\text{IV}}\text{Cl}_2(\text{SO}_4)$  obtained by the reaction  $2\text{HTi}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + 4\text{HCl} = \text{Ti}^{\text{III}}\text{Ti}^{\text{IV}}\text{Cl}_2(\text{SO}_4) + \text{Cl}_2 + 3\text{H}_2\text{SO}_4 + 8\text{H}_2\text{O}$ , at 200°. The compounds  $\text{Ti}^{\text{III}}\text{Ti}^{\text{IV}}\text{Br}_2(\text{SeO}_4)$  and  $\text{Ti}^{\text{III}}\text{Ti}^{\text{IV}}\text{Cl}_2(\text{SeO}_4)$  are also described.

S. I. L.

### Copper-Nickel-Lead and Copper-Iron-Lead Alloys. IX.

W. GUERTLER and F. MENZEL (*Z. anorg. Chem.*, 1923, **132**, 201—208).—Whilst copper and nickel mix completely in the liquid state and form mixed crystals in the solid state in all proportions, the binary systems copper-lead and nickel-lead show very limited miscibility in the liquid state, the limits for non-miscibility being 36—86.5% of lead in the first and 30—84% in the second; nevertheless, the ternary system shows complete miscibility in the liquid state in almost all proportions. Mixtures of the German coinage nickel (Ni 25%, Cu 75%) with lead in all proportions yielded clean homogeneous alloys of excellent lustre and appearance, the microscopical examination showing mixed crystals of copper-nickel in a ground mass of almost pure lead. Alloys containing 60% of lead with varying proportions of copper and nickel show complete miscibility in the liquid phase down to very small proportions of either nickel or copper (2.5% Ni, 6% Cu); this is attributed to the fact that a small proportion of either copper or nickel is sufficient to make an otherwise immiscible fluid layer of the other with lead completely miscible. The alloys promise to be of considerable value.

The immiscibility of the binary systems iron-lead and copper-lead on the other hand persists to a great degree in the ternary system. The cooled mixtures show two or three layers, the three consisting essentially of the three metals, each showing inclusions of the other two; where two layers are formed, one is iron containing inclusions of copper and lead, the other consists of copper crystals in a ground of lead, although in the liquid state the copper is completely miscible with the iron.

S. I. L.

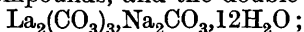
**Ternary System Copper-Lead-Antimony.** H. SCHACK (*Z. anorg. Chem.*, 1923, **132**, 265—272).—Of the three binary systems, which have already been worked out, lead and antimony and copper and antimony are miscible in the liquid state, but the latter form a compound  $\text{Cu}_5\text{Sb}_2$ , which decomposes on cooling into  $\text{Cu}_3\text{Sb}$  and  $\text{Cu}_2\text{Sb}$ ; the system lead-copper is not completely homogeneous in

the liquid state. The limits for incomplete miscibility in the ternary system are worked out and expressed in the usual triangular diagram; in this region the solidified alloys show two layers, the upper consisting of both the copper-antimony compounds, the lower of  $\text{Cu}_2\text{Sb}$  and lead embedded in a ground mass of the ternary eutectic. The alloys rich in copper have the general structure of the binary copper-antimony alloys, with a ground mass of lead; those rich in antimony are too brittle for technical use, but those rich in lead appear likely to be valuable industrially, the addition of copper tending to improve the technical lead-antimony alloys. S. I. L.

**Action of Ozonised Oxygen on Mercury.** V. O. J. HODGSON (*J. Chem. Soc.*, 1924, 125, 462—463).—The prolonged action of ozonised oxygen on dry mercury at the ordinary temperature and in the dark yields mercurous oxide only; in the light, photochemical decomposition of this oxide produces a trace of mercuric oxide as well. S. K. T.

**Arc Spectrum of Scandium.** S. PIÑA DE RUBIES.—(See ii, 214.)

**Baskerville and Catlett's Lanthanates.** F. ZAMBONINI and G. CAROBBI (*Gazzetta*, 1924, 54, 46—52).—The so-called sodium tetralanthanate, described by Baskerville and Catlett (A., 1904, ii, 260), is found to be a mixture composed of lanthanum oxide, various indefinite compounds, and the double carbonate,



this double carbonate results from the action of water on the product formed by fusing lanthanum oxide with sodium carbonate. The other supposed lanthanates described by Baskerville and Catlett (*loc. cit.*) are evidently mixtures similar to the above. T. H. P.

**Double Carbonates of Sodium and Metals of the Cerium Group.** F. ZAMBONINI and G. CAROBBI (*Gazzetta*, 1924, 54, 53—59).—The double carbonates of sodium and metals of the cerium group, prepared under the conditions indicated by Meyer (A., 1904, ii, 734), have compositions corresponding with the formula  $\text{R}'''_2(\text{CO}_3)_3 \cdot \text{Na}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$ . The lanthanum, cerium, praseodymium, neodymium, and samarium compounds are described (cf. Cleve, A., 1885, 636). T. H. P.

**Carbonates of the Rare Earths. I. Conditions of Formation and Hydrolysis of the Cerite-earth Carbonates.** J. PREISS and A. DUSSIK (*Z. anorg. Chem.*, 1923, 131, 275—286).—Precipitation of 2% solutions of the chlorides of cerium, lanthanum, neodymium, and praseodymium with hot, normal alkali carbonate furnishes strongly basic carbonates, the hydroxyl content increasing in the order La, Ce, Pr, Nd. Excess of alkali raises the hydroxyl content in the case of lanthanum and decreases it in the case of neodymium. When cold solutions are used, brightly coloured, nearly normal carbonates are precipitated in the amorphous state; they become crystalline on keeping. A solution of sodium hydrogen carbonate saturated with carbon dioxide precipitates brightly

coloured, normal carbonates in the amorphous state; they rapidly become crystalline. The precipitates after drying during eight days in air had the formula  $E_2O_3 \cdot 3CO_2 \cdot 8H_2O$ . Drying in a vacuum over sulphuric acid for 50 days reduced this to the dihydrate, which lost a further molecule of water when heated at  $100^\circ$  for 50 hours. It was necessary to heat the monohydrate at  $200^\circ$  in a stream of carbon dioxide for a week to form the anhydrous carbonate.

Hydrolysis of the normal carbonates by heating with excess of water leads to the formation of a basic carbonate, probably  $OH \cdot E \cdot CO_3$ . The hydrolysis is complete after about 3 hours (cf. following abstract). In the hydrolysis one-third of the content of carbon dioxide is eliminated, and this is regarded as a purely chemical stoichiometric proof of the tervalency of the rare earths.

In the case of neodymium, the temperature coefficient of the velocity of hydrolysis is 2.6 at  $70^\circ$ .

The strongly basic substances precipitated by hot sodium carbonate solution are mixtures of the normal carbonate with  $OH \cdot ECO_3$ .  
S. K. T.

**Carbonates of the Rare Earths. II. Thermal Decomposition of the Cerite-earth Carbonates.** J. PREISS and N. RAINER (*Z. anorg. Chem.*, 1923, **131**, 287—298).—When the normal carbonates are heated in a slow stream of dry carbon dioxide, loss of carbon dioxide occurs first at  $300^\circ$ , all the water being expelled below  $200^\circ$ . The loss is rapid at  $400^\circ$  and, in the cases of lanthanum, praseodymium, and neodymium, the basic carbonate,  $E_2O_3 \cdot CO_2$ , is formed without any intermediate steps. The products are readily soluble in dilute acids; the lanthanum compound is white, and stable between  $600^\circ$  and  $900^\circ$ , the praseodymium compound is dirty yellow, stable between  $550^\circ$  and  $815^\circ$ , and the neodymium compound, bluish-violet, stable between  $550^\circ$  and  $800^\circ$ . When the respective temperature limits are exceeded, the lanthanum and praseodymium compounds are rapidly converted, with no intermediate stages, into the oxides  $La_2O_3$  and  $Pr_2O_3$  (?  $Pr_4O_7$ ), respectively. In the case of neodymium, however, an intermediate compound,  $Nd_2O_3 \cdot \frac{1}{2}CO_2$ , is formed, which is stable over the range  $810$ — $870^\circ$ ; above this range it is completely converted into the oxide. The curves for dissociation in air are of similar form to those in carbon dioxide; the decomposition temperatures are lower, however, and the temperature-range of stability of the intermediate products is smaller.

The curve for cerium carbonate in carbon dioxide exhibits only one step; the  $Ce_2O_3 \cdot 3CO_2$  probably first forms  $Ce_2O_4 \cdot 3CO_2$ , which loses the greater part of its carbon dioxide at a lower temperature than the compound of  $Ce^{III}$  and yields  $Ce_2O_4 \cdot \frac{1}{2}CO_2$ , a lemon-yellow compound which, at  $900^\circ$ , is converted into  $CeO_2$ . The compound  $[Ce_2(CO_3)_3]_x [Ce_2O_4 \cdot \frac{1}{2}CO_2]$  was also prepared. These results correspond with the formula,  $(CO_3 \cdot E)_2CO_3$ , for the normal cerite carbonates.

In mixtures, the carbonates of these metals lose their individuality as far as thermal dissociation is concerned. Mixtures not containing cerium exhibit mean, sharp dissociation temperatures for each step;

mixtures containing cerium, however, follow the behaviour of the carbonate of this metal.

The thermal dissociation curve of the compound  $\text{OH}\cdot\text{NdCO}_3$  corresponds with that of neodymium carbonate and suggests that the structure of the compound is  $(\text{OH})_2\cdot\text{Nd}\cdot\text{CO}_3\cdot\text{Nd}\cdot\text{CO}_3$  (cf. preceding abstract).  
S. K. T.

**Constitution of Ternary Aluminium Alloys.** V. FUSS (*Z. Metallk.*, 1924, 16, 24—25).—In the fifteen possible ternary systems comprising aluminium and two of the elements, iron, copper, nickel, zinc, magnesium, and silicon, the aluminium corner of the ternary diagram is intersected by a quasibinary line only in the cases in which the addition of the two elements to aluminium has a specifically new influence on its properties, namely, in the systems Al-Mg-Si, Al-Mg-Zn, and Al-Mg-Cu. Aluminium decomposes the silicides of iron, nickel, and copper, liberating free silicon and forming intermetallic compounds, and addition of any of these elements or of zinc to aluminium results in the formation of these compounds. [Cf. *B.*, 1924, 259.]  
A. R. P.

**Range of the Mixed Crystal Phase rich in Aluminium in the Quaternary System Aluminium-Magnesium-Silicon-Zinc.** W. SANDER and K. L. MEISSNER (*Z. Metallk.*, 1924, 16, 12—17).—The amounts of zinc, magnesium, and silicon which aluminium can hold in solid solution increase from 8%, 2%, and 0.5%, respectively, at 20° to 65%, 12%, and 0.8%, respectively, at 450°; consequently all aluminium alloys containing quantities of these elements between the above limits will deposit them partly on cooling slowly. If the cooling is rapid, this action is suppressed, but takes place slowly at the ordinary temperature, and is accompanied by a gradual increase in volume, hardness, and tensile strength. The equilibrium-diagram of the quaternary system Al-Zn-Mg-Si is developed from a consideration of those of the four ternary systems involved. [Cf. *B.*, 1924, 259.]  
A. R. P.

**Hydrates and Hydrogels. III. Aluminium Hydroxides Poor in Water.** R. WILLSTÄTTER and H. KRAUT (*Ber.*, 1924, 57, [B], 58—63; cf. *A.*, 1923, ii, 167, 493).—Specimens of aluminium hydroxide *A*, prepared by the precipitation of aluminium sulphate by concentrated ammonia and prolonged digestion of the precipitate with ammonia, exhibit a totally different behaviour when desiccated in a current of air according to whether they are still moist or have been subjected to a rapid, preliminary drying in a high vacuum over phosphoric oxide. In the latter case, the weight remains almost constant below 150°, thus showing the water to be united chemically to the aluminium oxide. Comparison of the desiccation curves with those of aluminium hydroxide *C* proves that the dry specimens of composition varying between  $\text{Al}_2\text{O}_3\cdot 2\text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3\cdot \text{H}_2\text{O}$  cannot in the moist condition have the composition  $\text{Al}(\text{OH})_3$ , but are to be regarded as compounds or mixtures of compounds of the type  $\text{Al}_n(\text{OH})_{3n}-x\text{H}_2\text{O}$ . Desiccation of the precipitate to the ultimate composition  $\text{AlO}(\text{OH})$  has not yet been

effected by means of ammonia. Comparison of the desiccation curves of the dried and moist specimens in a current of air saturated with aqueous vapour at  $18^{\circ}$  shows that new hydrates, poorer in water, are produced by an increase in temperature, whereas this change is not observed in a dry atmosphere. The desiccation of moist gels is similar in its result to digestion with water or ammonia. The observations explain the failure of attempts to establish the presence of definite hydrates in the hydrogels of various hydroxides.  
H. W.

**Precipitation of Hydrated Aluminium Oxide by means of Ammonia.** G. JANDER and B. WEBER (*Z. anorg. Chem.*, 1923, **131**, 266—274).—Hydrated aluminium oxide is appreciably soluble in slightly ammoniacal solutions of ammonium salts, the solubility being less in cold than in hot solutions. The solutions are probably not colloidal since multivalent and univalent anions have the same influence on the solubility, organic solvents (*e.g.*, toluene) exert no precipitating effect, and the membrane filter (A., 1919, ii, 520) allows the solution to pass readily. [Cf. B., 1924, 254.] S. K. T.

**Equilibrium of Colloidal Aluminium and Lanthanum Hydroxides with Dilute Acids and Bases.** H. VON EULER and R. NILSSON (*Ber.*, 1924, **57**, [B], 217—222).—An extension of previous work to aluminium hydroxide which has undergone "ageing" (cf. von Euler and Nilsson, this vol., ii, 23).

Solutions of acetic acid are never completely neutralised by suspensions of aluminium hydroxide A (cf. Willstätter and Kraut, A., 1923, ii, 493), neutralisation being less complete as the concentration of the acid in the mixture is increased; an alteration in  $p_H$  does not occur with an initial acidity of  $p_H$  2.6. The addition of small quantities of acid to a suspension of lanthanum hydroxide results in complete neutralisation, and the alkalinity of the hydroxide suspension itself ( $p_H$  9.37) is almost attained. The difference between the results with the two hydroxides is not attributed to the differing properties of aluminium and lanthanum, but to the differing age of the specimens. Observations of the behaviour of freshly precipitated aluminium hydroxide towards solutions of hydrochloric acid and sodium hydroxide show the substance to be equally strong as acid or base.

Aluminium hydroxide does not appear to be stable in media in which the acidity lies beyond  $p_H$  5.5—7.1; the narrower limits depend on the type of the hydroxide.  
H. W.

**Tervalent Manganese. IV.** J. MEYER and W. SCHRAMM (*Z. anorg. Chem.*, 1923, **132**, 226—238).—The reaction of sulphur dioxide with manganic hydroxide suspended in water proceeds in two ways, the manganic sulphite first formed decomposing according to the equations  $Mn_2(SO_3)_3 = MnSO_3 + MnS_2O_6$ , and  $Mn_2(SO_3)_3 = MnSO_4 + MnSO_3 + SO_2$ ; there is no reduction to manganous salts, nor any decomposition of the manganic salt into manganous salts and the dioxide. No definite results could be obtained connecting the relative extent to which the two reactions occur with any

external factor. With manganese dioxide, two reactions also occur, according to the equations  $2\text{MnO}_2 + 4\text{SO}_2 = \text{Mn}_2(\text{SO}_3)_3 + \text{SO}_3 = \text{MnSO}_4 + \text{SO}_2 + \text{MnS}_2\text{O}_6$  and  $\text{MnO}_2 + \text{SO}_2 = \text{MnSO}_4$ ; the latter is favoured and the former repressed by increase of temperature.

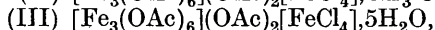
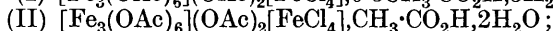
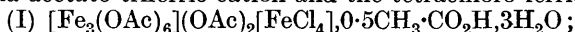
S. I. L.

**Effect of Silicon on the Equilibrium Diagram of the Iron-Carbon System in the Vicinity of the Eutectic Point.** H. A. SCHWARTZ, H. R. PAYNE, and A. F. GORTON (*Metal Ind.*, 1923, **23**, 226; from *Chem. Zentr.*, 1924, i, 237).—In the iron-carbon diagram, the  $A_1$  eutectic points of the stable and metastable systems are coincident in the absence of silicon. The  $\alpha$ — $\gamma$  transformation of the stable solid solution of a given composition takes place at a lower temperature than in the metastable system. At a given temperature and with a definite silicon content, ferrite is more soluble in "boydenite" than in austenite. Boydenite is the name given to the solid solution in the stable system corresponding with austenite in the metastable system.

G. W. R.

**Chemical Effects with Crystals. VII. Etching and Solution Phenomena of Magnetite.** F. RINNE and H. MIELKE (*Ber. Sächs. Ges. Wiss. Math.-Phys. Kl.*, 1923, **74**, 319—329; from *Chem. Zentr.*, 1924, i, 154).—Etching and solution experiments with magnetite, using hydrochloric acid ( $d$  1.21), showed that it belongs to the hexakisoctahedral class. The form resulting from the solution of a sphere of the material was a rounded cube. G. W. R.

**Constitution of the Compounds Formed by the Action of Acetic Acid and its Salts on Ferric Chloride and Ferric Nitrate.** R. WEINLAND, K. KESSLER, and A. BAYERL (*Z. anorg. Chem.*, 1923, **132**, 209—225).—By the action of glacial acetic acid on ferric chloride under appropriate conditions, a series of compounds of the hexa-acetato-triferric cation and the tetrachloro-ferric anion,



has been obtained. By treatment with alcohol, the compound, (V)  $[\text{Fe}_3(\text{OAc})_6(\text{OH})_2][\text{FeCl}_4] \cdot 5\text{EtOH} \cdot \text{H}_2\text{O}$ , is obtained. All these compounds are obtained as well-formed red or reddish-brown crystals, and by treatment with sodium chloroplatinate all give the same characteristic compound  $[\text{Fe}_3(\text{OH})_2(\text{OAc})_6]_2[\text{PtCl}_6] \cdot 10\text{H}_2\text{O}$ , an orange-red, crystalline substance. A further compound, (IV)  $[\text{Fe}_3(\text{OAc})_6]\text{Cl}_3 \cdot \text{CH}_3 \cdot \text{CO}_2\text{H} \cdot 5\text{H}_2\text{O}$ , is obtained from the mother-liquor from compound (III); by treatment of hydrated ferric chloride with glacial acetic acid, the closely related compound (VI),  $[\text{Fe}_3(\text{OAc})_6]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ , is obtained; both these give the characteristic chloroplatinate.

By treatment of one molecular proportion of ferric chloride in solution with two and one proportions of sodium acetate, respectively, the compounds (VII),  $[\text{Fe}_3(\text{OH})_2(\text{OAc})_6]\text{Cl} \cdot 7\text{H}_2\text{O}$ , and (VIII),  $[\text{Fe}_3(\text{OAc})_6(\text{OH})_2][\text{FeCl}_4] \cdot 6\text{H}_2\text{O}$ , are obtained; the action of alcohol on the latter gives the compound (V).

By treatment of ferric nitrate with acetic acid, the compound (IX),  $[\text{Fe}_3(\text{OAc})_6(\text{OH})]\text{OAc}\cdot\text{NO}_3\cdot 3(4)\text{H}_2\text{O}$ , is obtained; sodium acetate gives (X),  $[\text{Fe}_3(\text{OAc})_6(\text{OH})_2]\text{OAc}\cdot 4\text{H}_2\text{O}$  with large excess of acetate, (XI),  $[\text{Fe}_3(\text{OAc})_6(\text{OH})_2]\text{NO}_3\cdot 6\text{H}_2\text{O}$  with two molecular proportions of acetate, and (XII),  $[\text{Fe}_3(\text{OAc})_5(\text{OH})_2](\text{NO}_3)_2\cdot 12\text{H}_2\text{O}$ , with one molecular proportion of acetate. The latter is interesting as the first salt of a penta-acetato-triferric cation.

A series of four compounds obtained by interaction of ferric acetate and ferric nitrate are regarded as double compounds of salts of the hexa-acetato- and penta-acetato-triferric base; they are deep red compounds crystallising unchanged from cold water, and the ratios  $\text{NO}_3 : \text{OAc}$  for each 9 atoms of ferric iron are respectively 3 : 17, 3·5 : 17·5, 4 : 17, and 4·5 : 16·5; a further double compound,  $[\text{Fe}_3(\text{OAc})_6(\text{OH})_2]\text{NO}_3\cdot [\text{Fe}_3(\text{OAc})_5(\text{OH})](\text{NO}_3)_2\cdot 10\text{H}_2\text{O}$  separates from a solution of one molecular proportion each of ferric hydroxide and nitric acid and three molecular proportions of acetic acid. All these nitrate-acetates decompose on exposure to air, losing nitric and acetic acids.

S. I. L.

**Colloidal Nickel Hydroxide.** O. F. TOWER.—(See ii, 237.)

**Binary and Ternary Molybdenum Alloys.** DREIBHOLZ.—(See ii, 233.)

**Soft X-Rays from Tungsten.** C. B. BOZZANI and C. T. CHU.—(See ii, 215.)

**Hydrates and Hydrogels. IV. Stannic Acids.** R. WILL-STÄTTER, H. KRAUT, and W. FREMERY (*Ber.*, 1924, **57**, [B], 63—72).—The stannic acids have been regarded as hydrates with differing water content and, more recently, as colloidal modifications of hydrated tin dioxide in which the differing properties are due to differing sizes of the particles. It is shown that the latter conception is inadequate to account for the observed facts and that it is necessary to assume the existence of more or less definite hydrates.

The following stannic acids are described which are most sharply differentiated by determination of the concentration of hydrochloric acid necessary to bring them into solution as the tin base or to convert them into compounds which are soluble in water: Unstable monostannic acids of the composition  $\text{Sn}(\text{OH})_6\text{H}_2$ ,  $\text{Sn}(\text{OH})_4$ , or  $\text{SnO}(\text{OH})_2$ , obtained from stannic ammonium chloride, ammonium chloride, and ammonia or from  $\alpha$ -stannate and carbon dioxide in cold solution; they are soluble in hydrochloric acid (1%), nitric acid (1% and more concentrated), and sulphuric acid (1%); the other varieties of stannic acid are insoluble in the two latter acids.  $\alpha$ -Stannic acids, oligo- and poly-orthostannic acids are formed by intermolecular dehydration from several molecules of  $\text{Sn}(\text{OH})_4$ ; the group includes stannic acids soluble in hydrochloric acid, and hence not precipitated by this reagent; it is not possible to decide whether a particular individual is a higher member of this series or a lower member of the series  $\beta$ -stannic acids, which are derived from compounds of the  $\alpha$ -group by more or less extensive intra-



molecular dehydration; the group includes those stannic acids insoluble in hydrochloric acid or transformed thereby into polystannyl chlorides soluble in water. (For the preparation and properties of the individual members of each group the original communication must be consulted.)

Desiccation of these highly sensitive substances can be accomplished only by short exposure to the air. Under these conditions, the specimens retain the solubilities of the suspensions, but dissolve rather more slowly. When dried over phosphoric oxide in a high vacuum or when dried in air and subsequently heated at  $150^{\circ}$ , they lose their original solubility and yield compounds resembling those of the  $\beta$ -group. H. W.

**Electrolytic Preparation of Tin Sulphides and Thio-salts.** G. TOCCO and N. JACOB (*Gazzetta*, 1924, **54**, 32—38).—Tin sulphides and thio-salts are obtained by the alternating current electrolysis, with tin electrodes, of sodium thiosulphate solutions. [Cf. *B.*, 1924, 255.] T. H. P.

**Chemical Nature of Purple of Cassius.** A. HUBER.—(See ii, 229.)

**Hafnium Content of some Historical Zirconium Preparations.** G. HEVESY (*Nature*, 1924, **113**, 384—385).—Specimens of zirconium compounds prepared by various investigators, including those submitted to fractional purification and prepared for atomic weight determinations, have been found to contain hafnium in quantities up to 7%. In certain rare minerals, containing only small amounts of zirconium and a large number of other elements, an even larger amount of hafnium than of zirconium has been detected. The failure to detect hafnium in zirconium by atomic weight methods is ascribed entirely to the untrustworthiness of all the earlier methods employed. A. A. E.

**Normal Thorium Molybdate,  $\text{Th}(\text{MoO}_4)_2$ .** F. ZAMBONINI (*Gazzetta*, 1924, **54**, 39—45).—Anhydrous normal thorium molybdate, prepared by fusing partly dehydrated thorium chloride with excess of anhydrous sodium molybdate, forms microscopic, bipyramidal crystals belonging to the tetragonal system,  $a : c = 1 : 0.73565$ ,  $d^{7.5} 4.92$ . This value of  $a : c$  is approximately double that found for molybdates of the rare earth metals and of the metals of the calcium group. The molecular volume of the molybdate is 112.2, so that the value 56.1 for  $(0.5\text{Th})\text{MoO}_4$  agrees well with the values for the molybdates of the alkaline-earth metals, whereas the value 168.3 for  $(1.5\text{Th})(\text{MoO}_4)_3$  falls into line with the values for the molybdates of the rare earth metals.

Cerous and thorium molybdates exhibit mutual miscibility in the solid state. Confirmation is thus furnished of Urbain and Dauvillier's statements that the rare yttria earths are often found in zirconia, that minerals of the rare earths contain elements of every species, and that quadrivalent thorium always accompanies

the tervalent rare earth metals in minerals. Coster and Hevesy's conclusion that the element 72 is chemically homologous with zirconium because the latter most probably contains at least 0.01—0.1% of this element, is regarded as unauthorised. T. H. P.

**Structure of Vanadium.** H. COLLINS.—(See ii, 229.)

**Electrolytic Preparation of Antimony Sulphides and Thio-salts.** G. TOCCO (*Gazzetta*, 1924, **54**, 23—32).—Alternating current electrolysis of sodium thiosulphate solutions with antimony electrodes yields the sulphides and thio-salts of this metal in proportions varying with the conditions. [Cf. *B.*, 1924, 255.]

T. H. P.

**Hardness of Lead-Bismuth and Cadmium-Bismuth Alloys.** C. DI CAPUA and M. ARNONE (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 28—31; cf. this vol., ii, 111).—As is the case with lead-antimony, lead-tin, and zinc-cadmium alloys (cf. Kurnakov and Schemtschuschny, A., 1908, ii, 932), the hardness curves of lead-bismuth and cadmium-bismuth alloys exhibit maxima corresponding with the compositions of the eutectics. Further, as Glasunow and Matweeff found to be the case with zinc-cadmium alloys (*Int. Z. Metallog.*, 1914, **5**, 113), these maxima disappear when the alloys are subjected to prolonged re-heating. These results are regarded as confirmatory of the view that the marked hardness of the eutectic alloys is due to the very fine grain and great homogeneity of the alloys and to the internal stresses generated therein by the rapid separation of fine crystals during the solidification.

T. H. P.

**Complex Sulpho-acids of Platinum.** L. TSCHUGAEV and S. KRASSIKOFF (*Z. anorg. Chem.*, 1923, **131**, 299—302).—The action of sulphur dioxide on a hot solution of the chloride of the first Reiset base,  $[\text{Pt}, 4\text{NH}_3]\text{Cl}_2$ , gave a precipitate of pale yellow needles,  $[\text{Pt}, 4\text{NH}_3][\text{Pt}(2\text{NH}_3)(\text{SO}_3)_2]$ ; evaporation of the mother-liquor gave white plates,  $[\text{Pt}(2\text{NH}_3)\text{Cl}(\text{SO}_3)_2][\text{Pt}, 4\text{NH}_3]$ . Potassium chloroplatinate with the latter gave  $[\text{Pt}(2\text{NH}_3)\text{Cl}(\text{SO}_3)_2]\text{K}$ , together with the Magnus green salt,  $[\text{Pt}, 4\text{NH}_3]\text{PtCl}_4$ . The formation of the white plates is explained by assuming the  $2\text{NH}_3$  is replaced by  $2\text{SO}_2$ , this then being replaced by Cl and  $\text{SO}_3$ . Alternatively, the following reaction might take place:  $2[\text{Pt}(2\text{NH}_3)(\text{SO}_3)_2][\text{Pt}, 4\text{NH}_3] + 4\text{HCl} = 2\text{H}_2\text{SO}_3 + [\text{Pt}(2\text{NH}_3)\text{Cl}(\text{SO}_3)_2][\text{Pt}, 4\text{NH}_3] + [\text{Pt}, 4\text{NH}_3]\text{Cl}_2$ . The structures of the compounds were determined by warming with hydrochloric acid and by reaction with potassium chloroplatinate. According to Werner both these compounds are of the *trans*-form:



S. K. T.

## Mineralogical Chemistry.

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**Traversella Scheelite.** G. CAROBBI (*Gazzetta*, 1924, **54**, 59—64).—Analysis of a crystal of scheelite from Traversella gave the following percentage results:  $\text{H}_2\text{O}$ , 0.01;  $\text{WO}_3$ , 79.51;  $\text{MoO}_3$ , 0.58;  $\text{Nb}_2\text{O}_5$ , 0.08;  $\text{Ta}_2\text{O}_5$ , 0.02;  $\text{CaO}$ , 19.57;  $\text{BaO}$ , trace;  $\text{SrO}$ , trace;  $\text{MgO}$ , 0.05; yttria earths, 0.06;  $\text{Ce}_2\text{O}_3$ , 0.03;  $\text{La}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Pr}_4\text{O}_7$ , 0.05.  
T. H. P.

**Analcitic Lavas of North Africa, and Classification of Lavas containing Analcite.** A. LACROIX (*Compt. rend.*, 1924, **178**, 529—535; cf. Washington, A., 1915, ii, 275).—The basaltic lavas of Djebel Guerrien and Ben Ganah (N. Africa) are analcitic and not leucitic, since dilute hydrochloric acid extracts  $\text{Na}_2\text{O}$ , 5.11 and 4.07%, and  $\text{K}_2\text{O}$ , 0.76 and 0.72%, in the two cases respectively. The results of numerous analyses (by Raoult) of analcites are given, and the general conclusion is reached that the analcites of N. Africa are magmatic in origin.  
E. E. T.

**Mineralogical Constitution of Bauxites and the Limestones found in Contact with them.** J. DE LAPPARENT (*Compt. rend.*, 1924, **178**, 581—583).—A general discussion of the composition of French bauxites and the limestones associated with them.  
E. E. T.

## Analytical Chemistry.

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**Quantitative Chemical Analysis by Röntgen Radiation.** H. STINTZING.—(See ii, 216.)

**Automatic Burette with Improved Guard System.** F. J. CONSIDINE (*Chem. News*, 1924, **128**, 149—150).—The liquid is drawn into the burette from below through a stopcock, the caoutchouc tubing connecting the reservoir with the mouth of the burette being detachable in the middle at a short piece of glass tubing, in order that a closed system may be maintained.  
A. A. E.

**Chemical Analysis with Membrane Filters. IV. Nature of the Filter and its Application in Analytical Chemistry.** G. JANDER and W. JANDER [in part with H. MAAS] (*Z. anal. Chem.*, 1923, **63**, 273—291).—The rate of filtration through membrane filters is entirely unaffected by repeated use with all neutral salt solutions, acid solutions weaker than *N*, strong hydrochloric or acetic acid, or *N* solutions of sodium hydrogen carbonate or acetate. Strong solutions of nitric or sulphuric acid, alkali carbonate solutions stronger than *N*, alkali hydroxide solutions stronger than

0.2*N*, or ammonium sulphide solutions stronger than *N* rapidly cause the pores to close and filtration then ceases. The ash of a 15-cm. filter weighs from 6 to 12 mg.; most of this can be removed by soaking the filter for some time in *N* hydrochloric acid and nothing will be removed from the filter during the course of a subsequent analysis. The membranes do not adsorb even traces of salts during use either from acid or alkaline liquids, and precipitates like antimony or manganese sulphide or hydroxide may be completely removed from the filter by means of a jet of water. The amount of precipitate that adheres so strongly as not to be removed by this treatment rarely exceeds 0.2 mg. A. R. P.

**Indicators. VI. Theory and Practice of the Rational Use of Indicators in Acidimetry.** A. THIEL (*Z. anorg. Chem.*, 1923, **132**, 159—178).—A critical historical survey of the recent work of Noyes, Kolthoff, Bjerrum, Sørensen, and the author. The author's nomenclature given in earlier papers is elaborated. The term "acidity level" originally proposed by Friedenthal to express the logarithm of the hydrogen-ion concentration (Sørensen's  $p_H$ ) is supported, and definitions are given for the indicator-constant, characteristic, etc. The chief practical object of the study is to allow for errors as functions of the end-point with a particular indicator, of the concentrations and temperatures of the reagents, of concentrations of foreign substances, etc., and an exhaustive list is given of the points on which systematic knowledge must be available in order that the full possibilities of quantitative stoichiometry may be realised. S. I. L.

**Indicators for Use in Determining the Acidity of Soils.** E. RAMANN and H. SALLINGER (*Z. anal. Chem.*, 1923, **63**, 292—301).—Dyes made by a German firm for use in determining the acidity of soils by Clark and Lubs' method (*J. Wash. Acad. Sci.*, 1915, **5**, 609; A., 1916, ii, 571) are shown to give equally good results as those manufactured in America. The theory, construction, and application of Bjerrum's double wedge colorimeter for determining the hydrogen-ion concentration is explained. A. R. P.

**Potassium Carbonate and Potassium Hydrogen Carbonate as Standards [in Acidimetry].** G. BRUHNS (*Chem.-Ztg.*, 1924, **48**, 89—90).—The use of separate portions of potassium carbonate obtained by heating the hydrogen carbonate, instead of sodium carbonate, is recommended. If methyl-orange is used as the indicator in the subsequent titration, the sharpness of the end-point is improved by removing the greater part of the liberated carbon dioxide by agitation or aëration of the solution before the last few drops of acid are added. H. C. R.

**Neutralisation of Mixtures of Acids, and a Universal Buffer Mixture.** E. B. R. PRIDEAUX and A. T. WARD (*J. Chem. Soc.*, 1924, **125**, 426—429).—A buffer solution consisting of phosphoric, phenylacetic, and boric acids is described. The mixture is 0.02*N* with respect to each hydrogen ion and the whole is 0.1*N*. By adding alkali or strong acid of the same normality, a series

of solutions giving a  $p_H$  range of 2.5—11.5 is obtained. The neutralisation curve (cf. A., 1915, ii, 677) agrees well with that obtained by the hydrogen electrode.

S. K. T.

**Determination of the Moisture Content of Expressed Plant-tissue Fluids.** R. A. GORTNER and W. F. HOFFMAN (*Bot. Gaz.*, 1922, 74, 308—313).—The moisture content of plant-juices was calculated from the refractive index determined by a Abbe refractometer fitted with the ordinary "sugar" scale. The refractive indices of solutions of inorganic salts and proteins in the concentrations occurring in plant saps were sufficiently near to those of similar concentrations of sugars. There was close agreement between results so obtained and those determined by drying in a vacuum over sulphuric acid at the ordinary temperature.

A. G. P.

**Determination of the Hydrophilic Colloid Content of Expressed Plant-tissue Fluids.** R. NEWTON and R. A. GORTNER (*Bot. Gaz.*, 1922, 74, 442—446).—The freezing point of the expressed plant-juice is first determined. The total solids are determined by the refractometric method (see preceding abstract), a quantity of sucrose, sufficient to make a molar solution in the total water present, is added to the plant-juice, and the freezing point again determined. The magnitude of the excess depression over the calculated figure in the second determination is taken as a measure of the "bound" water, not available as solvent for the sugar. The "bound" water is shown to bear a definite relationship to the hydrophilic colloids of the plant-fluid.

A. G. P.

**Influence of certain Colloids on the Titration of Chlorides by Volhard's Method.** B. VAN DER BURG and C. A. KOPPEJAN (*Chem. Weekblad*, 1924, 21, 66—67).—The presence of colloids appears to make the process untrustworthy.

S. I. L.

**Modification of Isaacs' Colorimetric Determination of Blood Chlorides.** M. DUPRAY (*J. Biol. Chem.*, 1924, 58, 675—679).—Isaacs' method (A., 1922, ii, 716), depending on the conversion of silver chromate into sodium chromate by the chloride, and tintometric determination of the chromate solution, is made more sensitive by adding potassium iodide and 10% sulphuric acid and determining the iodine colorimetrically. The greater depth of colour makes it possible to use only 0.5 c.c. of blood.

G. M. B.

**Determination of Chlorides in Blood and Tissues.** D. D. VAN SLYKE [with J. SENDROY, jun.] (*J. Biol. Chem.*, 1923, 58, 523—529).—Organic matter is destroyed and the chlorides are precipitated as silver chloride by digesting the blood or tissue on a water-bath with standard silver nitrate solution prepared in concentrated ( $d$  1.4) nitric acid. The excess of silver nitrate is then titrated by Whitehorn's modification (A., 1922, ii, 272) of Volhard's method. The method may be used either on a macro- or a micro-scale.

E. S.

**Analysis of Alkali Bromides.** L. W. WINKLER (*Pharm. Zentr.-h.*, 1924, **65**, 37—39).—One g. of potassium bromide or sodium bromide is dissolved in 500 c.c. of water; 100 c.c. of this solution are acidified with 10 c.c. of concentrated sulphuric acid, and the boiling solution is titrated with 0.1*N*-permanganate solution until a permanent red coloration is obtained. Each 1 c.c. of the permanganate solution is equivalent to 0.0119 g. of potassium bromide. In the case of ammonium bromide, the solution must be boiled with the addition of sodium hydroxide to expel all the ammonia before the solution is acidified and titrated. To determine chlorides in alkali bromides, 1 g. of the sample is dissolved in 120 c.c. of water, the solution acidified with 20 c.c. of sulphuric acid, boiled, and titrated with 0.5*N*-permanganate solution; one drop of oxalic acid solution is then added and the chloride is determined by addition of silver nitrate solution and titration of the excess.  
W. P. S.

**Potassium Permanganate as a Standard for Iodometry.** J. M. HENDEL (*Z. anal. Chem.*, 1923, **63**, 321—324).—Results obtained by the use of potassium permanganate, previously standardised against pure sodium oxalate, as a standard for determining the strength of sodium thiosulphate solutions for iodometric work, agree to within 0.1% of those obtained by the use of iodine or potassium dichromate, provided that the acidity of the solution lies between 0.1 and 0.7*N*. The test is preferably made by adding 35 c.c. of the permanganate solution to 50 c.c. of 0.7*N*-sulphuric or hydrochloric acid and 3 g. of potassium iodide contained in a glass-stoppered flask. After keeping during 5 minutes in the dark, the solution is diluted to 450 c.c. and titrated with the thiosulphate solution.  
A. R. P.

**Application of Potassium Permanganate in Oxidimetry.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1924, **61**, 133—137).—In acid solution, the reaction may be written  $\text{MnO}_4' + 8\text{H}^+ \rightarrow \text{Mn}^{++} + 4\text{H}_2\text{O} + 5e$  ( $e$ =charge of a univalent cation); the oxidation potential is  $E = 0.00027/s \times \log ([\text{MnO}_4'] [\text{H}^+]^8 / [\text{Mn}^{++}]) + E_0$ , where  $E_0$  is a constant.  
S. I. L.

**Iodometric Determination of Sodium Sulphide.** E. BERL and W. PFANNMÜLLER (*Chem.-Ztg.*, 1924, **48**, 115—116).—Accurate results in this titration, using the hydrolytic precipitation method of Jellinek and Krebs (*A.*, 1923, ii, 871) to check the sodium sulphide solutions, are obtained by adding the diluted sulphide solution to an acidified iodine solution; with a neutral solution the results are too high. In alkaline solution, hydrolysis of the sulphide occurs.  
S. I. L.

**Determination of Sulphur Dioxide in Sodium Hydrogen Sulphite Solution.** L. DEBUCQUET (*J. Pharm. Chim.*, 1924, [vii], **29**, 66—68).—One c.c. of the solution is diluted with 20 c.c. of water and 25 c.c. of 5% mercuric chloride solution are added; the mixture is then titrated with 0.1*N*-sodium hydroxide solution,

using methyl-orange as indicator. The number of c.c. of the alkali solution multiplied by 0.0064 gives the amount of sulphur dioxide present.

W. P. S.

**Determination of Incoagulable Nitrogen (Residual Nitrogen).** F. FONSECA (*Biochem. Z.*, 1924, **144**, 175—178).—Comparative determinations have been made of the residual nitrogen of human blood sera after deproteinisation by colloidal iron, by sodium tungstate and sulphuric acid, by trichloroacetic acid, and by sodium tungstate and trichloroacetic acid (Pincussen). The colloidal iron method gives the lowest and the two last-mentioned methods the highest results, from which it is concluded that in the latter cases adsorption of the residual nitrogen compounds is at a minimum. On a protein diet, an increase in the residual nitrogen may be demonstrated by using any of the precipitants mentioned, with the exception of colloidal iron. Carbohydrate and fat have no influence on the residual nitrogen.

J. P.

**Rôle of Adsorption in the Determination of the Residual Nitrogen.** J. H. CASCÃO DE ANCIÃES (*Biochem. Z.*, 1924, **144**, 179—189).—Urea is not adsorbed by fibrin or by placental tissue; creatinine, amino-acids, and uric acid are adsorbed in amounts varying from 5 to 8%, whilst peptone is adsorbed to the extent of 25 to 30%. In the presence of 2—5% of sodium chloride, the adsorption of peptone is markedly reduced. Using the various methods of deproteinisation described by Fonseca (preceding abstract), the adsorption of amino-acids and more especially of peptone is considerable even in the presence of sodium chloride, but by washing the coagulum with 5% sodium chloride or 1.0*M* acetone the adsorbed nitrogen compounds may be partly recovered. It is concluded that in determining residual nitrogen considerable loss of compounds of high molecular complexity, such as peptones, occurs.

J. P.

**Determination of Nitrogen by Kjeldahl's Method and its Modifications.** P. FLEURY and H. LEVAILLIER (*J. Pharm. Chim.*, 1924, [vii], **29**, 137—147).—Using casein, the effect of introducing the following modifications and combinations thereof into the original process was tried: catalysts (metallic sulphates, mercuric chloride, stannic oxide), reducing agents (oxalic acid and oxalates), and substances raising the boiling point (potassium sulphate, phosphoric acid). The digestion of 0.25 g. of casein with 5 c.c. of sulphuric acid mixed with 15 c.c. of phosphoric acid and 5 g. of potassium sulphate gave a theoretical yield of ammonia, and the digestion was complete in fifteen minutes. The use of sulphates of copper, mercury, or iron as catalysts reduced the period of digestion at the expense of accuracy. The use of oxalic acid, however, gave satisfactory results. The boiling points of the various mixtures of acids and potassium sulphate were determined at various periods of the digestion; the best results were obtained with the mixtures of highest boiling point. In the case of mixtures

of acids and potassium sulphate of higher boiling point, the presence of catalysts, although it accelerates the decolorisation of the solution, retards the complete transformation of nitrogen into ammonia. The digestion should be continued for fifteen to thirty minutes after the solution has become colourless. The only disadvantage of phosphoric acid is that it attacks glass and silica.

H. C. R.

**Bromometric Determination of Ammonia, Sulphurous Acid, Hydrogen Sulphide, and Chromates.** W. MANCHOT and F. OBERHAUSER (*Ber.*, 1924, **57**, [B], 29—32; cf. this vol., ii, 199, 200).—The solution of bromine in hydrochloric acid (about 20%) may be replaced by a similar solution in approximately *N*-potassium bromide, which preserves its titre better.

For the determination of ammonia, a measured volume of 0.1—0.2*N*-bromine solution in potassium bromide is treated with approximately twice the calculated volume of about 0.5*N*-sodium hydroxide solution and the ammonium salt is added; when, after about 1—2 minutes, the evolution of nitrogen is complete, the solution is acidified with hydrochloric acid and treated immediately with an excess of arsenious acid. Unused arsenious acid is titrated with bromine in the presence of indigo-carmin as indicator.

Sulphurous acid is determined by allowing its solution to flow under the surface of a solution of bromine in hydrochloric acid and titration of the excess of halogen with arsenious oxide solution. The reaction does not require careful regulation of the concentration of the reactants as is the case with the iodometric determination of sulphurous acid. Solid sulphites and hydrogen sulphites are added directly to the solution of the halogen.

Hydrogen sulphide is determined analogously by adding its solution to an excess of bromine dissolved in hydrochloric acid. Reaction occurs in accordance with the equation  $\text{H}_2\text{S} + 4\text{H}_2\text{O} + 8\text{Br} = 8\text{HBr} + \text{H}_2\text{SO}_4$ . The troublesome separation of sulphur is not observed in sufficiently dilute solution.

For the determination of chromate, the solution is acidified with hydrochloric acid and treated with a sufficient quantity of potassium bromide and excess of arsenious acid solution. Unused arsenious acid is titrated with bromine in the presence of a solution of indigo-carmin (0.2 g.) and trinitroresorcinol (0.2 g.) in water (100 c.c.). The method can be extended to the indirect determination of lead and other metals which yield insoluble chromates.

H. W.

**Determination of Nitrates in Soils. Phenoldisulphonic Acid Method.** H. J. HARPER (*Ind. Eng. Chem.*, 1924, **16**, 180—183).—Full details of a simple procedure for accurately determining nitrates in soils by the phenoldisulphonic acid method are given. Perfectly clear and colourless soil extracts are obtained by using copper hydroxide precipitated in the soil suspension from copper sulphate and calcium hydroxide as the decolorising agent. This substance removes inappreciable quantities of nitrate from the solution by adsorption, whereas animal charcoal adsorbs appreci-



able quantities of nitrate. Losses of nitrate can be prevented by keeping the solution alkaline on evaporation, by removing the chlorides with silver sulphate, and by flooding the dry residue with 3 c.c. of phenoldisulphonic acid solution. The procedure described embodies the best points of several methods with certain modifications due to the author.

H. C. R.

**Direct Determination of Secondary Phosphate.** I. N. KUGELMASS and C. ROTHWELL (*J. Biol. Chem.*, 1924, **58**, 643—648).—An excess of saturated aqueous calcium sulphate precipitates secondary phosphates quantitatively according to the equation  $4\text{K}_2\text{HPO}_4 + 3\text{CaSO}_4 \rightleftharpoons \text{Ca}_3(\text{PO}_4)_2 + 2\text{KH}_2\text{PO}_4 + 3\text{K}_2\text{SO}_4$ , whilst primary phosphates are unaffected. In direct determinations, the phosphate in the precipitate is determined colorimetrically (A., 1922, ii, 718). In the presence of twenty times the amount of primary phosphate, the results are subject to an error of  $\pm 5\%$ .

G. M. B.

**Use of Bromine for the Volumetric Determination of Arsenic and Antimony, and in Winkler's Method for the Determination of the Bromine-Iodine Value (of Oils).** J. PRESCHER (*Pharm. Zentr.-h.*, 1924, **65**, 61—63).—Antimony trichloride in hydrochloric acid solution may be titrated with 0.1*N*-potassium bromate solution, using methyl-orange or indigo as indicator. The indicator is decolorised as soon as all the antimony has been oxidised. In the titration of arsenic trioxide, an indicator is not used; potassium bromide is added and the end-point of the titration denoted by the appearance of a faint yellow coloration. The following modification of Winkler's method is suggested with the object of avoiding the use of potassium iodide. The weighed quantity of oil is dissolved in 10 c.c. of carbon tetrachloride, 50 c.c. of 0.1*N*-potassium bromate solution, 1 g. of potassium bromide and 10 c.c. of 10% hydrochloric acid are added; after two hours, 10 c.c. of 0.1*N*-sodium arsenite solution and 20 c.c. of hydrochloric acid (*d* 1.19) are added and the mixture is titrated with potassium bromate solution.

W. P. S.

**Photosynthesis. An Electrometric Method of Determining Carbon Dioxide.** H. A. SPOEHR and J. M. MCGEE (*Ind. Eng. Chem.*, 1924, **16**, 128—130).—In determining changes in the carbon dioxide content of an air stream containing 0.2—0.6% by volume, with an accuracy of 0.002%, the carbon dioxide was absorbed in a solution of barium hydroxide and the conductivity of the latter measured. The electrolytic cell employed was in the shape of a two-bulbed pipette with electrodes 0.25 sq. cm. in area. When charged with 0.1*N*-potassium chloride solution, this had a resistance of about 6000 ohms, and errors due to polarisation and self-induction were found to be negligible. A resistance-concentration curve for the barium hydroxide solution was constructed by passing through it volumes of outdoor air, taken to have the fixed carbon dioxide content of 0.031% by volume.

C. I.

**Detection of Sodium and Potassium by Wet Analysis.**

G. G. LONGINESCU and (MLLE.) G. CHABORSKI (*Bul. Soc. Româna Stiin.*, 1923, **26**, 21—26).—Details are given of a method for detecting sodium and potassium by precipitation as pyroantimonate and hydrogen tartrate respectively, the remaining metals being removed by precipitation with barium carbonate. W. H.-R.

**Determination of Hardness of Water.**

N. TARUGI and G. GASPERINI (*Boll. Chim. Farm.*, 1924, **63**, 33—38, 65—70).—Boudron and Boudet's modification of Clark's method for determining the hardness of water, although in common use, is an empirical method and presents many defects. The authors discuss the numerous suggestions which have been made with the object of overcoming such defects, and propose the use of a palmitate solution for the purpose. [Cf. *B.*, 1924, 310.] T. H. P.

**Ash Determination by Aid of Oxygen.**

D. J. K. WETSELAAR (*Pharm. Weekblad*, 1924, **61**, 212).—In determining ash in organic materials, a great saving in time is effected if a gentle stream of oxygen is directed on to the carbon skeleton formed by heating in a porcelain or platinum boat. S. I. L.

**Alkalinity of the Ash of Foodstuffs. II. Simultaneous Titration of a Number of Components of the Ash.**

B. PFYL and W. SAMTER (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 241—275).—An improved method of determining phosphate consists in precipitating the tricalcium phosphate with sodium hydroxide in the boiling solution in the presence of excess of phosphate, when a finely crystalline precipitate is obtained which is very little hydrolysed on keeping. The influence of the following constituents of the ash of foodstuffs on the alkalinity and phosphate determination was systematically studied, and methods were worked out for preventing their disturbing effects: manganese, iron, aluminium, zinc, lead, tin, silicic, boric, and hydrosilicofluoric acids. Volumetric methods depending on acidimetric and alkalimetric titrations with phenolphthalein and methyl-orange as indicators are described for the determination of manganese, iron, aluminium, zinc, lead, and boric acid in the ash in conjunction with the determination of the alkalinity and phosphate content. A rapid volumetric method for determining calcium in the ash is also given. [Cf. *B.*, 1924, 229.] H. C. R.

**Determination of Copper as Cuprous Iodide.**

L. W. WINKLER (*Z. anal. Chem.*, 1923, **63**, 324—330).—The determination of copper as cuprous iodide by the following procedure yields results more accurate than those obtained by the gravimetric oxide or sulphide processes. The boiling neutral or faintly acid solution containing 0.01 to 0.1 g. of copper in a volume of 100 c.c. is treated in succession with 1 g. of ammonium chloride, 10 c.c. of 10% potassium iodide solution, and sufficient of a 10% sodium sulphite solution to remove the liberated iodine and to cause the liquid to have a slight odour of sulphur dioxide. After boiling during 1—2 minutes, the solution is set aside over-night in a dark place. The precipitate is collected on cotton wool, washed with 50 c.c.

of cold water, dried at  $130^{\circ}$ , and weighed. As a correction for the slight solubility of cuprous iodide, 1 mg. is added to the weight found. The process is applicable to the separation of copper from the alkali metals, magnesium, zinc, manganese, cobalt, and nickel. Cadmium salts exert a slight solvent action on the precipitate which may be suppressed by the addition of more iodide. Even very small quantities of lead are co-precipitated and impart a pale red colour to the cuprous iodide. Iron does not interfere if an excess of sodium sulphite is added before the potassium iodide.

A. R. P.

#### Critical Studies on Methods of Analysis. IV. Aluminium.

L. A. CONGDON and J. A. CARTER. V. Cadmium. L. A. CONGDON and R. C. CANTER. VI. Molybdenum. L. A. CONGDON and L. V. ROHNER (*Chem. News*, 1924, **128**, 98—100; 116—118; 118—120).—IV. Duplicate determinations of aluminium in aluminium chloride were made by seven different methods, from which it appears that hydrolysis of the solution by boiling with ammonium nitrite yields the most accurate results, whilst precipitation with ammonia in the presence of ammonium chloride gives high results and the iodide-iodate method low results. Volumetric methods involving determination of the free acidity after elimination of the aluminium as fluoride or alum, followed by direct titration of the total acid in a second sample, yield results comparable with those obtained by the nitrite method.

V. Precipitation of cadmium as sulphide and weighing as such after drying at  $100^{\circ}$ , or evaporation of the cadmium solution with sulphuric acid followed by ignition of the residue and weighing as cadmium sulphate, gave results with pure cadmium chloride closely approximating to the theoretical, whereas the figures obtained by precipitation with potassium carbonate and ignition to oxide, or by precipitation as cadmium ammonium phosphate followed by conversion to the pyrophosphate, were decidedly low. Of the volumetric methods tested, titration of the sulphide with iodine and titration of cadmium oxalate with permanganate gave good results, whilst indirect titration of the arsenate or sulphide gave slightly low results.

VI. In determining the molybdic acid in pure ammonium molybdate, precipitation with lead acetate, followed by weighing the ignited precipitate or distillation of the solution with hydrochloric acid and potassium iodide gave results very close to the theoretical. Low figures were obtained by precipitation as sulphide followed by roasting to, and weighing as, oxide, and high results by weighing as oxide after precipitation as mercurous molybdate.

A. R. P.

**Simultaneous Electrometric Determination of Iron and Manganese.** E. MÜLLER and O. WAHLE (*Z. anorg. Chem.*, 1923, **132**, 260—264).—The solution is titrated in presence of sulphuric acid at normal temperature with 0.1*N*-potassium dichromate solution, using a normal calomel electrode and a back *E.M.F.* of 0.57 volt; the whole is then heated at  $80^{\circ}$ , potassium fluoride

added, and the manganous salt titrated to the manganic state with 0.1N-permanganate solution as previously described (*ibid.*, 1923, **129**, 278; this vol., ii, 64). S. I. L.

**Critical Studies on Methods of Analysis. VII. Cobalt.** L. A. CONGDON and T. H. CHEN (*Chem. News*, 1924, **128**, 132—134).—In determining cobalt by precipitation as cobalt ammonium phosphate, accurate results are obtained only if the small quantity that escapes precipitation is recovered as sulphide and converted into oxide for weighing. The nitroso- $\beta$ -naphthol method yields more consistent and satisfactory results than any other method, whilst precipitation of a complex cobaltic molybdate gives high and inconsistent figures. A. R. P.

**Co-precipitation of Cobalt and Nickel by Stannic Sulphide. Colorimetric Determination of Cobalt.** V. AUGER and (MILLÉ.) L. ODINOT (*Compt. rend.*, 1924, **178**, 710—711).—The stannic sulphide precipitated from acid (hydrochloric) solutions containing cobalt or nickel contains these metals, the amount adsorbed varying inversely as the concentration of the acid. Stannous sulphide does not adsorb these metals. The determination of tin in such solutions is best effected by using cupferron. The blue colour obtained by dissolving cobalt salts in an excess of concentrated hydrochloric acid may be used for the colorimetric determination of cobalt. The influence of concentration of acid on the blue colour has been investigated. E. E. T.

**Detection of Chromium in the Presence of Manganese by Wet Analysis.** (MILLÉ.) G. CHABORSKI (*Bul. Soc. Romăna Stiin.*, 1923, **26**, 83—85).—The mixed hydroxides of iron, chromium, and manganese remaining after the separation of aluminium and zinc by sodium hydroxide solution, are treated with 1 to 2 c.c. of sodium hypochlorite solution, heated to the boiling point without actually being allowed to boil, and filtered. If chromium is present the filtrate is coloured yellow. In the absence of nickel a black residue obtained in the test for chromium indicates the presence of manganese, but if nickel was originally present the test is not conclusive, and a fresh portion of the mixed hydroxide precipitate is treated with 5—10 c.c. of sodium hypochlorite solution, boiled for 2—3 mins., and the remaining solid allowed to settle when, if manganese is present, the liquid will be coloured violet owing to the formation of permanganate. W. H.-R.

**Determination and Separation of Bismuth by Hydrolysis.** G. LUFF (*Z. anal. Chem.*, 1923, **63**, 330—348).—Bismuth may be quantitatively separated from lead, copper, and cadmium by precipitation as the basic nitrate,  $2\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ . The solution (80 c.c.) is neutralised with sodium hydrogen carbonate, the precipitate dissolved by adding *N* nitric acid, and the liquid boiled under a condenser. Precipitation of the basic nitrate may be brought about by the addition of either sodium nitrite or sodium hydrogen carbonate solution. The precipitate is ignited to,

and weighed as, oxide. In carrying out the oxychloride precipitation it is best to neutralise the nitrate solution, add ammonium chloride and hydrochloric acid, heat to boiling, and slowly add boiling water. To obtain the basic sulphate the neutralised nitrate solution is treated with 1 : 10 sulphuric acid until the precipitate dissolves, and boiling water added to the boiling solution; the bismuth is completely precipitated as microscopic colourless needles of the composition  $\text{Bi}_2\text{O}_3 \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$ . This compound remains unchanged when dried at  $100^\circ$ ; it contains 74.02% of bismuth, and is quantitatively converted to oxide by prolonged ignition over a blast burner.

A. R. P.

**Reduction of Bismuth Salts by Hydrazine Hydrate, and the Titration of Metallic Bismuth.** J. HANUŠ and A. JILEK (*Chem. Listy*, 1924, **18**, 8—12).—The bismuth salt solution is boiled with the addition of hydrazine hydrate, the resulting metallic bismuth is collected on a filter, and washed with water containing dissolved carbon dioxide; the filter and precipitate are then transferred to a vessel containing ferric chloride solution acidified with hydrochloric acid, a current of carbon dioxide is passed through the mixture, and, when the bismuth has dissolved, the ferrous chloride produced is titrated with 0.1N-permanganate solution. The presence of a small quantity of lead (less than 5% of the bismuth) does not interfere with the determination. W. P. S.

**The Resorcinol Test for Methyl Alcohol.** A. B. LYONS (*J. Amer. Pharm. Assoc.*, 1923, **12**, 323—327).—The presence of ethyl alcohol influences the resorcinol-sulphuric acid (formaldehyde) test, but rarely renders it invalid. CHEMICAL ABSTRACTS.

**Detection of Methyl Alcohol in Presence of Ethyl Alcohol;** C. H. LAWALL (*Trans. Wagner Free Inst. Sci. Philadelphia*, **10**, 55—62; *Amer. J. Pharm.*, 1923, **95**, 812—820).—To 5 c.c. of the mixture, diluted to contain about 5 vol.-% of ethyl alcohol, are added 5—6 drops of phosphoric acid and 2 c.c. of 3% aqueous potassium permanganate solution, the liquid being then allowed to remain for 10 minutes. Oxalic acid (1 c.c. of a 10% aqueous solution) is then added, and the mixture kept until it is transparent brown. Dilute sulphuric acid (1 : 3 mols.), then U.S.P. magenta-sulphurous acid test solution (5 c.c.) are added, well mixed, and allowed to remain for 10 minutes. The presence of methyl alcohol is indicated by a blue or violet colour observed against a white background. The test is sensitive to 1 part of methyl alcohol in 500 parts of ethyl alcohol; preliminary fractionation increases the sensitiveness to 1 in 10,000. The record of the test may be made permanent by dyeing white wool. Increasing the period of oxidation increases the sensitiveness, but heating after addition of permanganate produces formaldehyde from ethyl alcohol; increasing the volume of permanganate from 2 to 5 c.c. also caused ethyl alcohol to give a positive reaction.

CHEMICAL ABSTRACTS.

**Determination of the Copper Number of Cellulosic Materials.** The Fontès-Thivolle Molybdomanganimetric Method. H. GAULT and B. C. MUKERJI (*Compt. rend.*, 1924, 178, 711—713).—About 1 g. of the cellulose is added to 50 c.c. of Fehling's solution diluted with 100 c.c. of water and previously heated at 120° (calcium chloride bath). Heating is continued for exactly 15 minutes, the mixture then filtered, the cuprous oxide (or the copper obtained therefrom, by reduction) dissolved in the phosphomolybdic reagent, and determined by titration with permanganate.  
E. E. T.

**Rapid Analysis of Sugars. Purification and Concentration of Enzyme Solutions.** F. W. REYNOLDS.—(See i, 464.)

**Table for the Determination of Sugar in Blood.** G. A. WETSELAAR (*Pharm. Weekblad*, 1924, 61, 213—218).—A complete table has been prepared for determinations by Shaffer and Hartmann's method (A., 1921, ii, 417) as modified by Cohen and Tervaert (*Nederl. Tijdsch. Geneesk.*, 1921, 65, ii, No. 7). The figures were obtained by determinations after addition of known quantities of dextrose, and are accurate to the third significant figure. From the volume of 0.005N-thiosulphate solution used under specified conditions, the weight of dextrose (mg.) in 1 c.c. of blood is read directly.  
S. I. L.

**I. Folin and Wu's Method for the Determination of Blood Sugar. II. A Modification of the Method.** V. E. ROTHBERG and F. A. EVANS (*J. Biol. Chem.*, 1923, 58, 435—442, 443—451).—I. The results obtained with Folin and Wu's method (A., 1920, ii, 337) are trustworthy only when the concentrations of dextrose in the standard solution and that under examination are approximately the same. II. When the concentrations in the two solutions do not differ by more than 100%, this source of error can be overcome by diluting the blood filtrate, after addition of the phosphomolybdate-phosphotungstate reagent, until the colour is approximately the same as that of the standard solution, and introducing a volume factor into the calculation. All the precautions emphasised in the original method must be observed.  
E. S.

**Preparation of Dried Urease and the Determination of Urea in Normal and Pathological Urines.** G. REVOLTELLA.—(See i, 474.)

**Fluorescent Oxidation Products of Bilirubin and their Importance as Sources of Error in the Detection of Urobilin.** A. ADLER (*Biochem. Z.*, 1924, 144, 64—65).—A reply to the criticisms by Barrenscheen and Weltmann (A., 1923, ii, 800) of the author's work on the detection of urobilin in human fistula bile.  
J. P.

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## General and Physical Chemistry.

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**Foundations of the Quantum Theory.** I. H. A. SENFTLEBEN (*Z. Physik*, 1924, 22, 127—156).—A discussion of the principles underlying the quantum theory and its applications to intra-atomic changes. The mechanism of atomic radiation is considered. S. B.

**Quantum Defect and the New Bohr Theory of Atomic Structure.** F. S. BRACKETT and R. T. BIRGE (*J. Opt. Soc. Amer.*, 1924, 8, 213—230).—According to the new Bohr theory, successive increase in the atomic number is associated with the conversion of virtual orbits into orbits which are permanently occupied (cf. A., 1923, ii, 110, 478, 679). Direct calculations of the energies of orbits are only possible for atoms possessing one orbital electron (*e.g.* H and ionised He), but this theory makes possible a correlation of experimental data for more complex atoms. In the present paper, spectroscopic and X-ray data are used to calculate the energy values of the various atomic states of elements up to atomic number 56, and quantum numbers are assigned to each of these atomic states. The relation between the energies of corresponding levels in different elements is illustrated by curves which show many regularities. These diagrams may be used to predict the values of unknown orbits. The points on the curves obtained from "optical" and "X-ray" spectra show good agreement. The assignment of orbits differs from Bohr's in a few instances. S. B.

**Spectral Series of Divalent Elements.** R. T. BIRGE (*J. Opt. Soc. Amer.*, 1924, 8, 233—243).—New series of triplets found by Hopfield in oxygen and sulphur are assigned to a new energy level *OP*. The deviations from Rydberg's formula found in the same type of sequence of related elements are inter-related, so that it is possible to predict approximate values of unknown spectral terms (see preceding abstract). The missing *OS* level of calcium and zinc is probably identical numerically with the *IS* level, but has a different inner quantum number. It is suggested that any given type of orbit can exist in two states, when a virtual orbit or an X-ray orbit, but in only one possible state as a valency orbit. S. B.

**Simultaneous Action of Crossed Electric and Magnetic Fields on the Hydrogen Atom.** O. KLEIN (*Z. Physik*, 1924, 22, 109—118).—The disturbances of the hydrogen electron in crossed electric and magnetic fields are calculated by a method similar to that used by Bohr for the Stark effect; these results are employed to find the stationary states for such a system. S. B.

**Hydrogen Balmer Series, and the Impossibility of Further Corrections to the Quantising of Hydrogen Atoms.** A. E. RUARK (*Astrophys. J.*, 1923, 58, 46—58).—A series of plates

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obtained by Wood has been subjected to measurement, in order (i) to furnish better wave-lengths for the higher members of the series, (ii) to determine the Rydberg constant, and (iii) to test the necessity for corrections arising in the asymmetry of the nucleus or electron, or in the existence of an intrinsic magnetic moment in either, or in the possibility that part of the potential energy of the atom may be considered to move with the electron, so as to change its apparent mass. These three corrections are shown to be invalid; the relativity correction only is necessary to explain existing observations. Very accurate values of  $\lambda$  from H7 to H18 are tabulated. The mean value of  $R_H$  (computed for the lines 3 to 12 inclusive) is  $109677.26 \pm 0.23$ , whence  $R_\infty = 109736.45 \pm 0.23$ .

A. A. E.

**Doublet Separation of the Balmer Lines.** G. M. SHRUM (*Proc. Roy. Soc.*, 1924, **A**, 105, 259—270).—The doublet separations in the first five lines of the Balmer series of hydrogen have been determined at the temperature of liquid air, and found to be in almost exact quantitative agreement with the theory of Sommerfeld, this being the first direct proof of the theory in the case of hydrogen. The intensity of the Balmer lines relatively to that of the secondary spectrum, may be increased many times if the inner walls of the quartz tube in which the discharge takes place are coated with a very thin and even film of ice, which, together with adsorbed nitrogen, shields the atomic hydrogen from the catalytic action of the quartz, and so diminishes the intensity of the secondary spectrum which is due to hydrogen molecules. No evidence of the fine structure was observed even at the temperature of liquid hydrogen. W. H.-R.

**Intensities of Complex Spectral Lines.** H. B. DORZELO (*Z. Physik*, 1924, **22**, 170—177; cf. *ibid.*, 1923, **18**, 206).—The relative intensities of wide doublets and triplets have been measured. The intensity ratio of the alkali metal doublets was found to be 2 : 1, and the ratios for the alkaline-earth triplets to be 5 : 3 : 1. The intensity ratios of the components of simple doublets and triplets are fixed by the inner quantum numbers of the spectral terms which correspond to the series limits (Landé's  $J$ -values).

S. B.

**Fine Structure of Certain Spectral Lines.** E. LAU (*Physikal. Z.*, 1924, **25**, 60—68).—A critical discussion of methods of spectral measurement with special reference to the fine structure of the hydrogen and ionised helium lines. It is shown that measurements involving the use of step or line gratings or Lummer-Gehrcke plates in conjunction with photographic observations are subject to errors producing an apparent broadening of doublets of 40%. Interferometer methods or those involving photometric examination are held to be less liable to error. The most probable value for  $\Delta\nu_H$  is  $0.298 \text{ cm}^{-1}$  whereas the theory of Sommerfeld requires  $\Delta\nu_H = 0.365 \text{ cm}^{-1}$ . In the Fowler and the Pickering series of the helium spectrum, only the triplet 4686 Å. gives the theoretical  $\Delta\nu_H$  values; thus the relativity correction in the Bohr equation for the helium



spectrum should not be regarded as confirmed. The fine structure of the X-ray spectra is discussed. A. E. M.

**Direct Determination of the Relative Intensities of [the Components of] Multiple [Spectral] Lines.** W. GERLACH and O. BREZINA (*Z. Physik*, 1924, **22**, 215—221).—The slit of a spectrograph is illuminated by light which has traversed a pair of crossed Nicols. Interposed between the Nicols is a thin doubly refracting plate of mica, quartz, etc., cut so that the planes of vibration in the plate are inclined at  $45^\circ$  to the planes of vibration in the Nicols. The plate comprises a small central portion which can be rotated relatively to the outer and is separated therefrom by a narrow gap. The relative intensities of lines in the visible region are compared by rotating the inner portion of the plate until the intensity of the one line as viewed through the inner portion is adjusted to equality with the intensity of the other line as seen through the outer portion of the thin plate. Lines outside the visible region of the spectrum are photographed and an interpolation method is used. The results obtained are not vitiated by any possible unsteadiness of the light source employed. Contrary to the result obtained by Wood (A., 1914, ii, 398), the authors find that even in flames only slightly coloured by sodium, the relative intensities of the  $D_1$  and  $D_2$  lines are in the ratio 1 : 2. The mathematical theory of the method is given. J. S. G. T.

**Width of the Lines in the Spark Spectrum of Hydrogen.** M. HANOT (*Compt. rend.*, 1924, **178**, 1071—1073).—The "width" of a line is defined as the interval of wave-length corresponding with a diminution of the maximum intensity by one-half. The character of the spectrum is independent of the damping of the discharge, but increase of the period decreases the width of the lines,  $H\beta$  and  $H\gamma$ , which were investigated. The variation in width is attributed to the effect of the period on the temperature and pressure of the gas. A. B. H.

**Excitation of the Helium Spectrum by Electronic Bombardment.** A. UDDEN and J. C. JACOBSEN (*Physical Rev.*, 1924, **23**, 322—326).—At the higher voltages used, the ortho and parhelium spectra were of about equal intensity, but at low voltages the former was relatively much the stronger. In explanation, the supposition of the existence of the metastable state of the helium atom is favoured. Experimental work to test this view has so far been negative. A. A. E.

**Excitation of Spectral Lines by Electron Impact.** I. G. HERTZ (*Z. Physik*, 1924, **22**, 18—26).—It is still uncertain whether lines of a spectral series can be successively excited by gradual increase of the energy of electron impact, or whether they appear together (except the resonance lines) at the ionisation potential. In the present paper, small refinements of the hot cathode and grid anode apparatus usually employed for these investigations are described. Errors due to the space field in the ionising chamber are eliminated by using very small current densities, and by

introducing small quantities of a gas or vapour (usually mercury) of ionisation potential lower than the resonance potential of the gas under investigation. The successive development, in accordance with the Bohr theory, of lines in the mercury, neon, helium, and zinc spectra has been observed with this apparatus. S. B.

**Excitation of the Spectra of Argon, of Krypton, and of Xenon.** G. DÉJARDIN (*Compt. rend.*, 1924, **178**, 1069—1071).—A continuation of previous work on the rare gases (*Compt. rend.*, 1921, **172**, 1347, 1482; A., 1923, ii, 282). A study of the development of the spectra of the neutral atom, the monovalent ion,  $E_1$ , the doubly,  $E_2$ , and triply charged ions,  $E_3$ , as the potential increases from 10 to 100 volts. The arc-spectra appear when the potential of the electrons exceeds the ionisation potential, and the spark spectra of the first and second order appear at higher potentials. The excitation potentials of the different spectra of argon, krypton, and xenon are proportional amongst themselves.

A. B. H.

**Intensity Relations in the Helium Spectrum.** C. B. BAZZONI and J. T. LAY (*Physical Rev.*, 1924, **23**, 327—336).—The crossed orbit lines 4437, 4387, 4922, and 5016 Å. increased in relative intensity with voltage, although not uniformly, whilst the co-planar lines 4713, 5875, and 4471 Å. diminished to a minimum at 50 volts. The results are in general agreement with those obtained by Hughes and Lowe (*ibid.*, 1923, **21**, 714; A., 1923, ii, 804).

A. A. E.

**Excitation Stages in the Open Arc-light Spectra. III. Lead, Mercury, Thallium, Magnesium. IV. Hydrogen, Air, Water-vapour, Pressure Effect, Mixed Electrodes.** B. E. MOORE (*Astrophys. J.*, 1923, **58**, 86—103, 104—112; cf. A., 1922, ii, 242).—III. Photographic methods were applied in the observation of the lines, which are tabulated. At the pole tip, the temperature and velocities of the electrons were always high enough to produce appreciable dissociation of the atoms. In the case of lead, the lines represent very easy excitations and probably fall in stage I; two stages, and possibly a third, are found in the development of the lines of mercury, two in the case of thallium, and four for magnesium, corresponding respectively with resonance, first ionisation, subsequent resonance, and second ionisation.

IV. The substitution of hydrogen for air or nitrogen reduces the intensity of the spectra of the metals in the middle of the arc. It is concluded that hydrogen is completely dissociated into atoms within the polar illumination, and that the "second hydrogen spectrum" is the first hydrogen excitation. Decreased pressure is accompanied by a decrease in temperature and results in less contrast in the series lines. The effect of volatility of the electrodes is also considered. The changes due to pressure and temperature, together with the variations in electron velocity, are considered to be sufficient to explain all of the differences which have been noted in the spectra.

A. A. E.

**Series Spectrum of Ionised Carbon (CII).** A. FOWLER (*Proc. Roy. Soc.*, 1924, **A**, 105, 299—310; cf. A., 1923, ii, 447).—The spectrum of carbon has been examined under a variety of experimental conditions, and the discovery of previously unrecorded lines has led to the identification of the leading members of the series of ionised carbon (CII or  $C^+$ ) in the ordinary region of observation. The main series, however, lie in the extreme ultra-violet and have been identified in the observations of Simeon (A., 1923, ii, 709), and of Millikan (A., 1921, ii, 3). The series of CII form a doublet system, as would be expected from the spectroscopic displacement law, and previously unrecorded pairs of lines have been found at 7236.19 and 7231.12, 2174.14 and 2173.86, 2137.93 and 2137.45. The highest terms are the common limits of the sharp and diffuse series, 196612 and 196670, from which it may be deduced that the second ionisation potential of carbon is 24.28 volts, representing the energy necessary to remove the second electron when the first has already been removed. In the normal state of the atoms, two of the outermost electrons in ionised carbon probably move in  $2_1$  orbits, whilst the electron which generates the spectrum traverses a  $2_2$  orbit, as suggested by Bohr for neutral boron.

W. H.-R.

**Arc Spectrum of Silicon in Relation to Spectrographic Analysis.** C. PORLEZZA.—(See ii, 345.)

**Arc Spectrum of Chromium.** H. GIESELER (*Z. Physik*, 1924, **22**, 228—244).—Lines belonging to the quintet and septuplet systems characterising the spectrum of chromium are classified into series and the values of the series terms calculated. Details are given of the magnitudes of the Zeeman effect exhibited by lines of the series  $4^7_{13} - 4^7_{24, 23, 22}$ ,  $4^7_{13} - 4^{7a}_{24, 23, 22}$ , and of the series  $4^5_{12} - 4^5_{23, 22, 21}$  (notation of Landé and Paschen). The results confirm those obtained by Catalan (A., 1923, ii, 519). The normal orbit of the chromium atom is a 4s orbit. A number of terms relating to the systems of quintets and septuplets may be calculated by means of Ritz formulæ. The system of quintets are classified into twelve series, including four triplets of  $p$  terms. The  $f$  and  $d$  terms are of the order of magnitude of the  $p$  terms. Particulars are given of combination lines, the frequencies of which may be calculated by a combination of terms relating to the quintet and septuplet systems, respectively. Details are given of the Zeeman effect exhibited by the triplet 5208, 5206, 5204.

J. S. G. T.

**Regularities in the Arc Spectrum of Iron.** F. M. WALTERS (*J. Opt. Soc. Amer.*, 1924, **8**, 245—274).—Twenty-two polyfold energy levels (of the same total and azimuthal quantum numbers, and nearly the same energy value but with different inner quantum numbers) have been found in the arc spectrum of iron, producing 54 or more multiplets by intercombination. From the inner quantum numbers and Landé's scheme for the Zeeman effect, several polyfold levels have been identified with  $P$ ,  $D$ , and  $F$  terms. Lines in an iron multiplet show similar pressure effects, and behave alike in the electric furnace.

S. B.

**Higher Order Spark Spectra.** L. BLOCH, E. BLOCH, and G. DÉJARDIN (*Compt. rend.*, 1924, **178**, 766—769).—Previous work (A., 1923, ii, 350) has been applied to argon, krypton, and xenon. Three spark spectra are observed: the first (brightest) extends from the extreme red to the extreme ultra-violet; the second begins at the end of the violet and does not enter the visible spectrum; the third is mainly in the ultra-violet region. E. E. T.

**Secondary  $\beta$ -Rays produced in a Gas by X-Rays.** P. AUGER (*Compt. rend.*, 1924, **178**, 929—931).—Hydrogen saturated with water vapour has been investigated as previously described (A., 1923, ii, 601). The 163  $\beta$ -rays studied were sufficiently rectilinear to allow of measurement to within a few degrees of the angles made with the X-rays. The rays projected forward are virtually double as numerous as those projected backward, more than 85% of the electrons being emitted at inclinations to the direction of the X-rays ranging from  $45^\circ$  to  $115^\circ$ ; the emission is approximately symmetrical about the middle position,  $80^\circ$ . A theoretical interpretation of these facts is given. T. H. P.

**Direction of Ejection of Photo-electrons by Polarised X-Rays.** F. W. BUBB (*Physical Rev.*, 1924, **23**, 137—143).

**Symmetry of Incident and Emergent Photo-electronic Velocities.** R. J. PIERSON (*Physical Rev.*, 1924, **23**, 144—152).

**Scattering of X-Rays by Hydrogen.** G. A. SCHOTT (*Physical Rev.*, 1924, **23**, 119—127).—Measurements of the absorption and scattering of X-rays by Aurén (A., 1919, ii, 89; 1921, ii, 367) and by Olson, Dershem, and Storch (A., 1923, ii, 365) have been recalculated from the actual results, instead of from smoothed curves, using the method of least squares, and avoiding Aurén's approximations. By suitable choice of the quantity  $\sigma_0$ , the ring-electron theory and Compton's quantum theory can be made to fit the curve approximately, the former better at large, and the latter at small wavelengths. Sufficiently accurate experimental results could be secured only by using elementary hydrogen, either liquid, or gaseous under high compression. A. A. E.

**Rotatory Dispersion of Quartz.** F. BURKI (*Helv. Chim. Acta*, 1924, **7**, 328—330).—The author's rotatory dispersion formula,  $[\alpha] = C/\lambda^2 \cdot e^{\beta/\lambda^2}$  (this vol., ii, 218) has been used to calculate the rotation-dispersion of quartz. The calculated values accord more closely with experiment than those derived from Drude's formula,  $[\alpha] = k_1/(\lambda_2 - \lambda_0^2) + k'/\lambda^2$ . The values of the constants are  $C = 7.1505$ ,  $\beta = 0.01864$ . The sum of Drude's constants,  $k_1 = 12.200$  and  $k' = -5.046$ , is practically equal to the value of  $C$ . E. H. R.

**Molecular Absorption Spectra of Hydrogen Cyanide.** E. F. BARKER (*Physical Rev.*, 1924, **23**, 200—204).—Two maxima, very nearly symmetrical, and with nearly equal intensities, were observed at about  $6.94 \mu$  and  $7.23 \mu$ ; three others, unsymmetrical, were found at  $4.756 \mu$ ,  $4.723 \mu$ , and  $4.79 \mu$ , and a single narrow

maximum at  $3.564 \mu$ . Estimates of the moment of inertia of the molecule from various bands do not agree; measurements at  $7\mu$  give a value of about  $13.2 \times 10^{-40}$ .  
A. A. E.

**Absorption Spectra of Chromium and Iron Vapours.** H. GIESELER and W. GROTRIAN (*Z. Physik*, 1924, **22**, 245—260).—In continuation of previous work (A., 1923, ii, 106), the authors have observed the absorption spectra of chromium and iron vapours respectively at a temperature of about  $1230^\circ$ . For chromium vapour, absorption was observed in the case of the triplets  $4289.92$ ,  $4275.01$ ,  $4254.52 \text{ \AA}$ . and  $3605.49$ ,  $3593.64$ ,  $3578.81 \text{ \AA}$ ., constituting the principal series of the septet system. Contrary to anticipation, absorption was not observed in the case of the combination lines  $4p_i$  and  $4p_e$ , viz.,  $3732.18$ ,  $3730.95 \text{ \AA}$ . and  $3351.97$ ,  $3379.18 \text{ \AA}$ . The  $4s$  term of the septet system corresponds with the normal condition and the 24 electrons of the chromium atom are arranged in a  $4_1$  orbit. With iron vapour, absorption was observed at  $1230$ — $1250^\circ$  in the case of the lines  $3886.29$ ,  $3859.91$ ,  $3745.56$ ,  $3737.14$ ,  $3719.95$ ,  $3047.61$  (?),  $3021.08$ , and  $3020.64$  (not separated),  $2973.24$ ,  $2966.90$ , and  $2719.04$ . Absorption was most marked in the case of the line  $3859.91$ , and was only just discernible in the case of the lines  $2719.04$  and  $3047.61$ . The twenty multiplets classified by Walters in the ion arc spectrum (A., 1923, ii, 519) are arranged according to the energy levels associated with the respective quintet and triplet terms. The lines in the iron spectrum correspond with an electronic transition from the lower group of levels  $3d_{4,3,2,1,0}$  comprised within this arrangement of levels. The existence of triplet and quintet systems in the iron arc spectrum is in accord with Sommerfeld's extension of Rydberg's rule of alternation to multiplets (A., 1923, ii, 734). It is concluded that, most probably, the term  $3d_4$  represents the normal condition of the iron atom and that the 26 electrons of the iron atom are arranged in a  $3_3$  orbit. At about  $1600^\circ$ , the iron lines previously observed and their multiplets are shown to be present as absorption lines. In addition, marked absorption was observed in the region  $2447$  to  $2491 \text{ \AA}$ . The components of this multiplet are classified. A few additional unclassified lines in the region  $5500$ — $2300 \text{ \AA}$ . were feebly absorbed at about  $1600^\circ$ .  
J. S. G. T.

**Effect of Pressure on Optical Absorption.** F. G. WICK (*Proc. Amer. Acad. Arts Sci.*, 1923, **58**, 557—573).—With the aid of a modified form of Bridgman's apparatus (*ibid.*, 1911—12, **47**, 321; 1913—14, **49**, 627), experiments have been performed with aqueous solutions of neodymium, praseodymium, erbium (with yttrium), uranium, and cobalt compounds, and with synthetic ruby and samples of coloured glass, at pressures up to  $3500 \text{ atm}$ . In general, the changes which take place in the absorption spectra on increase of pressure are similar to those observed on lowering the temperature or decreasing the concentration. There is, however, a slight shift (in most cases towards the violet, but, for the band  $4272$ , towards the red) in the position of the neodymium bands on increase of pressure, but not under the latter conditions; only

neodymium solutions containing a dehydrating agent show an appreciable shift with rise of temperature. Bands barely visible under normal conditions are brought out more strongly by either increase of pressure or lowering of temperature, but not by dilution; the effect of the highest pressures used with neodymium solutions was, however, much less than that produced by lowering the temperature to that of liquid air, and was possibly equivalent to that observed at about  $-60^{\circ}$ . The pressure effect cannot be explained by any resulting changes of temperature or concentration; there must be more than one simple type of mechanism involved in the production of the absorption bands, since the three agencies affect only some of the bands, and those in different ways. Since absorption bands in solution are made sharper by pressure, those of the crystalline neodymium salts also being sharper, it is suggested that the structure of solutions under pressure tends towards that of the solid state.

A. A. E.

**Fluorescent Efficiency of Solutions of Dyes.** S. J. WAWILOW (*Z. Physik*, 1924, **22**, 266—272).—Employing a spectrophotometric method similar to that used by Wood and Dunoyer for the investigation of the resonance spectrum of sodium vapour (2nd Solvay Conf., 1921, p. 307), the author has determined the value,  $K$ , of the ratio of the energy of the secondary fluorescent radiation emitted by solutions of various dyes to the total energy absorbed. The strengths of the solutions employed ranged from  $10^{-5}$  to  $10^{-6}$  g./c.c. The error in  $K$  due to the small absorption of fluorescent radiation by the solution, and to reflection by the glass walls of the containing vessel, was 10 to 15%. The following values of  $K$  were determined: aqueous solutions of fluorescein, 0.80; rhodamin Scarlet G, 0.50; rhodamin 5 G, 0.37; rhodamin B, 0.25; eosin bl., 0.15; acridine red, 0.08; erythrosine,  $<0.02$  (?); solution of fluorescein in methyl alcohol, 0.74; solution of fluorescein in ethyl alcohol, 0.66; solution of Magdala red in ethyl alcohol, 0.54; solution of uranium in uranium glass, 0.23. The approximation of  $K$  to unity in the case of a typically fluorescent dye such as fluorescein would not be anticipated from the classical theory of thermal absorption. The respective maxima of the incident and fluorescent radiation were separated, in all cases, by about 230 Å. The value of  $K$  diminished rapidly as the strength of the solutions employed increased. The author considers that Wood's conclusion, that in the case of sodium vapour  $K$  is approximately equal to unity, is unjustified.

J. S. G. T.

**Cathodo-luminescence of Solid Solutions of Forty-two Metals.** T. TANAKA (*J. Opt. Soc. Amer.*, 1924, **8**, 287—318).—Extensive observations on the cathodo-luminescence of mixtures of various salts are described. The materials were excited by cathode rays in a vacuum tube, actuated at about 4000 volts by a Holst machine. The luminescence was examined by a Hilger spectrophotometer. Between 0.1 and 1% of the substance under examination was mixed with a "base" (calcium carbonate, fluoride, sulphate, barium sulphate, cadmium sulphate, etc.). A series of

the luminescent sulphides prepared by Lenard and Klatt was also examined. Three types of luminescence were observed, characterised by (1) fine line-like bands, (2) groups of broad bands, the members of each group overlapping, and (3) a whitish colour without any distinct maxima.

The following general conclusions were drawn. Whatever base is used, the metal of the added salt shows a characteristic series of bands, although a change of base may produce a slight shift of the bands. Each metal has from one to four characteristic band series; most frequently there are two such series. For each metal there exist two characteristic frequency intervals, totally independent of the base, and the mean of these intervals decreases quite regularly with increase in the atomic weight of the metal. Of the metals examined, the active metals of Lenard and Klatt's sulphides and the rare earths gave the brightest luminescence.

S. B.

**Phosphorescence of Fused Transparent Silica.** W. E. CURTIS (*Nature*, 1924, **113**, 495; cf. Chapman and Davies, this vol., ii, 220).—Experiments on the production and destruction of the phosphorescence of silica discharge tubes indicate that it is due to the ultra-violet radiations (constituting the "Lyman" series) of atomic hydrogen.

A. A. E.

**Chemi-luminescence and Energy Changes in the Oxidation of Phosphorus.** A. PETRIKALN (*Z. Physik*, 1924, **22**, 119—126; cf. A., 1912, ii, 709).—The ultra-violet bands in the glow of phosphorus have been photographed. Five groups of bands are described with "centres of gravity" at 3270, 2600, 2530, 2460, and 2390 Å. These agree in wave-length and intensity with bands in the arc spectrum of phosphoric oxide. The production of ozone which accompanies this oxidation is discussed from a thermochemical point of view, and it is concluded that the phenomenon cannot be photochemical.

S. B.

**Spectral Emissive Power and Melting Point of Tungsten.** A. G. WORTHING (*Z. Physik*, 1924, **22**, 9—17).—The emissive power of tungsten, as determined by the reflection method, is 0.465 and 0.453 for 6650 Å. at 300° and 1330° abs., respectively, and 0.507 and 0.493 for 4670 Å. at the same temperatures. From these data, the melting point of tungsten can be calculated by Wien and Planck's law. Previous determinations of this constant are tabulated, and the most probable mean is given as 3645° or 3665° abs. (according to the value assumed for the constant  $c_2$  in the Wien-Planck formula), with an experimental error of 20°.

S. B.

**Angular Momentum and Electron Impact.** P. M. S. BLACKETT (*Proc. Camb. Phil. Soc.*, 1924, **22**, 56—66).—A theory of the detailed mechanism of ionisation or excitation by electronic impact. Assuming that the total energy of the system consisting of one atom and one impacting electron is the same after as before the collision, and that there is an exact conservation of both energy

and linear angular momentum, an upper limit is arrived at for the probability of excitation by electronic impact, for energies just greater than the excitation energy. The probabilities so predicted are in rough agreement with some results of Franck and Knipping (A., 1921, ii, 150) and of Franck and Einsporn (*Z. Physik*, 1920, 2, 18).  
A. E. M.

**Critical Potentials of Hydrogen in the Presence of Nickel Catalyst.** A. W. GAUGER (*J. Amer. Chem. Soc.*, 1924, 46, 674—680).—The ionisation and resonance potentials of the nickel-hydrogen complex are measured by methods previously described (Franck, *Z. Physik*, 1920, 2, 18; Olson, A., 1923, ii, 455). A specially prepared nickel plate with surface-adsorbed hydrogen is bombarded with electrons, the radiation generated falls on a platinum plate, and a photoelectric current is produced which is studied as a function of the accelerating potentials, applied to the electrons producing the radiation.

The graphs obtained by plotting the electrometer deflection against the accelerating potential reveal seven critical potentials (at voltages of 10.4, 12.0, 13.6, 16.4, 18.2, 20.5, and 22.6). The first four of these are attributed to atomic hydrogen, the fifth to dissociation of the nickel-hydrogen complex together with ionisation of one hydrogen atom, and the last two to the presence of molecular hydrogen. It is considered that the hydrogen is activated (atomic), at least momentarily, and is concentrated in this condition at or near the surface of the metal.  
S. K. T.

**Normal Potential Gradient in the Discharge through Gases.** A. GÜNTHER-SCHULZE (*Z. Physik*, 1924, 22, 70—97).—The potential gradient in the uniform part of the discharge, away from electrode disturbances, is characteristic of the gas in the path of the discharge. Its value for a gas at 1 mm. pressure at 27° in volts per cm. is called the "normal gradient" for the gas. To obtain satisfactory measurements of this constant, large plane parallel electrodes must be used, in a vessel so large that the walls have no influence, and the temperature of the gas and the cathode must be controlled.

Measurements were made for the rare gases, oxygen, nitrogen, hydrogen, and water-vapour, and for various gas mixtures. The normal gradient was smallest in neon (0.493 volt/cm.) and largest for water (50 volts/cm.). From humps in the gradient-composition curves, it is suggested that oxygen forms temporary associations with argon and helium, in the path of the discharge. The mobility of the electrons at atmospheric pressure in helium, neon, and argon, is calculated to be 1880, 1330, and 590 cm.<sup>2</sup>/volt-sec., respectively. The degree of dissociation of the gases in the discharge is of the order of 10<sup>-8</sup>.  
S. B.

**Mobilities of Electrons in Helium [Hydrogen, and Nitrogen].** L. B. LOEB (*Physical Rev.*, 1924, 23, 157—168; cf. Townsend, A., 1923, ii, 721).—For helium,  $K = [7.57 \times 10^8 / (1.56 + E_0.760/p)]^{\frac{1}{2}}$ , whence, for  $E_0 = 0$ ,  $K_0 = 22,000$ ; hence the mean free path seems to have the value given by the kinetic theory.



Corrected empirical equations (cf. *ibid.*, 1922, 19, 24; 20, 398) are, respectively, for nitrogen  $K = [3.637 \times 10^5 / (11.9 + E_0.760/p)]$  and for hydrogen  $K = 4.32 \times 10^5 / [55.2 + E_0(760/p)^{1/2}]$ . The quantity assumed to be the mobility is possibly an improperly averaged figure.

A. A. E.

**Motion of Electrons in Nitrogen.** H. B. WAHLIN (*Physical Rev.*, 1924, 23, 169—177).—For low fields, the mobility of electrons in nitrogen is 18,000 cm./sec., but the value decreases rapidly for higher fields. The results are in conditional agreement with Compton's equation. The mean free path of electrons in nitrogen at 760 mm. and in thermal equilibrium with the molecules is 0.000131 cm., or 2.7 times the value required by the kinetic theory.

A. A. E.

**Ionisation of Salt Vapours.** V. KONDRATÉEV and N. SEMENOV (*Z. Physik*, 1924, 22, 1—8).—Thermionic electrons, with a definite velocity, were caused to collide with a stream of the salt molecules. The minimum ionisation potential for mercuric chloride and iodide is about 11 volts. The only negative ions detected were singly charged halogen atoms, but it is stated that in  $\text{HgI}_2$  vapour,  $\text{HgI}^+$ ,  $\text{Hg}^+$ , and possibly  $\text{I}^+$  and  $\text{Hg}^{++}$  are produced.

S. B.

**Ionisation of Cæsium Vapour and the Mobility of Electrons in the Bunsen Flame.** B. T. BARNES (*Physical Rev.*, 1924, 23, 178—188).—In experiments to test Saha's theory of the ionisation of metallic vapours at high temperatures (A., 1920, ii, 659), a dilute solution of a cæsium salt was sprayed into an air-gas flame, the conductivity being determined as a function of the concentration of the solution. The concentration of vapour in the flame was computed, and the black body temperature measured. A computation of Saha's equilibrium constant,  $K$ , and comparison with that given by Saha's equation, supported that author's theory. Selected values for the mobility of electrons in the flame are 75 and 82 m./sec. for 1 v./cm.

A. A. E.

**Electrical Properties of Flames containing Salt Vapours for High Frequency Alternating Currents.** A. B. BRYAN (*Physical Rev.*, 1924, 23, 189—194).—A study of the dielectric properties of salted flames.

A. A. E.

**Conductivity of [Salted] Flames for Rapidly Alternating Currents.** H. A. WILSON and A. B. BRYAN (*Physical Rev.*, 1924, 23, 195—199).

**Electron Emission from Metals as a Function of Temperature.** O. W. RICHARDSON (*Physical Rev.*, 1924, 23, 153—155).—Polemical, and mainly concerning priority.

A. A. E.

**Electron Emission from Metals.** S. DUSHMAN (*Physical Rev.*, 1924, 23, 156).—A reply to the above. The value of Richardson's constant  $A$  in  $i = AT^2 e^{-b/T}$  is valid only for pure crystalline substances, being less in the case of certain covered filaments.

This is in agreement with G. N. Lewis' interpretation of the third law of thermodynamics. A. A. E.

**Emission of Positive Ions by Heated Salts.** O. GOSSMANN (*Z. Physik*, 1924, **22**, 273—274).—In continuation of the work of Schmidt and Walter (this vol., ii, 13), the author finds that manganese chloride, antimony chloride, sodium fluoride, sodium nitrite, potassium iodide, potassium chloride, and cobalt chloride do not emit ions at temperatures below  $450^{\circ}$ . Within the same range of temperatures, the iodide, bromide, chloride, and nitrate of cadmium, the iodide, bromide, and chloride of zinc, the chloride and fluoride of aluminium, ferric chloride, calcium fluoride, the iodide, bromide, and nitrate of ammonium, sodium nitrate and potassium nitrate emit positive ions only. The conductivity of the respective vapours attains a maximum value after a short time and then decreases, rapidly at first and then slowly, attaining finally an approximately constant value. The form of the time-conductivity curve is the same whether the salts are heated by a platinum or a nickel wire, but ionic emission occurs at a temperature about  $30^{\circ}$  lower with the former. Addition of iodine or bromine to the halide salts increases the emission, whilst an excess of cadmium or zinc reduces the emission. The curve showing the relation of the applied *E.M.F.* to the current in the vapour has the customary form, and positive ions appear to be first emitted when the applied *E.M.F.* attains a constant value, independent of the salt employed, of about 1.3 volts. J. S. G. T.

**Light Sensitivity of Cuprous Oxide and Selenium.** V. P. BARTON (*Physical Rev.*, 1924, **23**, 337—344).—The change of electrical resistance produced by light was measured for cuprous oxide for the range 3900 to 6000 Å., a maximum decrease being observed at 4600 Å., and for selenium between 4300 and 9300 Å., the maximum decrease being at 7000 Å. The change in potential of the substance produced by light when cuprous oxide or selenium formed one of the plates in an electrolytic cell (photoelectrolytic effect), measured over the ranges, respectively, of 2700—5500 Å. and 2700—9000 Å., is, for cuprous oxide, at a maximum at 3500 Å. (upper limit about 5600 Å.) and for selenium at a maximum at 5700 Å. (upper limit about 9500 Å.). The effect is positive, and proportional in the former case to the intensity, *I*, and in the latter to  $I^{\frac{1}{2}}$ . The photoelectric wave-length limit is 2570 Å. for cuprous oxide and 2260 Å. for selenium. A. A. E.

**Determination of Dielectric Constants of Gases by High Frequency Method.** E. C. FRITTS (*Physical Rev.*, 1924, **23**, 345—356).—By the application of Hyslop and Carman's method (*ibid.*, 1920, **15**, 243) of heterodyne beats for the measurement of small capacities, the following values, reduced to 1 atm. at  $0^{\circ}$ , and accurate to about 1% of the difference from vacuum, were obtained for the dielectric constants: hydrogen, 1.000263; oxygen, 1.000507; nitrogen, 1.000555; air, 1.000540; carbon dioxide, 1.000948. A. A. E.

**Electrical Resistance and Thermo-electric Power of the Alkali Metals.** C. C. BIDWELL (*Physical Rev.*, 1924, **23**, 357—376).—Determinations of the electrical resistance and thermoelectric power of the alkali metals between  $-183^{\circ}$  and  $250^{\circ}$  indicate transformations in each case from an  $\alpha$ - to a  $\beta$ -form, occurring at approximately the following temperatures: lithium,  $50^{\circ}$ ; sodium,  $-20^{\circ}$  to  $+20^{\circ}$ ; potassium,  $-120^{\circ}$ ; rubidium,  $-35^{\circ}$ ; caesium,  $-80^{\circ}$ . In all cases, a sharp rise in thermoelectric power and resistance occurs near the m. p. Extrapolated values for the temperature coefficient of resistance at  $0^{\circ}$  are: lithium, 0.01404; sodium, 0.00758; potassium, 0.00604; rubidium, 0.00470; caesium, 0.00311; the values thus decrease smoothly with increasing atomic weight. The atomic heat of electrons in the alkali metals is computed to be approximately 0.24 cal. for sodium or potassium, and 0.58 cal. for rubidium or caesium.

A. A. E.

**Electrical Conductivity of Magnetite.** E. WILSON and E. F. HERROUN (*Proc. Roy. Soc.*, 1924, **A**, 105, 334—345).—The effects of impressed voltage, temperature, compressive stress, and magnetisation on the electrical conductivity of some varieties of magnetite have been examined. In general, the resistance was found to vary with the impressed voltage, the resistance decreasing as the potential difference was increased. The effect of heating the specimens and subsequently cooling them to the ordinary temperature, was to diminish both the resistance and the temperature coefficient, whilst the application of magnetic force or compressive stress also caused a decrease in resistance. A specimen with high magnetic retentivity behaved exceptionally, its resistance being scarcely affected by variation in the applied potential difference or by alternating changes of temperature; furthermore, the application of a magnetic field made relatively little difference in the resistance, although this was diminished by compressive stress as in the case of the other specimens.

W. H.-R.

**Effect of Changes in Total Carbon and in the Condition of Carbides on the Magnetic Properties of Steel.** A. W. SMITH, E. D. CAMPBELL, and W. L. FINK (*Physical Rev.*, 1924, **23**, 377—385).—Normal magnetisation curves were obtained by the magnetic potentiometer method, using the bar and yoke apparatus, the carbon content of the steel being controlled by heating at  $950^{\circ}$  in dry hydrogen, with or without the presence of steel of a different content of carbide. The minimum reluctivity (reciprocal of the maximum permeability) is a linear function of the carbon content, to 0.8% for hardened steels, whereas for annealed carbon steels its rate of increase is somewhat greater. For annealed chromium steels, the value is maximal at about 0.5% and minimal at about 0.8%. [Cf. *B.*, 1924, 425.]

A. A. E.

**Magnetic Susceptibility of Oxygen, Hydrogen, and Helium.** A. P. WILLS and L. G. HECTOR (*Physical Rev.*, 1924, **23**, 209—220).—Values for  $\kappa_0$  at 1 atm. and  $20^{\circ}$  were obtained as follows: oxygen,  $+0.1447 \times 10^{-6}$ ; hydrogen,  $-1.64 \times 10^{-10}$ ; helium,  $-0.807 \times 10^{-10}$ .

A. A. E.

**Magnetic Researches. XXVI. Measurements of Magnetic Permeabilities of Chromium Chloride and Gadolinium Sulphate at the Boiling Point of Liquid Hydrogen in Alternating Fields of Frequency 369,000 per Second.** G. BREIT and H. K. ONNES (*Proc. K. Akad. Wetensch.*, 1923, **26**, 840—849).—It has been suggested that at very low temperatures paramagnetic substances may show phenomena of hysteresis. To test this point, the authors have measured the magnetic susceptibility of anhydrous chromic chloride and gadolinium sulphate at the boiling point of liquid hydrogen and have compared the results with those obtained by the use of a direct field. The order of magnitude of the susceptibility is unchanged when the frequency of alternation of the field is increased to  $3.69 \times 10^5$ . The values obtained for chromic chloride and gadolinium sulphate in alternating fields are 0.75 and 0.51, respectively, of the values for a direct field. The authors consider that the observed differences may be due to causes other than the change in the character of the applied field. J. F. S.

**Characteristics of Iron in High Frequency Rotating Magnetic Fields.** L. TONKS (*Physical Rev.*, 1924, **23**, 221—238).

**Electrostatic Nature of the Molecular Field.** P. WEISS (*Compt. rend.*, 1924, **178**, 739—742).—Assuming an electrostatic moment to be superposed on the magnetic moment of an atom, the electrostatic moment of the combination is calculated to be  $0.85 \times 10^{-18}$  for the atom of nickel and  $1.25 \times 10^{-14}$  for the atom of cobalt. In the case of  $\beta$ -iron, an ambiguity arises, the moment being  $1.09 \times 10^{-18}$  or  $1.90 \times 10^{-18}$ , according as each atom or every third atom has a moment. For magnetite, the moment is  $1.74 \times 10^{-18}$ . Debye's calculation of this moment by a different method gave values between  $0.34 \times 10^{-18}$  and  $1.18 \times 10^{-18}$  for many liquids (water, lower aliphatic alcohols, acetone, etc.). The close agreement between the last figures and those for ferromagnetic substances supports the theory of an electrostatic origin for the molecular field. E. E. T.

**Magnetisation of Nickel-Chromium Alloys above the Curie-point.** J. ŠAFRÁNEK.—(See ii, 342.)

**Isotope Effects in the Band Spectra of Boron Monoxide and Silicon Nitride.** R. S. MULLIKEN (*Nature*, 1924, **113**, 423—424; cf. this vol., ii, 3).—The spectrum of boron nitride observed by Jevons (*A.*, 1915, ii, 33) consists of two superposed spectra of  $B^{10}O$  and  $B^{11}O$ , respectively, the bands being of the same pattern, but the scale being larger for the lighter isotope. The possibility that the bands may be due to boron nitride is not, however, entirely excluded.

Jevons' observations (*A.*, 1913, ii, 813) on the bands of silicon nitride were also examined in order to detect possible isotopy. Complete agreement exists between the experimental and theoretical values for the ratio of the vibration frequencies of  $Si^{29}N$  and  $Si^{30}N$  with respect to  $Si^{28}N$ ;  $Si^{29}$  appears to be a little more abundant

than  $\text{Si}^{30}$ , and there is no evidence of isotopes other than  $\text{Si}^{28}$  in appreciable amounts.

A. A. E.

**Spectroscopic Evidence of Isotopic Elements.** H. NAGAOKA and Y. SUGIURA (*Nature*, 1924, **113**, 532—534).—If, as has been assumed, there may be formation of pairs between atoms, especially in the ionised state, leading to the emission of non-series spectral lines, a method of calculating the difference of wave-length due to isotopes is available. Application to known isotopes gives satisfactory results; preliminary calculations also indicate that calcium contains a small quantity of  $\text{Ca}^{44}$ , sodium a trace of  $\text{Na}^{21}$ , whilst barium consists of  $\text{Ba}^{135}$ ,  $\text{Ba}^{137}$ ,  $\text{Ba}^{138}$ , and  $\text{Ba}^{139}$ , principally the last three.

A. A. E.

**Isotopes of Mercury and Bismuth revealed in the Satellites of their Spectral Lines.** H. NAGAOKA, Y. SUGIURA, and T. MISHIMA (*Nature*, 1924, **113**, 459—460).—Accurate measurements have been made of the position of the satellites of mercury and bismuth lines. The remarkable resemblance of non-series lines in gold and mercury indicates that the nuclei may have something in common—possibly a hydrogen-proton is slightly detached from the central nucleus, and quasi-elastically connected with it, so that when excited by electro-magnetic waves they may make coupled vibrations. The difference in wave-lengths of such nuclear vibrations arising from different isotopes is calculated, and the correspondence with the observed results is sufficient to show that the satellites in mercury and bismuth lines are due to the different isotopes.

A. A. E.

**Isotope Effect as a Means of Identifying Emitters of Band Spectra: Metal Hydrides.** R. S. MULLIKEN (*Nature*, 1924, **113**, 489—490; cf. this vol., ii, 3).—The considerations (a) that the spacing of bands in a band system should be less for the heavier isotope in approximately the ratio  $\rho$  of the respective molecular vibration frequencies, and (b) that the spacing of the lines in a given band should be less in approximately the ratio  $\rho^2$  for the heavier isotope, are applied to observations made by Frerichs (this vol., ii, 77) on copper, and by Kratzer (*Ann. Physik*, 1923, **71**, 102) on zinc, cadmium, and mercury. Satisfactory interpretation requires the supposition that the bands are of hydride origin; similar bands of silver, gold, and aluminium are probably due to hydrides, whilst magnesium and calcium hydrides are known emitters of band spectra.

A. A. E.

**Detection of Thorium Emanation (Thoron) in Thermal Springs by the Method of Induced Activity.** A. LEPAPE (*Compt. rend.*, 1924, **178**, 931—934).—A number of springs in the Pyrenees and in the Central Plateau of France have been examined to ascertain their content of radium and thorium emanations. The former occurs in various proportions in all the waters, but thorium emanation is found in traces only in those of the Central Plateau. Even in those cases in which thorium emanation is not detectable, it is probable that the water comes into contact with this emanation,

but that the time elapsing between the termination of this contact and the appearance of the water at the outlet of the spring exceeds 10 minutes, which is the duration of the life of thorium emanation.

T. H. P.

**Radium Emanation in Air from the Schneeberg Mines.**

P. LUDEWIG and E. LORENZER (*Z. Physik*, 1924, **22**, 178—185).—The appreciable amount of emanation present in the air in various mines in the Schneeberg-Oberschlema district has been measured. It is the probable cause of a local lung disease.

S. B.

**Particles of Long Range from Polonium.** L. F. BATES and J. S. ROGERS (*Proc. Roy. Soc.*, 1924, **A**, **105**, 360—369).—Three different sources of polonium have been examined by the scintillation method for the emission of long-range particles, and it has been found that for every  $10^7$   $\alpha$ -rays of range 3.93 cm. emitted, there are also present 98, 51, and 26 particles of ranges  $6.1 \pm 0.1$ ,  $10.0 \pm 0.1$ , and  $13.1 \pm 0.2$  cm., respectively, together with about 7 particles of longer range which are probably long-range hydrogen particles. From the brightness of the scintillations it is concluded that these particles are  $\alpha$ -rays, and, from a consideration of the materials used, it is shown that the rays must be emitted by a product of radium-*D*, i.e., either by polonium or by a substance chemically similar to it. As the relative number of long-range particles agreed closely in all three specimens, it is concluded that these particles are emitted by polonium itself, as no  $\beta$ -ray evidence of branch products has been noted, and no evidence of long-lived products similar to polonium has been obtained.

W. H. R.

**Bombardment of Elements by  $\alpha$ -Particles.** E. RUTHERFORD and J. CHADWICK (*Nature*, 1924, **113**, 457).—On the assumption that the particles of disintegration are emitted in all directions relative to the incident  $\alpha$ -rays, a simple method has been devised whereby the disintegration of an element can be observed with certainty when the ejected particles have a range of only 7 cm. in air; the presence of hydrogen in the bombarded material has then no effect, nor do the long-range particles found by Bates and Rogers interfere. In addition to the elements boron, nitrogen, fluorine, sodium, aluminium, and phosphorus, which give hydrogen particles of maximum range in the forward direction between 40 and 90 cm., the following give particles of range above 7 cm.: neon, magnesium, silicon, sulphur, chlorine, argon, and potassium; preliminary experiments with beryllium indicated a small effect. Hydrogen, helium, lithium, carbon, and oxygen give no detectable effect beyond 7 cm. The sulphur nucleus is clearly not built up solely of helium nuclei. Preliminary experiments, with indefinite results, have been carried out with the elements from calcium to iron; no effects were observed with nickel, copper, zinc, selenium, krypton, molybdenum, palladium, silver, tin, xenon, gold, and uranium.

A. A. E.

**Explanation of the Theory of the Rotation of the Atomic Nucleus.** V. H. HENSTOCK (*Chem. News*, 1924, **128**, 84—87; cf. A., 1923, ii, 400, 477, 679, 845).—With the aid of diagrams,

the author's view of the constitution of ozone, sulphur dioxide and trioxide, and phosphorus oxychloride is depicted. Considerations of polarity lead to the following generalisations: (i) When two or more atoms unite, the bonds uniting them are of opposite polarities in each atom. (ii) Normal stable compounds are formed only where each atom is united to its neighbours by single bonds, which are all positive or all negative throughout each atom. (iii) Normal stable compounds are formed only where atoms are united by double or triple bonds, having positive and negative bonds corresponding in each atom, which may be in conjunction with single bonds normal to each atom. (iv) Neutral atoms, like carbon, may unite normally by either positive or negative bonds, but the tendency will be for these compounds to be the more stable where bonds are all of one polarity in each atom. A. A. E.

**Physical Constants of Stereoisomeric Compounds.** K. VON AUWERS and B. OTTENS.—(See i, 513.)

**Structure of Oxygen.** H. COLLINS (*Chem. News*, 1924, **128**, 230—232).—From considerations of the relative volume and heat of formation of organic compounds containing oxygen, an attempt is made to show that the atom of oxygen has the constitution  $\text{Li}-\text{H}-\text{H}_3-\text{H}-\text{H}_3-\text{H}$ . The presence of two "free" helium portions causes it to be a non-metallic element, and since the mass of the metallic portion is not greater than that of the rest, there are left only two electro-negative valencies emanating from the two metallic portions. Neutral oxygen is formed from acidic oxygen by the complete absorption of the two helium portions by the metallic part and alcoholic oxygen by the withdrawal of only the  $\text{H}_3$  portions. A. R. P.

**Structure of Neon and Argon.** H. COLLINS (*Chem. News*, 1924, **128**, 81—83).—Numerical considerations are held to indicate that neon and argon atoms are both constructed of lithium and hydrogen atoms in a manner described. A. A. E.

**Periodic Law of Atomic Radii.** W. P. DAVEY (*Physical Rev.*, 1924, **23**, 318—321).—"The ratio of the radii of any two simple atoms belonging to the same vertical column in the periodic table is the same as the ratio of the radii of any other two simple atoms on the same horizontal lines of the table, provided that these atoms also belong to a common vertical column." The periodic relationship is conveniently expressed in the form of a curve obtained by plotting the atomic radii as a function of the number of electrons in the outer shell. Atomic radii are predicted (to  $\pm 2\%$ ) as follows: phosphorus, 1.08; sulphur, 1.03; scandium, 1.73; rubidium, 2.49; strontium, 2.16; yttrium, 1.91; niobium, 1.45; caesium, 2.85; barium, 2.48; lanthanum, 2.19. A. A. E.

**New Theory relative to Molecular Constitution of Chemical Compounds.** C. BULOW (*Compt. rend.*, 1924, **178**, 770—771).—The author states that in 1919 he put forward views similar to those of Armstrong and of Kling and Lassieur (*A.*, 1923, ii, 542, 543; cf. Auger, this vol., ii, 146). E. E. T.

**Atomic Structure and the Relationship of the Chemical Elements.** F. P. WORLEY (*Rept. Austral. Assoc. Adv. Sci.*, 1923, **16**, 212—219).—An electronic theory of valency. The four valency electrons in the carbon atom are supposed to revolve in planes parallel to the faces of a tetrahedron, two revolving in a clockwise and two in an anti-clockwise direction. The valency bonds are largely magnetic. The external structure of other elements is arrived at by modifying the different faces of the carbon atom. Nitrogen, oxygen, fluorine, neon, and other atoms are discussed. M. S. B.

**Calculation of Electrostatic Potential and Energy for Di- and Quadri-polar Lattices.** H. KORNFELD (*Z. Physik*, 1924, **22**, 27—43).—General formulæ are deduced for the electrostatic potential and energy of di- and quadri-polar space lattices and the energy of two special cubic lattices. S. B.

**Surface Energy of Crystals and Crystal form.** M. YAMADA (*Physikal. Z.*, 1924, **25**, 52—56).—A continuation of a previous paper (*ibid.*, 1923, **24**, 364), in which the surface energy is calculated from the work necessary to overcome the electrostatic forces across the cleavage planes. Surfaces inclined to the crystal axes are dealt with in this paper. A. E. M.

**Space Lattice of White Tin.** H. MARK and M. PÓLÁNYI (*Z. Physik*, 1924, **22**, 200).—Corrections to the diagrams and letterpress of a previous paper (*A.*, 1923, ii, 768). S. B.

**[Crystal] Lattice of Aluminium Nitride.** H. OTT (*Z. Physik*, 1924, **22**, 201—214).—Examination of crystals of aluminium nitride by the Laue method of X-ray analysis indicates that the crystals belong to the hexagonal system. Investigation by the rotating crystal and powder methods shows that the aluminium and nitrogen atoms are separately distributed in close, spherically packed hexagonal lattices slightly compressed in the direction of the six-fold axis of symmetry and displaced in the same direction by an amount determined by the parameter  $p = 0.38$ . The basal axis  $a$  is of length  $3.11_3$  Å., and the value of the axial ratio,  $c$ , is  $1.60_1$ . The basal group comprises two molecules, and each atom of either kind is surrounded tetrahedrally by four atoms of the other kind arranged at a uniform distance of  $1.89_4$  Å. The respective intensities of the lines in the X-ray spectra afforded no evidence of a possible polar structure of the crystals. J. S. G. T.

**Intensity of the X-Rays scattered from Rock Salt.** G. E. M. JAUNCEY and H. L. MAY (*Physical Rev.*, 1924, **23**, 128—136).—X-Rays from a molybdenum target were allowed to pass through a thin crystal slab of rock salt. The curve obtained by plotting the scattering angle against the intensity has two maxima, at  $15^\circ$  and  $30^\circ$ , respectively. Two maxima are also exhibited by the curve showing the relation between the spectra of scattered radiations and the electrometer deflection; the scattered rays are much harder than the primary rays. The experimental values correspond fairly well with Compton and Jauncey's quantum theory of scattering.



The mass scattering coefficient for rock salt, for the primary rays used ( $0.4\text{--}0.7\text{ \AA.}$ ), is  $0.23 \pm 0.02$ , as compared with Thomson's value of  $0.193$ . A. A. E.

**Refraction of X-Rays in Pyrites.** B. DAVIS and R. VON NORDOFF (*Proc. Nat. Acad. Sci.*, 1924, **10**, 60—63).—The bending of the molybdenum  $K_\alpha$ - and  $K_\beta$ -rays by refraction has been measured for pyrites. The effect has been greatly increased by grinding and polishing the crystal so that the surface makes an angle with the natural cleavage planes. The mean value of the bending of the rays,  $\delta$ , is  $3.33 \times 10^{-6}$  for the  $K_\alpha$  line and  $2.82 \times 10^{-6}$  for the  $K_\beta$  line, which are in good agreement with those calculated from the dispersion formula of Lorentz ("Theory of Electrons," 1909, 159). It is impossible to determine, however, whether the resonance effects required by the Lorentz theory are present or not. A. E. M.

**Liquid Crystals, Soap Solutions, and X-Rays.** J. W. MCBAIN (*Nature*, 1924, **113**, 534).—Terminological. A. A. E.

**The Scattering of X-Rays and Bragg's Law.** G. E. M. JAUNCEY (*Proc. Nat. Acad. Sci.*, 1924, **10**, 57—59).—A theoretical paper in which it is concluded that the experimental deviations from Bragg's law cannot be explained by a change of wave-length on reflection, but that the theory of Darwin (*Phil. Mag.*, 1914, **27**, 318) requiring that a crystal should have a refractive index for X-rays provides the only available explanation of these deviations. A. E. M.

**Excitation, Reflection, and Utilisation in Crystal-structure Analyses of Characteristic Secondary X-Rays.** G. L. CLARK (*J. Amer. Chem. Soc.*, 1924, **46**, 372—384; cf. A., 1923, ii, 468, 469, 856).—A continuation of previous work. The characteristic secondary X-rays of iodine from the 100 planes of potassium iodide and the 0001 planes of iodoform have been measured through several orders. Uranium nitrate hexahydrate is found to reflect secondary  $L$ -series uranium rays. The wave-lengths of these secondary spectra are identical with those of characteristic lines in the spectra of target elements but the relative intensities of the lines vary considerably from the characteristic primary rays. The reflection is only partly in accordance with the Bragg law  $n\lambda = 2d \sin \theta$ .

The secondary spectrum furnishes an easy way of obtaining accurately the distances between successive planes of atoms. In the case of iodine in KI,  $d = 3.52 \times 10^{-8}$  cm. and in iodoform,  $3.737 \times 10^{-8}$  cm.

The excitation and reflection of the characteristic secondary X-rays is considered not to be due to resonance, but to the transfer of radiation momenta in quanta (cf. Mie, *Z. Physik*, 1923, **15**, 56). By using finely divided crystalline materials as scattering radiators, no change in the wave-length of the scattered rays was observed (cf. Compton, A., 1923, ii, 280). On the other hand, with highly polished thin sheets of metals, e.g., copper or silver, tertiary X-radiations due to photo-electrons from both the  $K$ - and  $L$ -rings were noticed. These tertiary rays may account for the phenomena

observed by Compton and Ross. They have a frequency which is the difference between that of a primary ray and of the critical absorption frequency characteristic of the element of the secondary radiator. H. T.

**Abnormal Reflection of X-Rays by Crystals.** G. L. CLARK and W. DUANE (*Science*, 1923, **58**, 400—402).—In view of the experiments of Wyckoff (A., 1923, ii, 743), who failed to obtain any indication, with potassium iodide, of "abnormal X-peak reflection," the authors have reinvestigated the phenomenon. Using both the ionisation spectrometer and the photographic method, they have confirmed their previous conclusions. The success is ascribed to the use of a constant voltage of 75,000 volts instead of an alternating voltage of 50,000 volts, to the employment of a thicker crystal, and to the use of a single pin-hole, instead of the ordinary arrangement of two, to define the beam of X-rays incident on the crystal. A. A. E.

**Standard Melting Points at High Temperatures.** H. S. ROBERTS (*Physical Rev.*, 1924, **23**, 386—395).—After recrystallisation, the following m. p. were determined with calibrated thermocouples: potassium dichromate,  $397.5^\circ$ ;  $45 \text{ KCl} + 55 \text{ Na}_2\text{SO}_4$  by weight,  $517.1^\circ$ ;  $30.5 \text{ NaCl} + 69.5 \text{ Na}_2\text{SO}_4$  by weight,  $627.0^\circ$ ; potassium chloride,  $770.3^\circ$ ; sodium chloride,  $800.4^\circ$ ; sodium sulphate,  $884.7^\circ$ ; potassium sulphate,  $1069.1^\circ$  (all  $\pm 0.5^\circ$ ); calcium borate,  $\text{Ca}_2\text{B}_2\text{O}_5$ ,  $1304^\circ \pm 5^\circ$ . The transformation point of potassium sulphate is  $583^\circ \pm 1^\circ$ . A. A. E.

**Heat of Vaporisation, a Function of Temperature.** M. M. GREEN (*J. Amer. Chem. Soc.*, 1924, **46**, 544—545).—Assuming that  $L_e$ , the latent heat of vaporisation, is a function of temperature only and has the same form for all non-associated liquids, then Trouton's rule leads to Guldberg's relation (A., 1890, 1043), according to which the ratio of the boiling point to the critical temperature is constant. Within the limits given by the boiling point and critical temperatures the dependence of  $L_e$  on  $T$  is therefore probably the same for all non-associated liquids. S. K. T.

**Volume in the Liquid and Gaseous States.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, **132**, 36—40).—The values of  $\psi = (n^2 - 1)/(n^2 + 2)$  have been calculated for thirty-one substances in the liquid and gaseous states at their respective boiling points. There are no obvious relations between the values of  $\psi_e$  (liquid) and  $\psi_g$  (gas) for the substances examined. H. T.

**Pressure-Volume-Temperature Relations for Gaseous Ethyl Ether.** J. A. BEATTIE (*J. Amer. Chem. Soc.*, 1924, **46**, 342—357).—The isometrics for ethyl ether over the temperature range  $175^\circ$  to  $325^\circ$  and from specific volumes of 2.5 to 35 c.c. per gram have been accurately measured. There are practically straight lines from the largest specific volumes down to 15 c.c. per gram; at greater densities marked curvature becomes apparent, presumably due to association or dissociation of the molecular species.

The equations of Keyes (*Proc. Nat. Acad. Sci.*, 1917, **3**, 323) hold

with great accuracy at lower pressures but do not give satisfactory results in the regions of greater density. H. T.

**Equilibrium in the Liquid-Saturated Vapour System, Heat of Vaporisation, Law of Rectilinear Diameter, and Molecular Attraction.** V. KARPEN (*Bull. Acad. Sci. Roumaine*, 1923, 8, 175—180).—The slow vaporisation of a liquid is considered as the diffusion of liquid molecules at pressure  $p$ , through a thin diffusion layer at the surface of the liquid into the vapour at pressure  $p_2$ . By assuming that the molecular heat of vaporisation  $L$  is proportional to  $\Delta d$ , the difference in the densities  $d_1$  and  $d_2$  of the liquid and vapour phases, and adopting  $p(v-b)=RT$  as the equation of state, the expression  $L=RT_c \cdot \Delta d/d_c(1-bd_c)^2$  is deduced, the suffix  $c$  referring to the critical state. This equation is simplified to  $Ld_c=5T_c \cdot \Delta d$ , or  $\Delta d/L=\text{const.}$ , by taking  $2.7d_c=b^{-1}$ . Values of  $L$  calculated from this formula agree with the observed values within about 2%, but greater divergences are shown by methyl and propyl alcohols. The value of  $\Delta d/L$  for water increases with temperature.

Assuming  $2d_c=b^{-1}$ , the law of rectilinear diameter is deduced in the form  $\frac{1}{2}(d_1+d_2)=d_c+[T_c-T]/T_c]$  for the region of the critical point. Observed results for 22 substances out of 28 (e.g., argon, ether, benzene, chlorobenzene, ethyl acetate) conform to the formula fairly well, but hydrogen shows a large deviation.

When  $d_2$  is negligible in comparison with  $d_1$  and the latter can be considered constant,  $d_2=e^{[a-(b/T)]}$ ,  $a$  and  $b$  being constants, a formula which has been verified experimentally for water (30—150°) to within  $\pm 7\%$ . (Cf. Chapman and Appleby, T., 1914, 105, 734.) S. K. T.

**Solution and Molecular Attraction.** V. KARPEN (*Bull. Acad. Sci. Roumaine*, 1923, 8, 180—185).—Considerations similar to those outlined in the preceding abstract have been applied to solutions of gases in non-volatile solvents. Assuming Boyle's law to hold in the layer separating the gaseous and liquid phases, Henry's law is derived in the form  $p_2=p_1 e^{-L/RT}$  (1), ( $L$ =molar heat of solution of gas;  $p_1, p_2$ =pressures of free and dissolved gas, respectively). If  $L$  is independent of  $T$ , then  $T \cdot \log(p_1/p_2)=\text{const.}$ ; this is shown to hold approximately for ammonia, but not for sulphur dioxide.

The theory is applied to solutions of solids in liquids, and the limiting heats of solution are calculated from equation (1),  $p_1$  and  $p_2$  referring to the osmotic pressures of the dissolved substance. For lead chloride (25—100°)  $L=3360$  cal. and for potassium chloride (20—100°)  $L=920$  cal.

The expression  $p_1/p_2=e^{\Delta L/RT}$  is obtained for the partition coefficient ( $p_1, p_2$ =osmotic pressures of the solute in the two solvents;  $\Delta L$ =difference in molar heats of solution of the solute in the solvents). Boyle's law is assumed for each solution as a first approximation. The relation shows that  $T \cdot \log p_1/p_2$  should be constant if the composition of the phases is independent of the temperature. This has not been verified experimentally, although  $p_1/p_2$  is constant at constant temperature. S. K. T.

**Constitution of Solids.** V. KARPEN (*Bull. Acad. Sci. Roumaine*, 1923, **8**, 190—197).—Solids are regarded as heterogeneous mixtures of a solid and a liquid phase, the latter occupying pores disseminated throughout the former. An equilibrium, similar to that between a liquid and its vapour (cf. preceding abstracts), is set up between the molecules of the solid, crystalline phase, and those of the liquid phase. It is shown that many well-known phenomena can be satisfactorily interpreted in terms of the author's hypothesis, *e.g.*, increase of ductility with temperature, supra-conductivity, etc. It permits of the calculation of latent heats of fusion, the value obtained for ice being 85.7 as compared with the experimental value of 80. This is regarded as in favour of the theory. S. K. T.

**Physical Properties of Glass.** F. ECKERT (*Jahrb. Radio-activ. Electronik*, 1923, **20**, 93—275).—A comprehensive survey of the results obtained in the whole field of research on the physical properties of glass. Generally speaking, the subject is treated with reference to the effect of the constituent oxides, and where the properties are approximately additive in character (specific heat, thermal expansion, density, etc.) the factors for the individual oxides obtained by various workers are quoted. Deviations from the additive relationship are considered in the light of constitutive effects. In conclusion, a short summary is given of the prevailing theories as to the nature of glass; of interest in this connexion are the data obtained for glasses over the softening range. [Cf. *B.*, 1924, 335.] A. COUSEN.

**Solutions Considered as Binary Mixtures of Liquids.** G. G. LONGINESCU and I. N. LONGINESCU (*Bul. Soc. Româna Stiin.*, 1923, **26**, 3—18).—Solutions of gases, liquids, and solids may all be considered as binary mixtures of liquids, a dissolved gas being regarded as liquefied by the pressure to which it is subjected in the solution, whilst a dissolved solid undergoes fusion. The most soluble gases dissolve in water with evolution of heat, which is regarded as due to the latent heat liberated on liquefaction, and it is stated that no gas is soluble above its critical temperature, or below the critical solution temperature for the liquefied gas and the liquid solvent. If such solutions are thus considered as binary mixtures of liquids, it is shown that the density of a solution may be expressed by  $(cd + c'd')/100$ , where  $c$  and  $c'$  are the percentage concentrations,  $d$  and  $d'$  the densities of the two liquids. A more accurate expression can be obtained if it is assumed that the density of the dissolved substance varies with the concentration, so that the term  $d$  may be replaced by a term  $d_0(1 + K_1c + K_2c^2)$ , where  $d_0$ ,  $K_1$ , and  $K_2$  may be determined empirically from the densities of three solutions. It is shown that this equation affords accurate values for the densities of aqueous solutions of ammonia, hydrofluoric, hydrochloric, hydrobromic, and hydriodic acids, sulphur dioxide, glycerol, sugar, sodium sulphate, and copper sulphate; it is also applicable to mixtures of alcohol and ether. Tables show-

ing the densities of the above solutions, and the values of  $d_0$ ,  $K_1$ , and  $K_2$  are given for fifty-two substances. The equation may be employed to calculate the densities of substances in the free condition from the densities of their solutions. W. H.-R.

**Internal Friction of Liquid Systems.** W. HERZ and E. MARTIN (*Z. anorg. Chem.*, 1924, **132**, 41—53).—The relative merits of the formulæ  $\phi = a + bT$  (Meyer and Rosencranz, *Z. physikal. Chem.*, 1909, **66**, 238),  $\phi = a + bv$  (Batchinsky, A., 1913, ii, 928) and  $\phi = m - n \log (T_c - T)$  (van Aubel, A., 1921, ii, 575) for the representation of the internal friction of liquid systems have been compared by reference to the data for a large number of organic liquids. This comparison shows that the formulæ of Batchinsky and van Aubel correspond more exactly with experiment, the latter giving slightly better agreement than the former. In addition, the authors have investigated the influence of temperature on the viscosity of (1) a number of aqueous salt solutions, (2) water-alcohol mixtures and aqueous-alcoholic solutions of potassium iodide, and (3) pyridine and pyridine solutions. The applicability of the above formulæ to these observations has been examined. H. T.

**Aqueous Solubilities in Homologous Series.** H. FÜHNER (*Ber.*, 1924, **57**, [B], 510—515).—As a result of the examination of the solubilities in water of normal aliphatic hydrocarbons, alkyl halides, alcohols, esters, etc., the general rule is put forward that in homologous series of organic compounds the molecular solubility in water diminishes as we ascend the series, so that each member is three to four times less soluble than the previous member. Figures are given for the approximate solubilities of a number of aliphatic derivatives in water. F. A. M.

**Solubility of Picric Acid in Mixtures of Liquids.** E. ANGELESCU and D. DUMITRESCU (*Bul. Soc. Româna Stiin.*, 1923, **26**, 71—82).—The empirical formulæ put forward by Bodländer (*Z. physikal. Chem.*, **7**, 308), and by Hertz and Knoch (*Z. anorg. Chem.*, **46**, 193) are only applicable to a very limited range of concentration. The authors have determined the solubility of picric acid in mixtures of alcohol and carbon tetrachloride, alcohol and chloroform, and of alcohol and benzene at 12°. The results obtained are shown to be in agreement with the empirical equation  $S_c - S_0 = Kc^p$ , where, if one liquid is considered as the solvent,  $S_0$  is the quantity of picric acid which dissolves in 100 g. of the pure solvent,  $S_c$  is the quantity which dissolves in 100 g. of the solvent plus  $c$  g. of the second liquid, *i.e.*, in (100 +  $c$ ) grams of the mixture, and  $K$  and  $p$  are constants. The range of validity of the equation depends on the nature of the components of the mixed solvent; it extends from pure carbon tetrachloride, chloroform, and benzene to mixtures of these containing, respectively, 40, 60, and 73 g. of alcohol in 100 g. of mixed liquid. The equation has been applied to results obtained by other workers, and is found to be more satisfactory than other empirical equations. W. H.-R.

**Graphical Solution of certain Ratios in Temperature-Concentration Diagrams.** C. O. SWANSON (*Amer. J. Sci.*, 1924, [v], 7, 233—238).—The author gives a geometrical proof of the rules for determining, from the freezing-point diagrams of binary and ternary systems characterised by a single eutectic mixture, the relative proportions of the solid and liquid phases. In addition, for ternary systems, the ratio of the two constituents in the separated solid, when the systems considered are cooled from a higher to a lower temperature, is derived geometrically. Gibbs' method of representing the ternary system is employed, and it is assumed that no complications resulting from the formation of compounds or solid solutions are involved. M. S. B.

**Calibration of Cells for Conductance Measurements. III. Absolute Measurements of the Specific Conductance of certain Potassium Chloride Solutions.** H. C. PARKER and (MISS) E. W. PARKER (*J. Amer. Chem. Soc.*, 1924, 46, 312—335).—The values obtained for solutions containing 1, 0.1, and 0.01 equivalent per c.dm. at 0° are 0.065098, 0.0071295, and 0.00077284 ohm<sup>-1</sup> cm.<sup>-1</sup> respectively.

The conductivities for temperatures up to 30° have been calculated and compared with the older values of Kohlrausch and Maltby (A., 1900, ii, 61; 1901, ii, 82) and Kohlrausch, Holborn, and Diesselhorst (A., 1898, ii, 366). The former are 0.145% and the latter about 0.15% too high.

It is considered that the sum of all the errors in the new measurements does not exceed 0.02%. H. T.

**Dilution Law for Uni-univalent Salts.** B. SZYSZKOWSKI (*J. Physical Chem.*, 1924, 28, 193—211).—The author seeks to show that, by adopting Ghosh's hypothesis (A., 1922, ii, 125), it is possible to establish a theory of electrolytic dissociation which is in accordance with experimental data. The theory is developed from a thermodynamic point of view.

In deducing the expression for the intrinsic energy of the solution, Ghosh takes into account only the attractive forces between oppositely charged ions, because he looks on the ions as points, or as volumes carrying uniform positive or negative charges. Such a view is permissible at high dilutions, but not when the ions are more closely packed, for, regarding the ion as a central positive nucleus surrounded by negative electrons, it is evident that the relative strengths of the repulsive and attractive forces coming into play between two ions will vary as the distance between the ions varies. The authors' formula takes into consideration both these forces and is found to be applicable to the conductivity data of Kohlrausch and his collaborators for uni-univalent electrolytes over a wide range of concentrations. Salts undergoing hydrolysis exhibit deviations at high dilutions.

According to the author's theory, the decrease of equivalent conductivity with increase of concentration is exclusively due to the decrease of the ionic mobility.

The theory of complete ionisation applies only to salts and not to

acids, which must be assumed to be only partly ionised, even when strong. This behaviour is attributed to the peculiar constitution of the hydrogen ions, which have no exterior ring of negative electrons to exercise a repulsive force on the anion and so prevent combination.

M. S. B.

### Electrolytic Dissociation of some Salts in Furfuraldehyde.

F. H. GETMAN (*J. Physical Chem.*, 1924, **28**, 212—220).—Experiments have been carried out to test the Nernst-Thomson rule in the case of furfuraldehyde. The electrolytes employed were the iodides of lithium, sodium, potassium, and rubidium, and also ammonium and tetraethyl ammonium iodides. By plotting the equivalent conductivity against the cube root of the concentration, the curves obtained for the alkali iodides are approximately parallel; the equivalent conductivity falls off far less rapidly with increase of concentration than is the case for the ammonium and substituted ammonium iodides. Walden's relationship (A., 1921, ii, 423), connecting the viscosity and the dielectric constant of the solvent, is found to be inapplicable to furfuraldehyde solutions. The fact that the electrical conductivities of the four alkali salts are in the inverse order of the molecular weights suggests that there is ionic solvation. The solvation of the cations has been calculated by Walden's method (A., 1920, ii, 230) on the assumption that the iodide ion is not solvated. The values are of the same order as those calculated for the same ions in aqueous solution (Washburn and Millard, A., 1915, ii, 311).

The variation with dilution of the equivalent conductivity of the alkali iodides in furfuraldehyde is accurately expressed by Storch's equation (A., 1896, ii, 288).

M. S. B.

### Second Dissociation Constant of Sulphuric Acid. I. M.

KOLTHOFF (*Rec. trav. chim.*, 1924, **43**, 207—215).—Previously recorded values of the second dissociation constant of sulphuric acid,  $K_2$ , show little agreement. The hydrogen-ion concentration in a mixture of alkali sulphate and alkali hydrogen sulphate is given by  $[H'] = K_2[HSO_4']/[SO_4'']$ . Its value has been determined colorimetrically by comparison with buffer solutions. The  $SO_4''$ -ion concentration was obtained from conductivity measurements. The  $HSO_4'$ -ion concentration was determined on the assumption that the dissociation of sodium hydrogen sulphate is equal to that of uni-univalent salts. The average value obtained for  $K_2$  is  $3.0 \times 10^{-2}$  (with methyl-orange,  $2.8 \times 10^{-2}$ ; with tropæolin OO,  $3.2 \times 10^{-2}$ ).

It is shown that methyl-red gives the most accurate results when strong acids are titrated in presence of sulphates.

S. K. T.

### Strength of the Acid Function of the Oxygen Acids of Sulphur. I. M. KOLTHOFF (*Rec. trav. chim.*, 1924, **23**, 216—

220).—Jellinek has stated (A., 1911, ii, 362) that the second dissociation constant,  $K_2$ , of thiosulphuric acid,  $H_2S_2O_3$ , is approximately the same as that of sulphuric acid. This view is criticised and a redetermination of  $K_2$  has been made on the lines already

described (cf. preceding abstract). Decomposition of the thio-sulphate had no perceptible influence on the measurement, the mean value obtained being  $K_2 = 5.7 \times 10^{-2}$  at  $\pm 15^\circ$ . This result leads to the conclusion that sulphur has a stronger negative action than oxygen on the acid molecule. Similar measurements have been made with tetrathionic acid. The results, which are not quoted, indicate that this acid is one of the strongest dibasic acids. An experiment is described which shows qualitatively that the introduction of sulphur into the hydrogen sulphide molecule increases the acidity.

S. K. T.

**Activity Coefficients of Ions in Very Dilute Solutions.**

J. N. BRÖNSTED and V. K. LAMER (*J. Amer. Chem. Soc.*, 1924, **46**, 555—573).—The expressions given previously (A., 1922, ii, 482) for the osmotic and activity coefficients have been extended to include salts of higher valence types. The ratio of the logarithms of two activity coefficients is very nearly equal to the square of the ratio of the corresponding valences; this is only exact in the ideal region. The equations have been confirmed experimentally by measuring the change in solubility of four sparingly soluble cobalt-ammines on the addition of electrolytes of various valence types. In general, the deviations do not exceed the probable experimental error.

S. K. T.

**Activity of Water in Hydrochloric Acid.** H. J. E. DOBSON and I. MASSON (*J. Chem. Soc.*, 1924, **125**, 668—676).—The partial vapour pressures of water vapour and hydrogen chloride in equilibrium with solutions of hydrochloric acid from  $3N$  to  $10.5N$  at  $25^\circ$  have been determined by a modification of the method used by Bates and Kirschman (A., 1920, ii, 88). No great accuracy is claimed for the partial pressures of the hydrogen chloride, as the experimental conditions were designed primarily for the measurement of the aqueous vapour. The results are compared with those calculated from *E.M.F.* data by means of the Duhem equation, and good agreement is obtained.

L. J. H.

**Vapour Pressure of Hydrochloric Acid.** J. S. DUNN and E. K. RIDEAL (*J. Chem. Soc.*, 1924, **125**, 676—684; compare preceding abstract and A., 1920, ii, 88).—The partial vapour pressures of hydrogen chloride over its aqueous solutions from  $0.3$  to  $5.3M$  at  $25^\circ$  have been measured by a distillation method. The concentrations of the distillates were measured by conductivity and the ratio of the vapour pressures calculated on the assumption that both constituents obey the gas laws in the vapour state. The values of  $p_{H_2O}$  were obtained from the data of Linhart (A., 1918, ii, 28). From these measurements the activity of hydrogen chloride in its aqueous solutions was calculated and compared with the values deduced from *E.M.F.* measurements. Agreement is obtained up to  $2M$ , above which considerable divergence is found. The results are considered antagonistic to the theory of the total dissociation of strong electrolytes.

L. J. H.



**Reactions at the Interface of Two Immiscible Liquids and the Part Played by the Vapour of Each. Reaction between Water and Benzyl Chloride.** G. HARKER (*J. Chem. Soc.*, 1924, 125, 500—511).—An attempt was made to compare the hydrolytic action of steam and liquid water on benzyl chloride in the hope of comparing the reactivity of hydrol (simple  $H_2O$  molecules) in the pure state (as steam) with that in complex liquid water. It was found, however, that, under the conditions of the experiments, steam impinging on the surface of the oil produced no hydrolysis. On the other hand, the mixed vapour of benzyl chloride and steam impinging on the surface of water, with due precautions against condensation, was found to result in an amount of hydrolysis comparable with that obtained at the two liquid surfaces, probably indeed identical with it after making certain corrections. The conclusion is drawn that, at the interface of the two liquids, the mixed, saturated vapours are present.  
L. J. H.

**Relation between the Diffusion of a Gas Mixture and its Pressure.** R. WUSSOW (*Brennstoff-Chem.*, 1924, 5, 65—67).—The author utilises experimental results recorded by Fischer, Schrader, and Jäger (A., 1923, ii, 742) to test his formula giving the connexion between the partial pressures of the components in mixtures of gases before and after diffusion. The experimental data are in fairly close agreement with the calculated numbers.

T. S. W.

**Determination of Coefficients of Diffusion in Gels by means of Chemical Analyses, and a Comparison of Results Obtained with those Yielded by the Indicator Method.** C. E. T. MANN (*Proc. Roy. Soc.*, 1924, A, 105, 270—281).—The coefficients of diffusion of sodium, potassium, lithium, ammonium, magnesium, calcium, and barium chlorides in 2% agar-agar gel have been determined at 20° and 30°. The chlorides were allowed to diffuse from normal aqueous solution into a cylinder of the gel contained in a glass tube, successive layers of the gel being analysed after the experiment. The coefficients of diffusion calculated from these data are generally lower than those obtained by the indicator method. This difference is attributed to the fact that free ions diffuse more rapidly than undissociated molecules, and, consequently, the coefficient calculated from the indicator method, which measures the rate of penetration of ions, is greater than the coefficient calculated on the basis of chemical analysis, in which the total quantity of salt, dissociated and undissociated, is considered. A relationship, apparently linear, has been found to exist between the coefficient of diffusion and the degree of dissociation of the solute, the coefficient of diffusion being greater as the dissociation is increased. Consequently, the coefficient of diffusion of electrolyte tends to increase with the dilution.

W. H.-R.

**Rhythmic Formation of Layers. Liesegang's Phenomenon.** P. D. ZACHARIAS (*Koll.-Z.*, 1924, 34, 37—40).—The author reviews the various explanations which have been put forward to

explain the Liesegang phenomenon. As the result of observations on a natural water containing sulphur, the author advances the view that the formation of Liesegang rings is to be attributed to the diffusion of particles of different sizes, which have almost the same density as the dispersive medium. Although the formation of rings is affected by a number of factors, the jelly structure appears to be of predominant importance. J. F. S.

**Adsorption and Distribution between Two Immiscible Solvents.** E. ANGELESCU and D. DUMITRESCU (*Bul. Soc. Romăna Stiin.*, 1923, **26**, 27—38).—Equilibrium is rapidly attained when a substance is adsorbed from solution, and the solute may be regarded as distributed between two solutions, the one existing only at the surface of the adsorbing solid, and the other comprising the main bulk of the solution, the concentrations of the two solutions being connected by the equation  $C_1 = \alpha C_2^{1/n}$ . Experiments show that a similar relation holds for the distribution of iodine between an aqueous solution of potassium iodide and organic solvents, although in dilute solutions the partition of the iodine is in agreement with the simple law of distribution. If a given solution of iodine in potassium iodide is in equilibrium with solutions of iodine in carbon tetrachloride, chloroform, and carbon disulphide of concentration  $C_1$ ,  $C_2$ , and  $C_3$ , respectively, it is found that  $C_1$ ,  $C_2$ , and  $C_3$  are in the same ratio as the solubilities of iodine in the three organic solvents concerned. Consequently, it is possible to express the distribution of iodine between a solution of potassium iodide and the three organic solvents by one and the same equation  $C_{K1} = AC^{1/n}$  provided that the concentrations in the organic solvents are expressed as fractions of the corresponding solubilities. The experiments of Herz and Fischer (*Ber.*, 1903, **38**, 1138) indicate that the same equation applies to the distribution of acetic acid between water and aromatic hydrocarbons. W. H.-R.

**Adsorption of Binary Mixtures by Animal Charcoal and a Comparative Study of the Adsorptive Power of Different Varieties of Charcoal.** N. A. YAJNIK and T. C. RANA (*J. Physical Chem.*, 1924, **28**, 267—278).—The adsorption of the following electrolytes by purified charcoal has been studied: the chlorides of sodium, potassium, lithium, magnesium, strontium, and calcium, potassium and sodium hydroxides, sodium carbonate, and hydrochloric, nitric, and oxalic acids. Changes of temperature produce very little change in the adsorption, but increase of dilution causes increase of the relative adsorption. Experiments with pairs of the above electrolytes in solutions of varying concentrations show that there are three possibilities in the adsorption of binary mixtures: (a) the two substances may be quite independent of one another, indicating that adsorption depends very little on ionisation; (b) the adsorption may be reduced by the presence of another substance, this, no doubt, being the action in the poisoning of a catalyst; (c) the adsorption may be increased, that of the other substance, at the same time, either increasing or decreasing. No general rules can be

given by which the effect of one substance on another may be predicted.

The adsorptive powers of three varieties of wood charcoal (talia, acacia, and mulberry) have been compared with that of animal charcoal. For most substances mulberry charcoal appears to be the best of the three, and for a few substances the values for adsorption by animal charcoal are approached, and may even be exceeded, by all three.

M. S. B.

**Adsorption by Precipitates. VI.** H. B. WEISER (*J. Physical Chem.*, 1924, 28, 232—244; cf. A., 1922, ii, 262).—Experiments have been made to compare, for different types of sols, the precipitating values of mixtures of two electrolytes, of similar and also of widely varying precipitating power, with the precipitating values of the separate electrolytes. In addition, the adsorption of the different ions from mixtures of electrolytes has been studied.

In the presence of a smaller quantity of potassium chloride than is required for complete precipitation of the positive hydrated chromic oxide sol, the amount of added potassium sulphate or oxalate necessary for complete coagulation is less than the calculated amount by about 20%. Similar results were obtained with negative hydrated stannic oxide sol when precipitated by mixtures of lithium chloride with barium or magnesium chloride. They are not in agreement with the conclusion of Freundlich and Scholz (A., 1922, ii, 828) that the hydration of a colloid and of the precipitating ions results in ionic antagonism to such an extent that the behaviour of a colloid with mixtures of electrolytes may be used to determine whether it is hydrated or not.

The precipitating values of mixtures of potassium sulphate and oxalate, which have similar precipitating power, are practically additive.

In the case of the negative arsenic sulphide sol, which is regarded as not being hydrated, very marked antagonistic action may be observed where the two electrolytes differ widely in coagulating powers, e.g., lithium and barium chlorides, lithium and magnesium chlorides, and hydrochloric acid and magnesium chloride. As found for other colloids, however, the effect is almost additive when the precipitating powers are similar, e.g., barium and magnesium chlorides.

These phenomena are explained by the influence of each precipitating ion on the adsorption of the other by the sol. A strongly adsorbed ion will naturally affect the extent to which another ion in the same solution is adsorbed, and hence the coagulating power of the latter. The reduction below the additive values where no antagonistic action is observed is accounted for by the well-known fact that adsorption is proportionately greater at lower concentrations of the adsorbed ion.

The influence of the stabilising action of the anion in the precipitation of negative colloids, or of the cation in the precipitation of positive ones, is discussed.

Contrary to the conclusions of Tartar and Gailey (A., 1922, ii,

829), it has been shown that magnesium chloride may have the same precipitation value for widely different hydrogen-ion concentrations.

M. S. B.

**Amorphous Precipitates and Crystalline Sols.** J. BÖHM and H. NICLASSEN (*Z. anorg. Chem.*, 1924, **132**, 1—9).—Further experimental investigation has verified the conclusions reached by Haber (A., 1922, ii, 553) with regard to the conditions under which crystalline or amorphous precipitates or sols are obtained. In the case of substances with a low velocity of orientation, *e.g.*, the hydroxides of zirconium, thorium, and cerium, the sols as well as the precipitated forms are amorphous, but with the exception of precipitated  $\text{Zr}(\text{OH})_4$  these become crystalline under the more favourable conditions existing at higher temperatures.

The cold precipitated hydroxides of aluminium, scandium, beryllium, lanthanum, and neodymium are completely amorphous, but the sols produced under more favourable conditions, *i.e.*, at low concentrations, are crystalline. Strongly bipolar substances such as the halides of silver, the fluorides of the alkaline-earths, etc., are crystalline in both the precipitated and the sol forms. H. T.

**Osmotic Pressure of some Electrolytes of High Molecular Weight.** E. JORPES and E. G. HELLGREN (*Biochem. Z.*, 1924, **145**, 57—62).—The osmotic pressures of the ammonium, sodium, trimethylammonium, triethylammonium, and tripropylammonium salts of Congo red increase with increasing molecular volumes. This is explained by assuming that the large negative ion adsorbs on its surface the small positive ions and that this process becomes less complete with increase in the size of the latter, *e.g.*, in the homologous series of aliphatic amine salts investigated. J. P.

**Viscosity and Refractive Researches on the Coagulation of Lyophilic Colloids.** N. SCHOORL (*Rec. trav. chim.*, 1924, **43**, 203—206).—The viscosities of a 5% solution of air-dried egg-albumin mixed with  $2\frac{1}{2}\%$  hydrochloric acid were measured at  $15^\circ$  in an Ostwald viscosimeter at progressively increasing time intervals after mixing. The refractivities were also measured. The object was to determine whether variations in the colloidal state of blood-serum could be followed by refractivity changes, the colloid used in these experiments being similar to blood-serum, although the changes are slower. The decrease in refractivity during coagulation runs parallel with increase in viscosity. Both properties in their variation with time afford evidence of an autocatalytic process, and it is probable that either property may be used to detect variations in the colloidal state of blood-serum, the refractivity being convenient when only small quantities are available. S. K. T.

**Hydrophilic and Hydrophobic Colloids and the Influence of Electrolytes on Membrane Potentials and Cataphoretic Potentials.** J. LOEB (*J. Gen. Physiol.*, 1924, **6**, 307—328).—The depressing effect of neutral salts on the cataphoretic P.D. of hydrophobic colloids (mastic, Acheson's graphite, or collodion particles) which have been stabilised by the presence of  $N/256$ -sodium chloride

and also of denatured egg-albumin in  $N/5000$ -sodium hydroxide solution, depends on the valency and molar concentration of the cation, and not on its nature. This does not hold for heavy metals, e.g., silver nitrate has a greater depressing effect on the cataphoretic P.D. than sodium nitrate. The influence of dilute acids on the cataphoretic P.D. of gelatin-coated collodion particles depends only on the  $p_H$  and the valency of the acid used. These experiments agree with the view that the cataphoretic potential difference of protein particles is determined, largely at least, by the existence of a Donnan equilibrium between the medium and the surface layer of the particle, and, except where chemical changes are possible, as in the case of heavy metals, they accord with Wilson's suggestion ("The Chemistry of Leather Manufacture," 1923, 128) that in the case of hydrophobic colloids, the effect may be due first of all to the attraction of the particle for the anion causing stabilisation, followed by the operation of the Donnan equilibrium between the surface layer containing excess of anion and the bulk of the medium.

W. O. K.

**Process of Filtration.** K. SCHAUM, A. MOELLER, and T. MARX (*Koll.-Z.*, 1924, **34**, 1—12).—The time required for a liquid to flow through a filter plate is approximately proportional to the thickness of the plate. In order to obtain satisfactory support for the filter, it is best to use a thin plate with large pores covered by a fine-pored overlayer instead of a thick plate with fine pores. The arrangement of filter layers of different pore size, one after the other, is not efficient, since the time required for filtration by such a system is considerably greater than the sum of the times for the individual layers. The quantity of liquid flowing through a filter in unit time is proportional to the pressure above the liquid. For liquids of high viscosity, the total time of filtration may be reduced by dilution of the solution. Apart from the fact that the thickness of the cake of filtered material increases, it is found that the impermeability of a cake of given thickness increases with the time occupied by the filtration. The retardation may be partly prevented by stirring during filtration, or by removing the upper portion of the cake by means of a scraper. Filtration after sedimentation, when the latter takes place rapidly, is recommended as an efficient method.

J. F. S.

**General Colloid Chemistry. VIII. Analysis and Constitution of Colloidal Gold.** II. M. ADOLF and W. PAULI (*Koll.-Z.*, 1924, **34**, 29—34; cf. A., 1923, ii, 636).—A carefully dialysed gold sol contains particles the mean size of which corresponds with the cube edge =  $27\mu\mu$ . Using Scherrer's X-ray data, this gives approximately 1,444,000 atoms to each colloidal gold particle, and since there are 25 gold atoms to each charge, there must be 57,000 negative charges on the surface of the cube. The number of gold atoms in the surface of the average cubic particle is therefore somewhat greater than 76,000.

J. F. S.

**Colloid Chemistry of Night Blue.** F. V. V. HAHN (*Koll.-Z.*, 1924, **34**, 162—169).—The solubility of night blue in a number of

solvents is found to be connected with the dielectric constant of the solvent. When this constant is less than 5, the dye dissolves to a small extent only, and gives green solutions; in solvents with a higher dielectric constant, it is readily soluble and the solutions are blue. The solubility in mixed liquids is determined in a similar manner by the dielectric constant. Yet it is found that toluene, in which the dye is only sparingly soluble, will completely extract it from an aqueous solution. The residues obtained by evaporating solutions in different solvents show differences in solubility which indicate that the structure of the colloid has been modified by the solvent. Ultra-microscopical examination affords evidence of molecular dispersion in the green solutions, whilst the blue solutions contain colloidal aggregates which vary in size in different solvents, and are largest in an aqueous solution. Night blue precipitated from aqueous solution by sodium hydroxide dissolves in toluene in the same way as the pure dye, and does not appear to be a sodium salt. The surface tensions of toluene and of water are slightly raised by the addition of night blue, and the interfacial tension between these liquids is doubled when the dye is added. S. S.

**Colloid Chemistry of Cellulose.** H. WISLICENUS and W. GIERISCH (*Koll.-Z.*, 1924, **34**, 169—181).—Purified cellulose (filter-paper) disintegrated by long-continued milling in the dry state in a closed porcelain ball mill and in a Dreef's steel plate mill, was found on microscopical examination to have lost all traces of fibrous structure and to have the form of minute irregular particles which, especially when moistened, tend to collect into spherical aggregates. The disintegrated cellulose is more soluble in water than the original fibre, adsorbs methylene-blue more readily, and is more rapidly hydrolysed by sulphuric acid. Its reaction with iodine is much the same as that of the starting material, but the copper number of the heavily milled product is much higher, suggesting that some chemical change has taken place. S. S.

**Influence of Electrolytes on the Swelling of Agar.** S. DOKAN (*Koll.-Z.*, 1924, **34**, 155—161).—In dilute solutions, cations (hydrogen excepted) influence the swelling of agar according to the valency rule. In stronger solutions specific effects appear, and in normal solutions of the chlorides the influence of the cation increases in the order  $\text{Li} < \text{Mg} < \text{Ca} < \text{Na} < \text{Al} < \text{Ba} < \text{K} < \text{H}$ . Anions in dilute solutions do not affect the swelling of agar but in stronger solutions exhibit specific effects. The order of action of the anions in normal solutions is  $\text{I} < \text{CNS} < \text{NO}_3 < \text{OH} < \text{Br} < \text{Cl} < \text{OAc} < \text{SO}_4 < \text{citrate}$ . The influence of an electrolyte on the swelling of agar is regarded as the resultant of two effects: (a) the lowering of the charge on the colloid by the cation, and (b) the specific dehydrating effect of the ions, which becomes effective at higher concentrations. S. S.

**Electrical Resistance of Soap-Water Systems at the Setting-point.** M. H. FISCHER (*Koll.-Z.*, 1924, **34**, 140—145).—Previous observations (A., 1923, ii, 725, 823) suggested a sharp increase in electrical resistance at the temperature at which an emulsion of

soap in water changes into an emulsion of water in soap. Experiments on  $N/2$  solutions of sodium and potassium soaps confirm this conclusion. The temperatures at which the sudden increase in resistance takes place are for the sodium soaps: stearate,  $60^{\circ}$ ; palmitate,  $52^{\circ}$ ; myristate,  $34.5^{\circ}$ ; laurate,  $16.5^{\circ}$ ; oleate,  $7^{\circ}$ , and for the potassium soaps: stearate,  $44^{\circ}$ ; palmitate,  $23.5^{\circ}$ . The curves for potassium myristate, laurate, and oleate indicate that the inversion points lie below  $0^{\circ}$ . The solutions were allowed to cool without shaking, since mechanical treatment would destroy the outer phase of hydrated soap and produce an emulsion of less hydrated soap in an aqueous outer phase. S. S.

**Physical Properties of Mixtures of Alcohol and Serum.** R. FÜRTH and O. BLÜH (*Koll.-Z.*, 1924, **34**, 129—135).—With increasing additions of ethyl alcohol, the dielectric constant, optical activity, and electrical conductivity of bovine serum at first increase, attain maxima at 2, 3, and 7 parts of alcohol per 1000 by volume, respectively, and thereafter decrease continuously. Conversely, the viscosity curve exhibits a minimum at 2 volumes of alcohol per 1000, whilst the surface tensions of alcohol-serum mixtures lie on a curve parallel to that for water and alcohol mixtures. The refractive index of the serum is at first unaltered by small additions of alcohol, but increases linearly after 2 volumes per 1000 have been added. The results are discussed in terms of Drude's dipole theory. S. S.

**Electro-osmotic Experiments on the Reversal of the Electric Charge of Colloids and Precipitates and the Preparation of Stable Sols with a Charge Opposite in Sign to that Commonly Obtained.** J. N. MUKHERJEE and B. C. ROY (*J. Chem. Soc.*, 1924, **125**, 476—488).—Two types of adsorption by colloids are distinguished: (a) primary adsorption of ions due to chemical affinity, and (b) electrical adsorption of oppositely charged ions. It is supposed that the original charge of the surface is due to primarily adsorbed ions fixed on the surface as point charges, and that oppositely charged ions can be held by electrical attraction just opposite these. Consequently, a reversal of the charge of the surface is only possible by electrical adsorption when the valency of the oppositely charged ion is greater than that of those primarily adsorbed, but if the oppositely charged ion is affected by chemical affinity of the surface atoms, a reversal of charge is possible independent of the valency. It follows that the alkali-metal cations can never reverse the charge of colloidal surfaces, for these ions are univalent and their chemical behaviour is summed up in their tendency to exist as ions. Similarly, the alkaline-earth metal ions are not likely to reverse the charge, although they may do so by electrical adsorption if the primarily adsorbed ions are univalent. These views are confirmed by cataphoretic and electro-endosmotic experiments dealing with the effects produced by the nitrates and chlorides of different metals, and the hydrochlorides of organic bases, on various sols. L. J. H.

**Effect of Hydrophilic Colloids on Size and Distribution of Particles in Electrolytic Precipitation. I. Gelatin and Basic Lead Carbonate.** W. G. FRANCE and D. MCBURNEY (*J. Amer. Chem. Soc.*, 1924, **46**, 540—544).—The average size of basic lead carbonate particles electrolytically precipitated at 20° is reduced to approximately one-third by the presence of 0.013% of gelatin. The decrease after the first addition is not so large, being approximately proportional to the concentration of the gelatin added. The particles are of more uniform size when gelatin is present. Samples of dry commercial white lead contain particles which are larger and less uniform than those in the electrolytic product obtained in presence of gelatin. S. K. T.

**Gelatinisation of Nitrocellulose Solutions.** A. SZEGVARI (*Koll.-Z.*, 1924, **34**, 34—37).—Solutions of nitrocellulose when diluted with amyl acetate and benzine gelatinise on elevation of the temperature, but on lowering the temperature again they re-liquefy. The temperature of gelatinisation depends on the composition of the liquid medium. This phenomenon is attributed to solvation, and to variations in the relative affinity of the nitrocellulose for the solvent and the diluent with change of temperature. J. F. S.

**Electro-viscous Effect in Solutions of Soluble Starch.** H. G. B. DE JONG (*Rec. trav. chim.*, 1924, **43**, 189—202).—Specially prepared water sols of soluble starch ( $d_{20}^{20}$  1.0039) obey Poiseuille's law. The addition of small quantities of barium chloride causes a rapid decrease in the rate of flow of the sol in the viscosimeter (cf. A., 1923, ii, 132); this is attributed to the disappearance of the electro-viscous effect. At higher concentrations a more gradual change occurs which can be considered as a lyotropic influence on hydration. The lowering of the initial viscosity is independent of the anion, but increases with the valency of cation. These results are comparable with those obtained with agar sols (A., 1922, ii, 357), from which it is inferred that the starch sol possesses a negative charge, which is apparently below the critical value, since the sol is so readily coagulated by excess of alcohol or by small amounts of tannic acid. Addition of hexaethylenediamine-hexoltetracobaltic nitrate,  $[\text{Co}\{\text{(OH)}_2\text{Co en}_{2\frac{1}{3}}\}(\text{NO}_3)_6 \cdot 3\text{H}_2\text{O}]$ , causes reversal of the charge of the starch sol and at the isoelectric point hydration keeps the sol stable. With a partly dehydrated sol (addition of alcohol), neutral electrolytes cause complete precipitation, but the above complex salt behaves irregularly, a coagulation region (0.05—0.3 mg. equiv. per litre) being followed by a region of stability (0.3—2 mg.) and finally at higher concentrations by coagulation. It was confirmed by cataphoresis experiments that in the stable region the starch sol was partly hydrated and positively charged. The behaviour of the starch sol towards hydrochloric acid and sodium hydroxide confirmed the results of Samec (A., 1913, i, 17, 1155). The behaviour of the acid resembles that of neutral salts: that of sodium hydroxide points to starch sols being true colloidal solutions. It appears as if the hydration increases considerably with increasing



concentration of sodium hydroxide (or calcium hydroxide), the phenomenon resembling the lyotropic effect of neutral electrolytes. In explanation, it is supposed that the weakly acid starch sols are neutralised by sodium hydroxide, the mobile hydrogen ions being replaced by the comparatively slow sodium ions. In this process the charge remains constant and hence the electro-viscous effect increases. Further addition of sodium hydroxide brings into play other factors which tend to remove the quasi-viscous properties.

S. K. T.

**Ultramicroscopical Investigations with Unidirectional Illumination. The Ultramicroscopic Mie-effect.** A. SZEGVARI (*Z. Physik*, 1924, **21**, 348—357).—When a beam of light falls on a particle which is smaller in diameter than half a light-wave length, the light is scattered in all directions, but the intensity is greatest in the direction of the primary beam. The latter phenomenon becomes more pronounced with increasing size of the particle. The author calls this the "Mie-effect" (see Mie, *Ann. Physik*, 1908, [iv], **25**, 37).

It has been shown that, if unidirectional illumination is obtained in the ultramicroscope by means of the azimuth screen, which is a screen with a small aperture, allowing only a thin beam of light to fall on the colloidal solution to be examined (Szegvari, *Physikal. Z.*, 1923, **24**, 91), one portion of the circular image obtained displays, as a result of the Mie-effect, a more intense brightness than the rest. By rotating the screen, rotation of the luminous portion of the image is also obtained, but no change in intensity is observed if the particle is spherical. This may be applied to the study of immovable colloidal particles such as those of a precipitate. In a similar way, the appearance of scintillation phenomena when a colloidal solution showing Brownian movement is illuminated through an azimuth screen indicates that the particles are not spherical. Along with the azimuth screen, a screen with variable aperture for the objective should also be used. By this means, disturbing effects due to particles of larger size, or to excessive density of particles in suspension, may be eliminated.

In order to take full advantage of the Mie-effect, the direction of illumination should not be at right angles to the direction of observation, but should approach a coaxial position.

M. S. B.

**Contraction [of Volume] accompanying Formation of Compounds.** F. EPHRAIM (*Helv. Chim. Acta*, 1924, **7**, 298—307; cf. Ephraim and Michel, A., 1919, ii, 268).—For the chlorides, bromides, and iodides of manganese, iron (ferrous), nickel, copper, zinc, cadmium, and mercury, the percentage contraction is nearly independent of the halogen, although the iodides generally show a somewhat smaller contraction. Mercuric chloride is exceptional. The chlorides and bromides of univalent copper, silver, and thallium show a similar relationship, but the iodide is in each case different from the chloride and bromide, on account of its different crystalline structure. A similar regularity appears to hold for the halogen compounds of phosphorus, boron and antimony. The halide salts

of magnesium, calcium, strontium, barium, lead, and tin show no such regularities.

The hexammines derived from the halide salts of nickel, cobalt, iron, manganese, and zinc show practically the same contraction as the corresponding halide salts of the alkali metals. It is significant that all these compounds in which the influence of the halogen predominates belong to the regular system. When the contraction is calculated from the volumes of the salt and ammonia, the ammines of the zinc and manganese salts give values entirely different from the others. It follows that the lattice structure of the ammines must be entirely different from that of the free salts. Some of Biltz's conclusions regarding the formation and structure of compounds of salts with ammonia (this vol., ii, 167) are criticised. There is no contradiction between Kopp's rule as applied to homologous series of organic compounds and the author's percentage contraction rule, as Kopp's factors refer to already contracted radicals.

E. H. R.

#### Electromotive Forces of Cells and Molecular Attraction.

V. KARPEN (*Bull. Sci. Acad. Roumaine*, 1923, 8, 185—190).—By the introduction of the author's diffusion-layer theory (cf. this vol., ii, 301) the Nernst electrode-potential formula is modified to  $E = (\Delta l/n) - (RT/n) \log p_1/p_2$ ,  $\Delta l$  being the difference between the attractions of the metal ions in the metal and in the solution. No application of the second law of thermodynamics is made in the deduction of this equation, which gives comparable values for the solution pressures of metals. The application of the revised formula to the *E.M.F.* of cells of the type Pt/saturated amyl alcohol solution of caustic soda/saturated aqueous solution of caustic soda/Pt is discussed. A cell of this type with carbon electrodes has been found to yield a current uninterruptedly for 7 months with no apparent internal change.

S. K. T.

**Influence of Salts on the Constants of the Silver Bromide and Silver Electrode.** I. M. KOLTHOFF (*Z. anorg. Chem.*, 1924, 132, 117—124).—The value given in an earlier paper (A., 1922, ii, 20) for the normal potential of the silver electrode, referred to the normal hydrogen electrode at 18°, has been corrected to  ${}_0E_h = 0.801$  volt. The dependence of the potential referred to the null electrode on the concentration can be expressed by  $-\log[Ag^+] = p_{Ag} = (1.0780 - \pi)/0.05768$  at 18°, and in the case of the silver-silver bromide electrode  $-\log[Br'] = p_{Br} = (\pi - 0.3570)/0.05768$  at 18°. From these values it follows that the ionic solubility product for silver bromide  $= 3.4 \times 10^{-13}$ .

The influence of uni- and multi-valent cations on the potential of the silver electrode and of uni- and multi-valent anions on the potential of the silver-silver bromide electrode have been investigated. Ferro- and ferri-cyanides have a very marked effect, but the others examined exert no perceptible influence.

H. T.

**Oxidation Potentials at Mercury Electrodes. III. Ter- and Bi-valent Titanium.** G. S. FORBES and L. P. HALL (*J. Amer. Chem. Soc.*, 1924, 46, 385—390).—A mixture of titanium

di- and tri-chlorides obtained by heating finely divided titanium of 99.9% purity in a stream of dry hydrogen chloride, was introduced, in the absence of air, into a half cell with a mercury electrode, and the *E.M.F.* of this combined with a calomel electrode was determined. By subsequent analyses the ratio of di- and tri-valent titanium was determined. The average value of  ${}_0E_h$  for the reaction  $\text{Ti}^{+++} + \ominus \rightleftharpoons \text{Ti}^{++}$  is  $-0.369$  volt. This value is independent of the acid concentration, provided the latter does not exceed  $0.1N$ . At higher concentrations, the dihalide is rapidly decomposed. By combining the above value with that for the reaction  $\text{Ti}^{+++} + \ominus \rightleftharpoons \text{Ti}^{+++}$  (A., 1908, ii, 350) it follows that for the reaction  $\text{Ti}^{+++} + 2\ominus \rightleftharpoons \text{Ti}^{++}$   ${}_0E_h = -0.16 \pm 0.01$  volt. H. T.

**Polarisation of Electrodes. III.** J. E. VERSCHAFFELT (*Rec. trav. chim.*, 1924, **43**, 125–134; cf. A., 1923, ii, 115, 369).—A theoretical paper in which mathematical reasoning is adduced to show (1) that the concentrations of anions and cations in a solution may be considered as equivalent; (2) the variation of electrode-potential with current density; (3) the relationship between current density and electromotive force in an electrolyte which is dissociated into two ions, the liquid being separated into three portions, anodic, cathodic, and intermediate, the last being continually stirred, and (4) that the osmotic theory of the electromotive forces leads to the generalisation that the product of the ionic concentrations must be constant for saturated solutions. H. J. E.

**Overvoltage Phenomena. II. Connexion between the Overvoltage of Hydrogen as Pure Metal Surface and certain Properties of the Metals.** A. THIEL and W. HAMMERSCHMIDT (*Z. anorg. Chem.*, 1924, **132**, 15–35).—The overvoltage of hydrogen at the surfaces of a large number of pure metals has been determined by a method similar to that previously used (A., 1913, ii, 104). There appears to be a connexion between the overvoltage of hydrogen and the position of the metal in the periodic classification, metals of the first and eighth groups having low, and those of the second, third, and fourth high overvoltage values. Of the metals investigated, manganese and vanadium, both of which are difficult to obtain pure, are the only “misfits.” The so-called solubility theory for the explanation of overvoltage phenomena is rejected as untenable. Tafel’s theory (A., 1900, ii, 588), according to which the metal is supposed to accelerate or retard the spontaneous change  $2\text{H}^+ \rightarrow \text{H}_2$ , is considered the most satisfactory. An attempt is made to link up this theory with the results obtained by Sabatier, according to which the most active metals in the process of hydrogenation are those with a low overvoltage, and also with the work of R. W. Wood on the decomposition and re-formation of molecular hydrogen under the influence of an electric discharge. H. T.

**Life Period of Overvoltage Compounds.** E. NEWBERRY (*J. Chem. Soc.*, 1924, **125**, 511–518).—The velocity of decomposition of the overvoltage hydrides of certain metals (cf. A., 1917, ii, 64,

290) has been determined, using an intermittent current with variable commutator speeds. Those of zinc and chromium appear to be comparatively stable, those of graphite, silver, and platinum less so, whilst those of cadmium, copper, nickel, and lead are either very unstable, or variable in their composition or proportion on the electrode surface. The "direct" method of measuring overvoltage is criticised, and the use of alternating current ammeters with intermittent unidirectional currents shown to be inadmissible. In part polemical (cf. Glasstone, A., 1923, ii, 531). L. J. H.

**Depolarisation of the Chlorine Electrode by Organic Compounds.** M. A. YOUTZ (*J. Amer. Chem. Soc.*, 1924, **46**, 545—554).—The influence of organic compounds on anode decomposition potentials has been examined. With carbon anodes in potassium chloride solution, ethylene, maleic, oleic and 10% acetic acids show slight depolarising action. The current-anode potential curves do not rise smoothly as is the case when no depolariser is present. The phenomenon is reproducible with solutions of ferrous chloride, but does not occur with hydrochloric acid solutions of the organic compounds, and is often influenced by stirring. Phenol is oxidised to benzoquinone, and 70% acetic acid in 1.2*N*-hydrochloric acid gives chloroacetic acid, although ordinary chlorine under the same conditions gives no trace of this substance. With carbon anodes, toluene, *m*-xylene, mesitylene, amylene, or ether exerts no depolarising action; crotonic acid depolarises slightly and aniline very strongly. Strong solutions of acetone (50% and above) depolarise; weaker ones do not. This is shown to be due to the differences in the free energies of hydrochloric acid in water and acetone solutions. The potential of a chlorine electrode (platinum) with an overvoltage of 0.5 is not reduced by addition of acetone, acetic acid, chloroacetone, or chloroacetic acid. Neither method is suitable for deciding whether organic compounds can or cannot be chlorinated. S. K. T.

**Method for Studying the Rapid Absorption of Gases by Liquids.** P. G. LEDIG and E. R. WEAVER (*J. Amer. Chem. Soc.*, 1924, **46**, 650—657).—The rate of absorption in caustic soda solutions of small reproducible bubbles of carbon dioxide has been measured in a special apparatus. The absorption was measured by registering photographically on a rotating drum the movement of a mercury thread contained in a capillary tube connected with the absorption vessel, and by recording simultaneously the vibrations of a tuning fork. The absorption of a fresh bubble proceeds in three stages and the maximum rate is not attained immediately. The rate of absorption depends on the size of the bubble, and the viscosity of the solution is shown also to have a great effect. In presence of an inert gas (air), the rate varies inversely as the square root of the carbon dioxide pressure. Sodium carbonate solution (2.5*N*) absorbs carbon dioxide at less than half the rate for pure water and less rapidly than a sucrose solution of the same viscosity. Mass action may exert some effect here. S. K. T.

**Electrical Method of Determining the Velocity of Detonation of Explosives.** J. E. P. WAGSTAFF (*Proc. Roy. Soc.*, 1924, **A**, 105, 282—298).—For the measurement of the velocity of detonation of explosives, a method has been devised in which the length of the column of the explosive need not be greater than 15—60 cm. The method involves the measurement of time intervals of the order  $10^{-4}$  sec., and depends on the rate of discharge of a condenser during the short interval required for the detonation of a column of explosive. The method has been tested by finding the time of impact of steel balls, and the conditions necessary for high accuracy in the case of explosives have been investigated. The velocities of detonation of tetryl, trinitrotoluene, and other explosives have been determined, the results obtained agreeing closely with those found with much longer lengths of material in the Mettegang apparatus (Mettegang, Rep. of 5th Cong. Appl. Chem., vol. 2, 327, and Kast, "Spreng und Zundstoffe," 1025).  
W. H.-R.

**Explosion Limits and Ignition Temperatures of Combustible Liquids.** H. STRACHE (*Oesterr. Chem.-Ztg.*, 1924, **27**, 19—24).—The paper contains vapour-pressure curves of several combustible organic compounds and a table showing their upper and lower ignition temperatures, explosion limits with air, and the calorific value of the air-vapour mixtures at the ignition temperature, and discusses the bearing of the composition and ignition temperature of petrol on its storage. [Cf. *B.*, 1924, 364.] A. R. P.

**Influence of Cooling [Due to the Walls of the Container] on the Measurement of Explosive Pressures.** H. MURAOUR (*Mém. Poudres*, 1923, **20**, 323—329).—The influence of the cooling effect of the walls of the closed vessel on the pressure recorded in the combustion of propellants has been investigated by introducing a plate of gun steel, bent into the form of an incomplete hollow cylinder, into the closed vessel and so varying the extent of the cooling surface in contact with the hot gases. The effect on the pressures generated by propellants of different rates of combustion is given in a table and by means of a graph in which the loss of pressure in kg. due to the cooling effect of the interior surface of the closed vessel is plotted against the duration of combustion expressed in thousandths of a second. For the most rapidly burning powders, this loss of pressure amounts to about 50 kg. per sq. cm., and increases rapidly with the duration of combustion until a loss of 190 kg. is reached with the most slowly burning powders. Given equal periods of combustion, the loss of pressure varies very little with the temperatures of the gases. This curious result is ascribed to the fact that the products of combustion of the hotter propellants (such as ballistite) consist largely of carbon dioxide and water, the specific heats of which are much greater, especially at high temperatures, than the specific heats of carbon monoxide and hydrogen, which form a large proportion of the products of combustion of the cooler propellants containing large proportions of mineral jelly. For a given quantity of heat given to the walls,

the fall of temperature and pressure will therefore be less in the case of the ballistite than in that of the cooler propellants. The fall of pressure due to the cooling effect of the walls of the closed vessel may amount to 10% of the total pressure in the case of slow-burning propellants. H. C. R.

**Addition Reactions, Molecular Compounds, and the Hydrolysis of Tantalum Pentachloride.** K. LENDNER and H. FEIT (*Z. anorg. Chem.*, 1924, **132**, 10—14).—Pure tantalum pentachloride dissolved in a suitable solvent, e.g., carbon disulphide, gives rise to additive products with a number of organic substances. Some of these can be separated in the crystalline condition. The pyridine compounds,  $\text{TaCl}_5 \cdot 2\text{C}_5\text{H}_5\text{N}$ ,  $4\text{TaO}_2\text{Cl} \cdot 7\text{C}_5\text{H}_5\text{N}$ , and  $2\text{TaOCl}_3 \cdot 3\text{C}_5\text{H}_5\text{NHCl} \cdot 2\text{C}_2\text{H}_5 \cdot \text{OH}$ , and the piperidine compound  $\text{TaCl}_5 \cdot 6\text{C}_5\text{H}_{11}\text{N} \cdot 2\text{C}_2\text{H}_5 \cdot \text{OH}$  have been isolated. H. T.

**Physical Theory of Chemical Reactions.** P. LASAREFF (*Compt. rend.*, 1924, **178**, 773—775).—A qualitative theory of chemical reaction based on the Bohr atom. E. E. T.

**Chemical Aspect of Theories of Quanta, and Thermodynamics of Photochemical Reactions.** D. BERTHELOT (*Bull. Soc. chim.*, 1924, iv, **35**, 241—302).—A lecture delivered at the College de France.

**Catalysis by the Action of Subdivided Metals. II. Thermal Effect of the Hydrogenation of Ethylene at the Surface of Finely-divided Nickel.** B. FORESTI (*Gazzetta*, 1924, **54**, 132—146; cf. A., 1923, ii, 747).—Theories of catalysis are discussed with special reference to the hydrogenation of ethylene in presence of nickel. The various phases involved in this reaction consist of (a) adsorption of the gases by the nickel, (b) combination of the adsorbed molecules to yield adsorbed ethane, and (c) evaporation of the ethane from the surface of the metal. Consideration of the thermal changes accompanying these phases indicates that the catalyst does not diminish the critical increment of the total reaction, but renders possible a certain number of intermediate reactions with lesser critical increments without excluding the possibility that the sum of such increments may exceed the critical increment of the total reaction. Conclusions analogous to these were reached by Pratolongo from the results of his studies on chemical kinetics. Rideal's views are criticised adversely by the author.

The mean experimental values obtained for the molecular heats of adsorption at 0° of ethylene and ethane at constant volume by reduced nickel are 5845.6 cal. and 5004.7 cal. respectively.

T. H. P.

**Hæmoglobin and Methæmoglobin as Oxidative Catalysts.** M. E. ROBINSON (*Biochem. J.*, 1924, **18**, 255—264).—Hæmoglobin, methæmoglobin, and hæmin are efficient catalysts of the autoxidation of linseed oil. Hæmatoporphyrin does not have such action. The catalysis is most probably due to the presence of iron in the molecule. The concentration of iron, in the form of blood

pigment, capable of producing this catalytic effect is very much smaller than that required if the iron is present in the form of an inorganic salt. The addition of neutralised potassium cyanide, in an amount equivalent to that of the iron present, has no inhibitory influence on the catalytic action. S. S. Z.

**Promoting Action of Palladium on Copper. I. Catalytic Combustion.** W. W. HURST and E. K. RIDEAL (*J. Chem. Soc.*, 1924, **125**, 685—694).—A mixture of hydrogen, carbon monoxide, and oxygen, approximately in the proportions 8 : 1 : 1, was passed over catalysts of pure copper or copper with small amounts (up to 5%) of palladium, and the ratio  $\text{CO}/\text{H}_2$  burnt was determined over the temperature range 130—270°. For constant composition of the catalyst and varying temperature, it was found, in all cases, that this ratio increases up to about 175° and then diminishes rather rapidly up to the highest temperatures investigated. This temperature, where the ratio is a maximum, is identical with that at which cupric oxide, instead of cuprous oxide, is formed by contact of copper with oxygen. At constant temperature, increasing palladium content (up to 0.2%) increases the ratio, after which it steadily diminishes. With 1.7% of palladium in the catalyst the ratio has the same value as with pure copper. The results support the theory that the promoting action must be due to a peculiarity of the Pd-Cu interface, but on continued addition of palladium the augmented activity is decreased apparently by some specific action of that metal. L. J. H.

**Promoting Action of Palladium on Copper. II. Adsorption of Hydrogen and Carbon Monoxide.** W. W. HURST and E. K. RIDEAL (*J. Chem. Soc.*, 1924, **125**, 694—705).—The adsorption of carbon monoxide and hydrogen, separately and mixed (11% CO), by (a) copper and (b) copper containing 0.2% of palladium, was determined at 0°, room temperature, and 100°. This was made possible by the development of a method of analysis of the gas mixture giving an accuracy of 0.1% with only 1.3 c.mm. of the gas. The method depends on the measurement of the thermal conductivity. The adsorption of hydrogen is independent of the pressure down to about 150 mm., indicating that the surface is completely saturated, probably with a unimolecular layer, whilst the adsorption of considerably more carbon monoxide suggests a multimolecular layer. The adsorption from the mixed gases is far less than that calculated from the assumption of proportionality, and these results are discussed in the light of the authors' hypothesis concerning the adsorption of polar and non-polar molecules. From the mixed gases both constituents are always adsorbed, but the composition of the adsorbed layer varies continuously with the composition and pressure of the surrounding gas and also with the composition of the solid. The ratio  $\text{CO}/\text{H}_2$  in the adsorbed layer obtained with promoted copper compared with that for pure copper is in the proportion of 1.20 to 1 at 13° and 760 mm. pressure (cf. preceding abstract, 1.32 : 1 at 175°). L. J. H.

**Formation of Hydrogen Iodide by the Silent Electrical Discharge.** E. WARBURG (*Z. Physik*, 1924, **21**, 372—380).—Experiments have been carried out to determine the rate of formation of hydrogen iodide in the Siemens ozone tube at different temperatures, namely, room temperature, 30°, and 40°. The alternating current used had a frequency of about 50. A stream of pure hydrogen was passed through a U-tube containing iodine kept at constant temperature. It thus became charged with iodine vapour and was next passed through the Siemens tube. The hydrogen iodide formed, and part of the remaining iodine were absorbed by water, and the rest of the iodine by potassium iodide. The fraction of iodine transformed into hydrogen iodide increases with increasing strength of current and with diminishing rate of flow of the gas, but reaches a limit at approximately 90%, when the velocity of formation of the iodide equals the velocity of decomposition. The fraction of a gram-molecule of gas formed per coulomb of electricity has been calculated and is found to be of the same order as the amounts of oxygen (to form ozone), ammonia, and carbon dioxide which are decomposed per coulomb. The number of collisions between positive ions of molecular size and the gas molecules in the formation of ozone is found to be of the same order as the number of oxygen molecules decomposed. M. S. B.

**Yield of Photochemical Reactions with Complex Light.** M. PADOA and N. VITA (*Gazzetta*, 1924, **54**, 147—156).—The authors have investigated (1) the oxidation of hydrogen iodide, and (2) the reaction,  $2\text{FeCl}_3 + \text{H}_2\text{C}_2\text{O}_4 = 2\text{FeCl}_2 + 2\text{HCl} + 2\text{CO}_2$ , when these reactions are effected by the light from an arc lamp both before and after passage through various light-filters. For reaction (1) the sum of the effects produced by the blue, red, green, and violet zones is 3.17 times the effect produced by the unfiltered light. For reaction (2) in the absence of a catalyst, the spectral region over which the action takes place is somewhat limited, but the sum of the effects obtained in the blue and violet regions is 1.123 times that of the white light. In presence of quinine hydrogen sulphate, the zone of active radiations is widened and the total action in blue, green, and violet lights is 2.125 times that in the white light. Experiments with Eder's solution give analogous results.

Possible explanations for the above observations are discussed.

T. H. P.

**Metal to Glass Joint.** H. N. RIDYARD (*J. Amer. Chem. Soc.*, 1924, **46**, 287—290).—By coating a glass, silica, or porcelain tube with a mirror of platinum and then dipping this platinised end momentarily into a molten lead bath, a closely adhering film of lead is obtained on the glass. This lead-coated glass tube can readily be soldered into a suitable metal tube. Joints made in this way will hold a vacuum of  $10^{-4}$  mm. at temperatures up to 150° for some days and up to  $10^{-6}$  mm. for short periods.

H. T.

**Laboratory Gasometer.** R. SCHLEIPER (*Chem.-Ztg.*, 1924, **48**, 160—161).—A laboratory gasometer adapted for continuous work-



ing consists of two 3500 c.c. graduated Woulfe's bottles each having three necks and connected in such a way that the gas can be passed into either bottle as desired. The gas displaces the water from one bottle and measures it in the other, and the same water is used continually, so that no error is introduced by reason of the solubility of the gas, and the pressure is always that of the atmosphere.

A. R. P.

**Bifilar Quartz-fibre Manometer.** A. S. COOLIDGE (*J. Amer. Chem. Soc.*, 1924, **46**, 680—681).—The behaviour of the bifilar quartz-fibre manometer (A., 1923, ii, 612) at low pressures has shown the ineffectiveness of the gold-leaf trap. The substitution of a plain trap cooled to  $-25^{\circ}$  reduces the damping by condensation of mercury vapour. The temperature of the gauge need not be known when it is used in the lower range, although when used for measuring pressures in systems at different temperatures a correction for thermal transpiration must be made. At higher pressures, the viscosity of the gas influences the results, but a calibration curve for one temperature can be adapted to another by simple displacement. In the previous work (*loc. cit.*) the pressure was never high enough to be affected by this correction.

S. K. T.

**A Six-prism Glass Spectrograph, and a Neutral Wedge.** J. S. FOSTER (*J. Opt. Soc. Amer.*, 1924, **8**, 373—379).—Constructional details are given of a spectrograph of which the dispersion can be varied by using any number of prisms from one to six. A maximum dispersion is attained of 2 Å. per mm. in the violet. A neutral wedge is described which is used with the spectrograph for comparing the intensities of spectral lines. Methods of determining the density of the wedge for different wave-lengths are discussed, and owing to difficulties encountered in maintaining a constant discharge through a vacuum tube, a method utilising a continuous spectrum is adopted.

S. B.

**Tri-colour Mixing Spectrometer.** F. ALLEN (*J. Opt. Soc. Amer.*, 1924, **8**, 339—341).—A description of a new instrument combining features of the Helmholtz colour-mixing and the Hilger wave-length spectrometers. Mixtures of two or three colours can be made, and the wave-lengths and intensities of the components controlled and measured.

S. B.

**Iron-Mercury Calorimeter.** F. H. SCHOFIELD (*J. Scient. Instr.*, 1924, **1**, 141—144).—The calorimeter is designed for specific heat measurements on materials of low conductivity which react with water, and consists of an iron block with a hole into which the hot specimen is dropped from a furnace. Rapid interchange of heat between the block and specimen is secured by flooding the hole with mercury.

S. B.

**Radium Balance.** L. H. CLARK (*J. Scient. Instr.*, 1924, **1**, 137—141).—An apparatus for simple and rapid determinations of radium. Two insulated chambers are maintained at a constant difference of potential. An insulated electrode entering both

chambers makes electrical connexion between them. The chambers are exposed simultaneously, one to the  $\gamma$ -radiation from the radium under examination, the other to the  $\alpha$ -radiation from a very small mass of radium. The two consequent ionisation currents cause the potential of the insulated electrode to rise to a steady value, when a balance is set up. A gold leaf indicator is attached to the electrode. The accuracy attained is of the order of 2%.

S. B.

**Lecture Experiments to Show the Inflammability of Hydriodic Acid and Hydrogen Sulphide.** G. G. LONGINESCU and C. N. THEODOSIU (*Bul. Soc. Romăna Stiin.*, 1923, 26, 19—20).—A small portion of a thick paste of potassium permanganate and sulphuric acid, on the end of a glass rod, is introduced into a vessel completely full of hydriodic acid, when the latter immediately takes fire with incandescence and liberation of violet fumes of iodine. A similar method may be used to illustrate the inflammability of hydrogen sulphide. An alternative experiment with hydriodic acid consists in passing a stream of chlorine through a glass tube into the vessel containing the hydriodic acid, when the latter at once takes fire.

W. H.-R.

**Diffusion Gas Electrode.** A. SCHMID (*Helv. Chim. Acta*, 1924, 7, 370—373).—A gas electrode for use as a hydrogen electrode in a hydrogen-chlorine cell consists of a hollow, porous carbon support on which is deposited a skin of electrolytic platinum. The platinum, although having a smooth metallic appearance, has microscopic pores, impervious to liquids but permeable to gases. The gas passes from the inside of the carbon support through the platinum skin by capillary diffusion and forms a true solution at the active metal surface. The activity of such an electrode is so high that it is not polarised even by free halogen in the solution. Using this electrode for hydrogen and a similar carbon electrode, without the platinum surface, for chlorine, hydrochloric acid free from chlorine can be produced continuously. The potential of the hydrogen-chlorine cell, measured with this apparatus, is 1.360 volt, of the hydrogen-bromine cell 1.080, and of the hydrogen-iodine cell 0.54 volt, at 20° against a normal solution of the corresponding acid. The temperature coefficient of the potential between 0° and 80° for these three cells is — 0.0010, except in the interval 20—40° for the bromine and iodine cells, when it has only one-fourth of this value.

E. H. R.

**Derivation of the Word "Mercaptan."** T. S. PATTERSON (*Chem. and Ind.*, 1924, 43, 196—198).—Zeise discovered mercaptan about the year 1824 and gave this name to the substance; he derived it from *corpus mercurium captans* (*J. pr. Chem.*, 1834, 1, 186), and not from *corpus mercurio aptum*.

W. P. S.

## Inorganic Chemistry.

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**Solubility of Helium and Hydrogen in Heated Silica Glass and the Relation of this to the Permeability.** G. A. WILLIAMS and J. B. FERGUSON (*J. Amer. Chem. Soc.*, 1924, **46**, 635—639; cf. A., 1922, ii, 841).—The relative rates of effusion of hydrogen and of helium through silica glass are not in accordance with the law of Graham and Bunsen. Measurements of the increase of pressure observed on heating silica glass which had absorbed helium or hydrogen indicate that the solubilities of these gases differ but slightly (cf. A., 1915, ii, 319), showing that solubility differences do not influence the rates of effusion of these gases through silica glass. The dependence of permeability on temperature is shown to be similar for many of the cases which have been investigated by other workers. S. K. T.

**Periodic Dissolution of Metals in certain Reagents.** E. S. HEDGES and J. E. MYERS (*J. Chem. Soc.*, 1924, **125**, 604—626).—A survey of the literature indicates that few examples of periodic actions are known, and these are treated as isolated examples. The authors have studied a large number of reactions involving the liberation of hydrogen by the dissolution of metals in various agents by recording continuously the pressure of the gas as it is evolved. In all cases examined, the rate of evolution of hydrogen varies periodically with time, and it is shown conclusively that this is essentially part of the chemical change, supersaturation of the solution or of the metal with gas playing no part. Generally, the wave-length increases throughout the course of the reaction, and the peaks of the waves have a practically constant value; the "pulses" are superimposed on the ordinary reaction curve and do not correspond with alternate periods of activity and passivity of the metal. The phenomenon is quite general, and occurs only in the presence of a third substance; it appears to be a periodic catalysis of the regular reaction. The frequency of the periods is proportional to the concentration of the reagent, increases with rise of temperature, and is greatly reduced by small quantities of catalytic poisons (e.g., a concentration of 1 in  $10^6$  of chloroplatinic acid completely inhibits the production of waves in the case of aluminium dissolving in hydrochloric acid). The quantity of the active substance required to produce the periods is exceedingly small. Occasionally the reactions normally proceed in a periodic manner, because the reaction vessel used may contain the necessary catalyst, but the periodic phenomena may be produced at will by the addition of a freshly prepared colloid (gelatin or the dye night-blue being very reactive), or of a second metallic component which has been suitably treated. Thus the case of chromium investigated by Ostwald (A., 1900, ii, 730) is simply a particular instance of a very general phenomenon. In the first case, the appearance of waves depends

on the nature of the vessel employed and on the simultaneous presence of certain metals, since in some vessels periods could not be produced even by the addition of colloids. Successive heating and cooling in a vacuum renders many metals (platinum, palladium, gold, silver, copper, chromium, and iron) active, so that the addition of any of these metals after treatment makes the system periodic. On the other hand, cobalt and nickel are found to be normally active and are rendered inactive by the "vacuum-heat" treatment. Platinum can be activated by boiling with aqua regia, strong nitric or hydrochloric acid, and by bombardment with cathode rays, and copper by scraping the surface heavily with a knife-blade. The second metallic component may also be present in the form of an alloy with the dissolving metal. It is supposed that all methods of activation produce a metastable form, the metal having an amorphous surface after treatment, and the slow crystallisation of this amorphous metal corresponds with the dying of the activity. That the seat of periodicity is in the second metallic component is demonstrated experimentally by the evolution of hydrogen from a solution of chromous chloride in the presence of platinum. Using ordinary platinum, the evolution of the gas is quite regular, whilst well-developed waves are obtained when active platinum is employed.

J. W. B.

**Hydrogen Peroxide. IV. Action of the Halogens and Halogen Hydrides.** O. MAASS and P. G. HIEBERT (*J. Amer. Chem. Soc.*, 1924, **46**, 290—308).—The rate of decomposition of hydrogen peroxide by hydrogen chloride was investigated throughout all ranges of concentrations. With low concentrations of acid, the reaction is unimolecular, oxygen but no chlorine being evolved. For any concentration of hydrogen peroxide, however, there is a critical concentration of hydrogen chloride above which chlorine is simultaneously given off. Here the reaction is no longer unimolecular, the velocity constant being proportional to the concentration of the undissociated halogen hydride. The following reactions are suggested as explaining this result as well as the evolution of chlorine: (a)  $\text{H}_2\text{O}_2 + \text{HCl} \rightleftharpoons \text{H}_2\text{O}_2 \cdot \text{HCl}$ ; (b)  $\text{H}_2\text{O}_2 \cdot \text{HCl} \rightarrow \text{Cl} - \text{H}_2\text{O} - \text{OH} \rightarrow \text{H}_2\text{O} + \text{HOCl}$ ; (c)  $\text{HOCl} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{HCl}$ ; (d)  $\text{HOCl} + \text{HCl} \rightleftharpoons \text{Cl}_2 + \text{H}_2\text{O}$ . Similar results were obtained with hydrogen bromide; hydrogen fluoride, however, acts as a stabiliser.

H. T.

**Kinetics of the Photosynthesis of Hydrochloric Acid.** A. BERTHOUD (*Helv. Chim. Acta*, 1924, **7**, 324—328).—The conclusions of Chapman (T., 1923, **123**, 3062) regarding the course of the reaction between hydrogen and chlorine under the influence of light are criticised. The results recorded by Chapman agree well, for low concentrations of hydrogen, with the semi-molecular equation  $k = 2[(a-x_1)^{-1} - (a-x_2)^{-1}]/(t_2 - t_1)$  and are therefore in agreement with the theory of this reaction suggested by Nernst (A., 1919, ii, 208).

E. H. R.

**Photochemical Reaction between Bromine or Iodine and Potassium Oxalate.** A. BERTHOUD and H. BELLENOT (*Helv. Chim. Acta*, 1924, 7, 307—324).—The reaction between iodine and potassium oxalate has been studied both in darkness and in white light by Dhar (A., 1916, ii, 237; T., 1917, **111**, 707; 1923, **123**, 1856), but some of his results are conflicting. Determinations made at 78° in the dark show that the velocity of the reaction varies inversely as the concentration of potassium iodide. This result can be explained if it is assumed that there is an equilibrium between iodine,  $I_2$ , and the ions  $I'$  and  $I_3'$ ,  $[I_2][I']/[I_3'] = K$ . The concentration of  $I_2$  is then inversely proportional to that of the ions  $I'$ , and the influence of the iodide is explained if only the molecules  $I_2$  are active. Measurements were made under the influence of artificial light at 40°. The reaction velocity in the light is proportional to the concentration of potassium oxalate. All wave-lengths from the violet to the red are active; the activity of the red end of the spectrum was unexpected. Comparative experiments were made with blue light filtered through an ammoniacal copper sulphate solution and with red light filtered through an aqueous iodine solution. With blue light, there is almost total absorption, and with red light very little absorption. The reaction velocity in blue light is inversely proportional to the square root of the concentration of iodine, the reaction being therefore of the order  $-\frac{1}{2}$ , whilst in red light the velocity is proportional to the same square root, the reaction being of the order  $\frac{1}{2}$  (semi-molecular). In white light, the reaction follows neither of these courses, although Dhar (*loc. cit.*) found the reaction under these conditions to be semi-molecular. In both blue and red light, as in the dark, the velocity varies inversely as the concentration of iodide. The thermal coefficient between 25° and 40° is practically the same for blue light (3.04) and red light (3.10). The above facts indicate that the reaction does not follow Einstein's law of the photochemical equivalent. A reaction of the order  $-\frac{1}{2}$  seems not to have been previously observed. The observed orders of the reaction under the different conditions can be accounted for by applying the theory put forward by Nernst (A., 1919, ii, 208) to explain the photosynthesis of hydrochloric acid. It is assumed that the light activates molecules of iodine, eventually decomposing them into atoms which react with the oxalate thus:  $C_2O_4'' + I = C_2O_4' + I'$ . The departure from Einstein's law may be accounted for by the regeneration of atomic iodine by the reaction  $C_2O_4' + I_2 = 2CO_2 + I' + I$ . The velocity of the reaction, in both blue and red light, is proportional to the square root of the intensity of the light. The reaction in blue light is expressed by the equation  $d[I_2]/dt = kI_0^{\frac{1}{2}} \cdot [K_2C_2O_4]/[I_2^{\frac{1}{2}}][I']$ , and in red light by  $d[I_2]/dt = kI_0^{\frac{1}{2}} \cdot [K_2C_2O_4][I_2^{\frac{1}{2}}]/[I']$ , where  $I_0$  is the intensity of illumination and  $[I_2]$  the concentration of iodine after time  $t$ .

The velocity of the reaction between bromine and potassium oxalate in the dark is proportional to the concentration of bromine and inversely proportional to that of the potassium bromide. The temperature coefficient between 0° and 11.5° is 5.99. The photo-

chemical action is delayed in presence of ammonium ions, although this is not the case with iodine. In white light, with relatively concentrated solutions of bromine, the reaction velocity is constant (zero order), and proportional to the concentration of oxalate. Since only light of short wave-length is active, the same result is obtained with blue light. With weaker bromine solutions, the reaction is approximately semi-molecular. The velocity is little affected by variations in concentration of the bromide, from which it is concluded that not only bromine molecules but the ions  $\text{Br}'_3$  are activated by light. E. H. R.

**Sorption of Iodine by Carbons prepared from Paraffin Hydrocarbons, Carbon Dioxide, Aromatic Hydrocarbons and Derivatives, and from the Products of Oxidation of Wood Charcoal with Fuming Nitric Acid.** J. B. FIRTH, W. FARMER, and J. HIGSON (*J. Chem. Soc.*, 1924, 125, 488—492; cf. A., 1923, ii, 129).—The relative density (by the water displacement method) and the volume occupied by 1 g. of each carbon (dried at 120°) were determined. The results indicate that carbons prepared under defined conditions from various carbon compounds approximate to definite activity values, and that there appears to be no direct relation between the activity of the carbon and the molecular complexity of the original carbon compound. The presence of nitrogen, sulphur, and halogens makes scarcely any difference in the activity of the carbon or else reduces its activity value to about one-half (cf. Knecht, A., 1911, ii, 471). The preparation of a highly active carbon from wood charcoal by means of fuming nitric acid is described. J. W. B.

**Equilibrium between Iodine and Barium Iodide.** J. N. PEARCE and W. G. EVERSOLE (*J. Physical Chem.*, 1924, 28, 245—255).—By studying the distribution of iodine between carbon tetrachloride and aqueous solutions of barium iodide, the authors have tried to determine the nature of the polyiodides formed in solution. Concentrations have been determined on the basis of mols. per 1000 g. of solvent, instead of on the volume basis as by previous investigators (Jakowkin, A., 1894, ii, 271; 1896, ii, 295). The distribution ratio of iodine between carbon tetrachloride and water at 25° is thus found to be 52·5. Four different constants have been calculated assuming the following equilibria between the iodide and iodine in solution: (1)  $\text{BaI} \cdot \text{I}_3 \rightleftharpoons \text{BaI}_2 + \text{I}_2$  (Herz and Kurzer, A., 1910, ii, 1045); (2)  $\text{BaI} \cdot \text{I}_5 \rightleftharpoons \text{BaI}_2 + 2\text{I}_2$ ; (3)  $\text{BaI}_3 \cdot \text{I}_3 \rightleftharpoons \text{BaI}_2 + 2\text{I}_2$  (Jakowkin, *loc. cit.*); (4)  $\text{BaI}_5 \cdot \text{I}_5 \rightleftharpoons \text{BaI}_2 + 4\text{I}_2$ . The value of the equilibrium constant  $k_3$ , based on assumption 3, is found to be practically constant between the limits of iodide concentration of 0·02 to 0·14 mol. per 1000 g. of water, and of iodine 0·004 to 0·09. Apparently, for solutions unsaturated with iodine, the compound  $\text{Ba}(\text{I}_3)_2$  is practically the only polyiodide present.

Measurements of the solubility of iodine in solutions of barium iodide up to concentrations of about 1·2 mols. per 1000 g. of water, have also been made. The calculated values of the above four equilibrium constants, assuming that the uncombined iodine in the

solution is equal to the solubility of iodine in pure water, *i.e.*, 0.001329 mol. in 1000 g. (cf. Bray and Mackay, A., 1910, ii, 820), are considered to indicate that, in concentrated solutions of barium iodide saturated with iodine, some penta-iodide,  $\text{Ba}(\text{I}_5)_2$ , is also formed.

The work of Parsons and Corliss (A., 1910, ii, 1061) on the non-existence of polyiodides in solution is criticised. M. S. B.

### **Oxidation of Hydrogen Iodide in the Dark and in the Light.**

C. WINTHER (*Z. physikal. Chem.*, 1924, **108**, 236—274).—A repetition of earlier work (A., 1920, ii, 427), greater accuracy now being attained. The light absorption of solutions containing potassium iodide and hydrochloric acid is measured photographically (A., 1923, ii, 519); substitution of the acid by an equivalent amount of potassium chloride has no effect. With increasing concentration of the iodide, absorption in the long wave band increases and in the short wave band decreases. With increasing iodine concentration the absorption decreases considerably over all wave-lengths. The velocity of oxidation of acid potassium iodide solution in the dark increases with increasing iodine concentration; this points to two simultaneous reactions: (*a*) oxidation of the iodide ions (practically constant velocity constant,  $k$ ) and (*b*) oxidation of the tri-iodide ions,  $k_1$  here depending on the concentration. The total velocity is then given by  $\delta c/\delta t = k + k_1 c$ . The temperature-coefficient depends largely on the composition of the solution. In presence of radiations of wave-lengths ranging from 436 to  $254\mu\mu$ , the velocity of oxidation increases with increase of radiation energy up to a certain point, after which it remains constant.

To explain the results, it is assumed that in each second a fixed fraction of the molecules is in such a state that it can absorb only a certain wave-length; the fraction is calculated from the experimental results to be 1/3000 per second in approximately *N*-solution (*N*-potassium iodide + *N*-hydrochloric acid) for  $366\mu\mu$ . In 50 minutes all the molecules will have assumed this state. It is then shown that in one experiment each molecule absorbed about 8.2 quanta. It is further supposed that only those tri-iodide ions which have absorbed one quantum give rise to free iodine, those absorbing two quanta or more being not activated thus. The photochemical induction factor  $K$  (number of iodide ions oxidised by activated tri-iodide ions per 5 c.c.) is independent of the total energy and is given by an expression which agreed with observed values except in the case where the concentration of potassium iodide was varied; this discrepancy is thought to be due to more than experimental error. Expressions for the velocity constants  $k$  and  $k_1$  fitted the results fairly well.

The ratio  $k_1/K$  gives the fraction of active tri-iodide ions formed per minute (in the dark), and this is tabulated for varying concentrations of oxygen, hydrochloric acid, and potassium iodide at 20° and 30° on the assumption (not quite correct) that  $K$  is independent of the temperature. It is inferred from the figures that this ratio is independent of the oxygen and acid concentration,

but increases with the iodide concentration. The variation of absorption with iodide concentration is shown to depend on the energy partition between the tri-iodide ions, but acid, oxygen, and iodine concentration has no effect on this partition.

The principles discussed are applied to other photochemical reactions, *e.g.*, the decomposition of ozone mixed with nitrogen, oxygen, or helium (A., 1913, ii, 652; T., 1923, **123**, 2767), and the slow oxidation of phosphorus (A., 1895, ii, 213). S. K. T.

**Structure of Oxygen.** H. COLLINS.—(See ii, 297.)

**Properties of Colloidal Sulphur.** G. ROSSI (*Koll.-Z.*, 1924, **34**, 20—23).—The coagulating action of electrolytes towards a solution of colloidal sulphur and the adsorption of the coagulating electrolytes is dependent on the quantity of the electrolytes, sulphuric acid, and sodium sulphate present. The amount of adsorption of a crystalloid is proportional to the quantity present. The adsorption in sulphur solutions which contain less sulphuric acid and sodium sulphate is greater than in solutions which have not been dialysed. J. F. S.

**Reaction of Sulphur with Alkali and Alkaline Earth Hydroxides in Aqueous Solutions.** H. V. TARTAR and C. Z. DRAVES (*J. Amer. Chem. Soc.*, 1924, **46**, 574—581).—When sulphur is boiled for a short time with *N*-sodium hydroxide solution the polysulphides formed are slightly higher than the trisulphide. Long boiling with excess of hydroxide reduces these to disulphides; this reduction is less rapid for more dilute hydroxide solutions. Continued boiling reduces the disulphides very slowly to monosulphides. Similar results hold for solutions of potassium and barium hydroxides, the composition of the polysulphides depending on the initial concentration of the hydroxide and on the duration of the reaction period. The reaction is hence probably ionic: (i)  $3\text{OH}' + 4\text{S} \rightarrow 2\text{S}'' + \text{S}_2\text{O}_3'' + 3\text{H}'$ ; (ii)  $\text{S} + \text{S}'' \rightleftharpoons \text{S}_2''$ , (iii)  $\text{S} + \text{S}_2'' \rightleftharpoons \text{S}_3''$ , etc. It is shown that potassium disulphide and not the trisulphide (A., 1914, ii, 269) is the stable form in presence of excess of alkali. Further boiling appears to reduce the di- to the mono-sulphide, although much more slowly. The ratio of the monosulphide sulphur to the thio-sulphate sulphur is always slightly below unity.

For the determination of the monosulphide equivalent of the polysulphides the following method was devised. To 50 c.c. of a borax-boric acid buffer 0.1*N*-iodine solution was added in excess above the monosulphide sulphur equivalent of the solution. The latter was then added with constant stirring and the excess iodine titrated with thiosulphate as usual. S. K. T.

**Vapour Pressures of Fuming Sulphuric Acid and their Application to the Problem of the Absorption of Sulphur Trioxide.** J. W. McDAVID (*J. Soc. Chem. Ind.*, 1924, **43**, 57—61*T*).—The vapour pressure of fuming sulphuric acid containing from 0 to 45% of free sulphur trioxide has been determined for temperatures between 40° and 90° and the results are reproduced in graphical and tabular form. Across the graph of the vapour-



pressure curves a number of horizontal lines denoting the percentage concentration by volume of sulphur trioxide corresponding with the pressures in mm. of mercury have been drawn, so that it is possible to read off directly the maximum strength of fuming sulphuric acid that can theoretically be produced from any gas at any temperature within the range given above. These data indicate the number of absorption vessels required for complete absorption of sulphur trioxide from the gases issuing from the contact plant. The course of the absorption depends on the total weight of sulphur trioxide entering the apparatus in a given time, its concentration in the gas entering the system, the strength of the fuming sulphuric acid being produced, the strength of the acid fed into the last absorption vessel, and the temperature.

A. R. P.

**Stability of Thiosulphuric Acid in the Presence of Fuming Hydrochloric Acid. Preparation of Solutions of Thiosulphuric Acid.** J. C. GIL and J. BEATO (*Anál. Fís. Quím.*, 1924, 22, 84—91).—(See this vol., ii, 104.)

G. W. R.

**Determination of the Specific Gravity of Solutions of Ammonia.** N. J. PRICE and C. S. L. HAWKINS (*J. Soc. Chem. Ind.*, 1924, 43, 113—117T).—The specific gravities of ammonia solutions from  $d$  0.875 have been determined in a weighing pipette designed to be used both as a weighing bottle and as a specific gravity bottle. Over the range  $d$  0.880 to 0.885 the figures are lower than those of Lunge (A., 1890, 107), the maximum difference being about 0.33%  $\text{NH}_3$ . For weaker solutions the values are slightly higher than those of Lunge. The linear relationship which exists between the specific gravity and ammonia content at low specific gravities changes to a curvilinear one at about a point corresponding to  $\text{NH}_3 \cdot 3\text{H}_2\text{O}$ .

**Ammonia Equilibrium at High Pressures.** A. T. LARSON (*J. Amer. Chem. Soc.*, 1924, 46, 367—372; cf. this vol., ii, 104).—The equilibrium values for the reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  at 300, 600, and 1000 atmospheres and at temperatures of 450°, 475°, and 500° have been determined, the following values for the percentage amount of ammonia at equilibrium being observed: at 300 atm., 450°, 35.5; 475°, 31.0; 500°, 26.2; at 600 atm., 450°, 53.6; 475°, 47.5; 500°, 42.1; at 1000 atm., 450°, 69.4; 475°, 63.5. The equilibrium constants are shown to increase with increase of pressure. The empirical formulæ for calculating the percentage of ammonia at equilibrium have been extended up to 1000 atm.

H. T.

**Catalytic Decomposition of Nitroamide and its Physico-chemical Significance.** J. N. BRÖNSTED and K. PEDERSEN (*Z. physikal. Chem.*, 1924, 108, 185—235).—Nitroamide is a weak acid and the simplest explanation of its decomposition in alkaline solution is to assume the spontaneous decomposition of the ion  $\text{HN}_2\text{O}_2' \rightarrow \text{OH}' + \text{N}_2\text{O}$ . All substances having basic properties

catalyse the reaction; the decomposition is now studied with acid anions, aniline, etc., as basic catalysts.

The nitroamide, prepared from nitrourethane (Thiele and Lachmann, A., 1896, ii, 207), was decomposed by shaking with the catalyst, the nitrous oxide evolved being collected.

From the results obtained with various catalysts (mineral and organic acids, organic bases, aquo-compounds, etc.), equations showing the progress of the decomposition are deduced, on the assumption that the reaction is partly spontaneous and partly catalytic, and the velocity constants have been calculated. Methods are suggested for the use of nitroamide for determining the degree of hydration of the metal in aquo-compounds, and for calculating the dissociation constants of weak acids.

S. K. T.

### Chemi-luminescence in the Oxidation of Phosphorus.

A. PETRIKALN.—(See ii, 289.)

### Hypophosphorous Acid. VI. Reaction with Chromic Acid.

A. D. MITCHELL (*J. Chem. Soc.*, 1924, 125, 564—575).—Although this reaction is comparatively slow, no information on the part played by the active form was obtained (cf. T., 1920, 117, 1322). The measurable reaction is between the dichromate ion and the active hypophosphorous acid which is derived from 1 mol. of the normal form, is unimolecular with regard to each reactant, and does not involve hydrogen ions. It may be represented:  $\text{Cr}_2\text{O}_7'' + \text{H}_3\text{PO}_2 = \text{H}_3\text{PO}_3 + \text{Cr}_2\text{O}_6''$ , thus postulating the existence of a quinquevalent chromium ion (cf. Luther and Rutter, A., 1907, ii, 555), which then reacts rapidly with more of the hypophosphorous acid in either its active or normal form:  $\text{Cr}_2\text{O}_6'' + 2\text{H}_3\text{PO}_2 + 8\text{H}^+ = 2\text{Cr}^{++} + 2\text{H}_3\text{PO}_3 + 4\text{H}_2\text{O}$ . The intermediate compound is extremely reactive, and it can oxidise the very stable normal form of hypophosphorous acid, which resists the action of many reagents that oxidise the active form. The velocity coefficients obtained for the reaction vary inversely as the one-seventh power of the initial concentration of the chromic acid, and it is suggested that over a considerable range of concentration its activity coefficient may be represented empirically in this manner. Confirmatory evidence is obtained that it is the undissociated molecule of hypophosphorous acid that gives rise to the active form (cf. Lowry, A., 1923, ii, 313). The decrease in the velocity coefficient caused by considerable excess of chromic acid is attributed to the activity coefficient, which in solutions of high ionic concentration falls off rapidly.

A considerable error is caused by the presence of hypophosphorous acid when ferrous salts are titrated with potassium dichromate, and a possible cause is suggested. Certain points affecting the delicacy of the end-point of the reaction are also discussed.

J. W. B.

**Action of Arsenic Trioxide in Water Solution on certain Metallic Hydroxides.** L. G. STORY and E. ANDERSON (*J. Amer. Chem. Soc.*, 1924, 46, 533—539).—The absorption of arsenic trioxide by calcium, barium, lead, or magnesium hydroxides in water was

examined. The attainment of equilibrium required from 3 days at 99° to more than a week at lower temperatures.

In the system calcium hydroxide–arsenious oxide–water, when the concentration of the arsenic trioxide is equal to or greater than 0.06 g. per 100 c.c. (*i.e.*, 0.07 g. at 50° and 0.078 g. at 99°) the meta-arsenite,  $\text{Ca}(\text{AsO}_2)_2$ , is formed. At lower concentrations, the basic compound,  $\text{OH}\cdot\text{CaAsO}_2$ , is produced. Similar results were obtained with barium, the two arsenites,  $\text{OH}\cdot\text{BaAsO}_2\cdot 2\text{H}_2\text{O}$  (up to 0.6 g. of arsenic trioxide per 100 c.c. solution) and  $2\text{BaO}\cdot 3\text{As}_2\text{O}_3\cdot 4\text{H}_2\text{O}$ , being formed. With lead, a meta-arsenite,  $\text{Pb}(\text{AsO}_2)_2$ , was detected; a basic compound may also be formed at lower concentrations. No arsenite was formed by magnesium hydroxide; 1.035 g. of the latter absorbed 0.12 g. of arsenic trioxide from aqueous solutions, irrespective of the concentrations of the latter. S. K. T.

**Distillation of Arsenious, Antimonious, and Stannic Chlorides.** W. BÖTTGER (*Oesterr. Chem.-Ztg.*, 1924, 27, 24).—Arsenic and antimonious chlorides may be reduced to the trivalent state by means of pyrogallol, but hydrobromic acid appears to be the most satisfactory reducing agent. Distillation with a large excess of hydrobromic acid on the water-bath while passing a current of carbon dioxide through the solution effects a satisfactory separation of arsenic from a solution containing antimonious and mercuric chlorides; in the absence of these substances the temperature may be raised to 130° with a corresponding decrease in the time required for the distillation. Both antimonious and stannic chlorides may be distilled from solutions containing strong sulphuric acid if 47% hydrobromic acid is continually dropped into the solution.

A. R. P.

**Constitution of Arsenic Trisulphide Sols.** W. PAULI and A. SEMMLER (*Koll.-Z.*, 1924, 34, 145–155).—The hydrogen-ion content of arsenic trisulphide sols, freed from excess of hydrogen sulphide by a current of hydrogen, has been determined (*a*) from the electrical conductivity of the sol assuming the mobility of the colloid anion to be 50, and (*b*) by conductometric titration with barium hydroxide solution. The two methods give the same value for sols which have stood for several days, but freshly prepared or freshly dialysed sols have a lower conductivity than would be expected from the figure obtained by the barium hydroxide titration. Such sols increase in conductivity on keeping. Dialysis of a sol gave first a sharp decrease in conductivity followed by a slow increase; these phenomena are ascribed to a slow ionisation of the colloid. By precipitating a sol with barium chloride and determining the barium in the filtrate and washings, it was found that four equivalents of barium are present in the precipitate for each equivalent of hydrogen ion found in the sol. The colloid is regarded as having the constitution  $(x\text{As}_2\text{S}_3, \text{H}_2\text{As}_2\text{S}_4, \text{HAS}_2\text{S}_4)\text{H}^+$ , only one of the hydrogen atoms being ionised in solution, but all four being replaced on precipitation (*cf.* Bhatnagar and Rao, A., 1923, ii, 756).

S. S.

**Arc Spectrum of Silicon in relation to Spectrographic Analysis.** C. PORLEZZA.—(See ii, 345.)

**Sol of Silicic Acid, and its Preparation.** R. SCHWARZ (*Koll.-Z.*, 1924, **34**, 23—29).—The solubility of silicic acid, prepared from silicon tetrafluoride, has been determined in ammonia solutions of various concentrations between 0.001*N* and 10.3*N* at 25°. The peptising action of the ammonia makes itself noticeable at a concentration of 0.001*N*; for 3*N*-ammonia the amount of dissolved silicic acid lies between 63.4% and 67.4% for different specimens of the gel. Between the concentrations 3*N*- and 6*N*-ammonia the solubility does not change materially, and from this concentration upwards the solubility decreases. Attempts to titrate silicic acid with ammonia by the conductivity method failed to give an end-point. Sols of silicic acid can be prepared by allowing a solution of silicic acid in ammonia to evaporate slowly over dilute sulphuric acid. The properties of such a sol are compared with those of silicic acid sols prepared by other methods. J. F. S.

**Spectrum of Ionised Carbon.** A. FOWLER.—(See ii, 285.)

**Active Charcoal. II. Activity and Content of Foreign Atoms.** O. RUFF and E. HOHLFELD (*Koll.-Z.*, 1924, **34**, 135—139).—The hypothesis previously put forward (A., 1923, ii, 411) that the activity is proportional to the content of certain foreign atoms, *e.g.*, oxygen and nitrogen, has been tested further. The influence of temperature on the activity is connected with the type of chemical change which takes place when the activating gas comes into contact with the charcoal. Thus with water vapour as activating agent at 500°, only carbon dioxide is evolved, the hydrogen formed being adsorbed by the charcoal, which is inactive. At 850°, carbon monoxide, carbon dioxide, and methane are produced and an active charcoal is formed. Increasing the velocity of the stream of nitrogen which carries the activating gas gives an enhanced activity, since the products of the reaction are removed more completely, and for the same reason, under constant experimental conditions, a greater activity is found for charcoal prepared in a horizontal tube than in the same tube in a vertical position. The analyses previously quoted are seriously in error owing to the presence of adsorbed air in the charcoal. New methods give results which show that the earlier hypothesis can no longer be maintained. Thus a Merck's blood charcoal of high activity retained its activity when heated for 4 hours in a vacuum, although the oxygen content fell from 2.5% to 1.2%, and for other charcoals it is not possible to correlate the activity with the oxygen or nitrogen content. S. S.

**Structure of Neon and Argon.** H. COLLINS.—(See ii, 297.)

**Compressibility of the Alkali Salts.** E. SAERENS (*Bull. Soc. chim. Belg.*, 1924, **33**, 17—57).—By means of the piezometer the coefficients of compression of the halogen salts of the alkali and alkaline-earth metals and of cadmium and lead chlorides have

been determined. In the case of the alkali metals, the coefficient of compression increases from lithium to rubidium, decreasing, however, for the cæsium salts. With the alkaline-earth metals, on the other hand, the compressibility of the salts decreases with increase in the atomic weight of the metal. In the case of any one metal, the compressibility decreases in the order iodide, bromide, chloride. Rubidium bromide and iodide and cæsium bromide have two coefficients of compression, showing that these salts exist in two modifications with different affinities. Under ordinary pressure, the more compressible form is stable at high temperatures; the other modification, stable at the ordinary temperature, has a low coefficient of compression. The coefficient of the first modification increases with the pressure. R. B.

**Viscosity of Binary Mixtures of Sulphuric Acid, Potassium and Sodium Hydroxides.** L. J. SIMON (*Compt. rend.*, 1924, **178**, 1076—1079).—Measurements have been made of the viscosity of solutions containing various proportions of acid and alkali of a constant total molecular concentration. In the case of acid and sodium hydroxide, the minimum value of the viscosity is found to correspond with the formation of  $\text{NaHSO}_4$ ; in the case of potassium hydroxide with that of  $\text{K}_2\text{SO}_4$ . Rubidium is in this respect similar to potassium. The viscosities of mixtures of sodium and potassium hydroxides are slightly less than the mean of the viscosities of the constituents. A. B. H.

**Decomposition of Potassium Chlorate and its Catalysis by Potassium Chloride.** C. E. OTTO and H. S. FRY (*J. Amer. Chem. Soc.*, 1924, **46**, 269—276).—The kinetics of the reactions (1)  $4\text{KClO}_3 = 3\text{KClO}_4 + \text{KCl}$  and (2)  $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$ , which occur when potassium chlorate is heated have been investigated by an experimental method similar to that previously described (A., 1923, ii, 474). Reaction (2) is unimolecular. With reaction (1), the velocity of the transformation at constant temperature increases as the reaction proceeds, and this increase is due to the catalytic action of potassium chloride (cf. A., 1903, ii, 645);  $dy/dt = K_1c(a-x)$  where  $c$  = concentration of the potassium chloride, and  $(a-x)$  that of the potassium chlorate. In the decomposition of the chlorate, no chlorine was evolved. H. T.

**Cosmic Clouds of Calcium and Sodium.** B. GERASIMOVICH (*Nature*, 1924, **113**, 458—459).—The most probable explanation of the existence of cosmic clouds of calcium and sodium is that due to Saha (*ibid.*, 1921, **107**, 488); the position is, however, modified by the discovery, apparently incomprehensible from the point of view of the quantum theory, that in the spectra of helium stars there are not only the stationary lines *H* and *K*, but also the sodium *D* lines. A theory is put forward to account for this observation. A. A. E.

**Production of Large, Clear, Cubical Crystals of Sodium Chloride.** W. E. GIBBS and W. CLAYTON (*Nature*, 1924, **113**, 492—493).—Brine containing 0.1% of sulphuric acid and 0.1%

of lead nitrate, maintained at  $75^{\circ}$  in a silica pan, will in 12 hours yield brilliantly clear cubes, usually about 6 mm. side, and containing about 270 parts of lead per million. By further growth in the mother-liquor, cubes of 30 mm. side may be obtained.

A. A. E.

**Ternary and Quaternary Equilibria in the System:  $\text{NaClO}_4\text{--}(\text{NH}_4)_2\text{SO}_4\text{--}\text{NH}_4\text{ClO}_4\text{--}\text{Na}_2\text{SO}_4\text{--}\text{H}_2\text{O}$  at  $60^{\circ}$  and  $25^{\circ}$ .** F. A. FREETH (*Dissertation, Leiden, 1924*).—This investigation was undertaken primarily with a view to discover the best method of preparing ammonium perchlorate from sodium perchlorate.

The binary systems not previously examined,  $\text{H}_2\text{O--NaClO}_4$  and  $\text{H}_2\text{O--NH}_4\text{ClO}_4$ , have been studied. Sodium perchlorate forms a monohydrate, the transition point to the anhydrous salt being  $50.8^{\circ}$ . The four ternary systems, from which the quaternary system is built up, have also been considered. The existence of the double salt,  $\text{Na}_2\text{SO}_4, (\text{NH}_4)_2\text{SO}_4, 4\text{H}_2\text{O}$ , at  $25^{\circ}$  (Dawson, T., 1918, **113**, 675; Matignon and Meyer, A., 1918, ii, 66, 302), has been confirmed, but it is not obtained at  $60^{\circ}$ . Finally data are given for the quaternary equilibria in the reciprocal salt pair at the two temperatures considered, and methods are deduced for the separation of the different pairs of salts. It is also shown that, when equivalent quantities of sodium perchlorate and ammonium sulphate interact, sodium sulphate separates out at  $60^{\circ}$  and ammonium perchlorate on cooling. From a study of the quaternary diagrams, the author concludes that the preparation of ammonium perchlorate by this method is most efficient when the initial solution contains equivalent quantities of the salts. The mother-liquor may be used to treat further quantities of salt.

A general rule is given for the preparation of equivalents of incompatibles from any reciprocal salt pair.

M. S. B.

**Photochemical Studies. II. Reduction of Silver Bromide in the Presence of Gelatin.** A. REYCHLER (*Bull. Soc. chim. Belg.*, 1924, **33**, 7—12).—The presence of gelatin prevents the reduction of silver bromide in the dark by the three developers examined—potassium ferrous oxalate, quinol, and metol—quinol. The presence of gelatin inhibits reduction by the oxalate even in the light; with quinol, reduction is incomplete even on prolonged exposure to the light. In the case of metol—quinol reduction takes place in the light even in the presence of gelatin. The gelatin appears to form on the silver salt a very thin protective layer which can be ruptured by mechanical or actinic means (cf. following abstract).

R. B.

**Photochemical Studies. III. Reduction of Silver Bromide in the Photographic Plate.** A. REYCHLER (*Bull. Soc. chim. Belg.*, 1924, **33**, 12—16).—Development of an emulsion before and after exposure to the light confirmed the previous observation (preceding abstract) that in the dark the gelatin prevents the reduction of the silver bromide. [Cf. B., 1924, 356.]

R. B.

**Hydrates of Calcium Oxide.** R. T. HASLAM, G. CALINGAERT, and C. M. TAYLOR (*J. Amer. Chem. Soc.*, 1924, **46**, 308—311).—The solubility curve of calcium oxide in water has been redetermined, but no evidence was obtained for the existence of the dihydrate (cf. Karcz, *Chem.-Ztg.*, 1898, **22**, 38); its attempted preparation was also unsuccessful, the monohydrate with up to 7% of adsorbed water being always obtained. H. T.

**Hydration of Anhydrite. III.** G. WEISSENBERGER and B. SOINI (*Koll.-Z.*, 1924, **34**, 40—48; cf. this vol., ii, 109).—The influence of a number of electrolytes on the viscosity of anhydrite suspensions of various concentrations has been examined. The action is to a great extent dependent on the concentration, and may be either positive or negative. There exists for each electrolyte a concentration at which its action is strongest. The position of the maximum is dependent on the temperature, but for a given temperature it is constant. J. F. S.

**Preparation of Calcium Persulphate.** A. H. ERDENBRECHER (*Chem.-Ztg.*, 1924, **48**, 189).—The salt may be extracted by means of absolute ethyl alcohol from the dried mixture resulting from the action of ammonium persulphate on calcium oxide. [Cf. *B.*, 1924, 377.] S. I. L.

**Behaviour and Properties of Magnesium Oxide from Different Sources.** M. LE BLANC and K. RICHTER (*Z. physikal. Chem.*, 1923, **107**, 357—402).—Magnesium oxide has been prepared under identical conditions from light and heavy basic magnesium carbonate, normal magnesium carbonate, magnesium ammonium carbonate, magnesite, and magnesium nitrate. These starting materials were all prepared under reproducible conditions, and their chemical composition and relative volumes determined. In the conversion of finely crystalline substances into the oxide, the external appearance is unchanged, and in cases where sintering took place, this is not in relation to the reduction of the mass. It is therefore concluded that the microscopic secondary particles must be composed of a large number of primary particles, and since röntgenographic investigation shows that all forms of magnesium oxide possess a cube structure, the secondary particles must be produced by an aggregation of the primary particles. The individual oxides differ much in their relative dry volumes, and in the volume under pressure, which indicates that the secondary particles and the pores must have very different volumes. The stability of the secondary particles is very great. The densities of the various specimens differ, and this is attributed to the differences in the volumes of the pores. The much greater differences, recorded in the literature, between the various specimens are to be explained by the incomplete removal of air from the specimens. The highest value found for the density, 3.59, agrees well with the value calculated from röntgenographic measurements. The active surface, as determined by the adsorption of dyes, differs very much with various specimens, just as does the adsorptive power.

From this it is concluded that the size of the primary particles must be different in the different cases, since these determine the size of the active surface. The power of hydration of the various oxides has been determined. All oxides give an S-shaped hydration curve. The velocity of combination with water in the case of the oxide from basic carbonates is dependent on the method of formation of the basic carbonate. The presence of electrolytes, particularly alkalis, during the precipitation, reduces the power of hydration. A too long or a too short heating of the precipitate in contact with the solution also reduces the ease of hydration. This is attributed to the more or less strongly marked coagulation of the carbonate particles by the electrolytes. A prolonged washing increases the ease of hydration because of an increased dispersion produced by this means, whilst the presence of impurities such as the sodium and sulphate ions decreases the power of hydration. The rate of solution of the oxides in various acids is dependent on the size of the external surface of the secondary particles. The difference in the rate of solution of the oxides is also found in the rate of solution of the hydroxides prepared from these oxides. From the smaller rate of solution of the hydroxide in comparison with the rate of solution of the oxide, it is concluded that the solution of the latter does not take place through the hydroxide. The electrical conductivity of saturated solutions of magnesium oxide in contact with the solid oxide is greater than the value obtained when the solid oxide has been all converted into the hydroxide.

J. F. S.

**Fractional Crystallisation of Common Lead.** R. H. ATKINSON (*Nature*, 1924, **113**, 495; cf. A., 1923, ii, 689).—The fractions of lead previously obtained have absolute  $d_{20}^{20}$  11.358 and 11.327, respectively, the freezing points being identical. Whilst the reality of the corresponding differences in the atomic weight is not yet beyond doubt, the results for the two fractions fall on the periodic atomic volume curve. Similar considerations may apply to gallium (cf. Richards and Craig, A., 1923, ii, 495).

A. A. E.

**Polymorphous Forms of Lead Oxide.** V. KOHLSCHÜTTER and P. SCHERRER (*Helv. Chim. Acta*, 1924, **7**, 337—341).—In a previous paper, it was suggested that yellow lead oxide is always formed from a molecular state of division, that is, from solution or from the vapour, whilst the red form is produced by topochemical reactions (A., 1923, ii, 164). According to this view, the two kinds of lead oxide are polymorphic forms, differing in molecular complexity, but Glasstone (T., 1921, **119**, 1689, 1914) considers that the difference is optical, depending on the state of subdivision of the oxide. If this were the case, however, the yellow form should be red by transmitted light, which is not the case. Examination of the two forms with X-rays shows that they are structurally different. Preparations made following Glasstone's directions are found to be inhomogeneous. His solubility determinations, therefore, always gave the same result since he determined that of the more soluble form. Appleby (T., 1922,



**121**, 2129) found different solubilities and densities for the two forms. The transition point from red to yellow found by Jaeger and Germs (A., 1922, ii, 65) at  $587^{\circ}$  could not be confirmed. The change occurs somewhere in the neighbourhood of this temperature, but not the reverse change. The conditions used by Jaeger and Germs favour the oxidation of lead oxide to red lead. Glasstone claimed that, by heating large crystals of lead hydroxide,  $3\text{PbO}\cdot\text{H}_2\text{O}$ , yellow lead oxide is obtained, and red from small crystals, but experiment shows that the yellow oxide is formed through water being retained internally and dissolving the oxide, forming a solution from which the yellow form is deposited. When the hydroxide is heated in a vacuum so that the water is readily removed, only the red, pseudomorphic form is obtained. No structural similarity could be found between the hydroxide  $3\text{PbO}\cdot\text{H}_2\text{O}$  and the red oxide by X-ray examination.

E. H. R.

**Light Sensitivity of Cuprous Oxide and Selenium.** V. P. BARTON.—(See ii, 292.)

**Photo-chemical Properties of Cuprous Oxide.** A. GARRISON (*J. Physical Chem.*, 1924, **28**, 279—284; cf. A., 1923, ii, 728).—Conductivity determinations, made to ascertain whether, in view of the change of potential of cuprous oxide electrodes under illumination, the solubility of cuprous oxide alone in water is increased by the action of light, show no difference between the values in the dark and in the light.

It had previously been observed that the potential of a cuprous oxide electrode, in 0.1N-potassium sulphate solution against a 0.1N-calomel electrode, depends on the thickness of the layer of oxide covering the copper core, being less negative for a thin layer than for a thick one. When a thinly coated electrode is illuminated by white light, a positive photo-potential is set up, but this is replaced by a negative one, which may become very great, with increasing thickness of oxide. This effect is ascribed to the diminishing "concentration" of metallic copper in contact with the electrolyte. If the more heavily coated electrodes be scratched the potentials approach those of the thinly coated ones. A repetition of the conductivity experiments using a fine suspension of copper, treated so that the particles are coated with cuprous oxide, and therefore comparable with the cuprous oxide electrode, has shown a definite increase of solubility of the oxide under the influence of light. The conductivity of a copper suspension, with a cuprous chloride coating partly hydrolysed to cuprous oxide, is reduced by light.

A positive photo-potential probably results when the electrode potential is determined by the reaction  $\text{Cu}^+ \rightleftharpoons \text{Cu} + \oplus$ . This happens when solid copper and cuprous oxide are present. A negative photo-potential results when the potential is determined by the reaction  $2\text{O}^{2-} \rightleftharpoons \text{O}_2 + 4\ominus$ , i.e., when the amount of copper is infinitely small. A temporary negative photo-potential may also be realised by the reaction  $\text{Cu}^+ \rightarrow \text{Cu} + \oplus \rightarrow \text{Cu}^{++} + \ominus$ .

It is suggested that, in the cuprous oxide suspensions, a more

negative potential is developed, as in the electrodes with the thick coating. Thus although, as was shown by the oxidised copper suspensions, the solubility of the cuprous oxide is increased by light, the positively charged cuprous ions will be prevented from leaving the negatively charged particle. The positive photo-potential where copper is present would not mask the change in conductivity.

In the system  $\text{Cu}_2\text{Cl}_2\text{--Cu}_2\text{O--Cu--H}_2\text{O}$  the reaction is  $\text{Cu}_2\text{Cl}_2 + \text{H}_2\text{O} \xrightleftharpoons[\text{dark}]{\text{light}} \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{Cl}^-$ . The system in the dark will have the higher conductivity.

The results obtained appear to confirm Baly's theory (A., 1915, ii, 440) that the molecular "force fields" are opened by radiations in the same manner in which they are opened by a solvent.

M. S. B.

**Action of Nitrogen Peroxide on Cuprous Oxide.** J. R. PARTINGTON (*J. Chem. Soc.*, 1924, **125**, 663—665).—The cuprous oxide formed in the primary action of nitrogen peroxide on copper (cf. this vol., ii, 183) is not a peculiar active form, since the anhydrous, ignited crystalline oxide obtained from several sources takes up 30% of its weight of nitrogen peroxide in 48 hours without any indication of chemical change. There is no change in the appearance of the cuprous oxide; no reduction of the nitrogen peroxide, and no rise in temperature is observed. The product evolves a small quantity of nitrogen peroxide on keeping in a closed tube and reacts violently with water. Cuprous oxide has no visible action on liquid nitrogen peroxide.

J. W. B.

**Hardness of Amalgams of Tin, Lead, Zinc, Cadmium, and Copper, and of the Ternary Amalgam Silver-Tin-Mercury.** G. TAMMANN and Q. A. MANSURI (*Z. anorg. Chem.*, 1924, **132**, 65—76).—The addition of mercury to lead, tin, cadmium, and zinc results in the formation of solid solutions within limits, the amalgams formed being harder than the metal. This increase in hardness passes through the maximum attained with the following weight-percentages of mercury added to the metal named: (1) lead, 5%; (2) tin, 5.2%; (3) cadmium, 7.6%, and (4) zinc, 25%. With copper, the compound  $\text{CuHg}$  and one of unknown composition are formed (Stassfurth, "Jahrb. philos. Fakultät Gottingen," 1922, 57). The maximum hardness is attained with about 34% of copper, but its magnitude depends on the previous history of the amalgam.

An alloy of 50% of tin and 50% of silver reaches a maximum hardness when approximately 30% of mercury is added. An increase in the silver content also increases the hardness. H. T.

**Crystalline Structure of Corundum and Hæmatite.** C. MAUGUIN (*Compt. rend.*, 1924, **178**, 785—787).—If Bragg's structures for corundum and hæmatite crystals are accepted, the oxygen atoms in these substances cannot have the same periodic distribution as those of aluminium and iron. An X-ray examination showed that the atoms are arranged in two enantiomorphic lattices, one right- and one left-handed (cf. A., 1923, ii, 417).

E. E. T.

**Product of the Dehydration of Kaolin.** V. AGAFONOFF and W. VERNADSKY (*Compt. rend.*, 1924, **178**, 1082—1084).—The density of the product obtained by heating kaolin at 450—550° was 2·32—2·38. It is homogeneous, soluble in acids, and is considered to have the formula  $\text{Al}_2\text{Si}_2\text{O}_7$ . A. B. H.

**Arc Spectrum of Iron.** F. M. WALTERS.—(See ii, 285.)

**Magnetic Properties of Steel.** A. W. SMITH, E. D. CAMPBELL, and W. L. FINK.—(See ii, 293.)

**Desulphurisation of Iron Pyrites.** F. C. THOMPSON and N. TILLING (*J. Soc. Chem. Ind.*, 1924, **43**, 37—46r).—Iron pyrites is practically completely desulphurised in dry air between 800° and 900°; in air saturated with steam the rate of removal of sulphur is greater below 650°, and smaller above that temperature, than the rate in dry air. In steam alone iron pyrites commences to lose sulphur at 380° and the desulphurisation curve then rises steeply to 500°, then more slowly to 680°, at which temperature the solid phase consists of ferrous sulphide, which, on further heating, is oxidised to ferrosiferrous oxide, whilst the issuing gases contain hydrogen and hydrogen sulphide. Below 900° carbon dioxide exerts no oxidising action on iron pyrites, but dissociation into sulphur and ferrous sulphide commences at 580° and is complete at 670°. In carbon monoxide, sulphur begins to be removed at 350°, and the rate increases to 590°, when ferrous sulphide is left; apparently carbon oxysulphide is formed at the lower temperatures. In hydrogen, the action starts at 440°, and at 530° pyrites is completely converted into ferrous sulphide. From determinations of the soluble sulphur content of the residue after heating iron pyrites in air at different temperatures, it appears that a soluble sulphur compound, probably a persulphate, is an intermediate product in the oxidation of pyrites to iron oxide. The amount of persulphate formed increases to a maximum at 430°, at which temperature the amount of soluble sulphur present is also a maximum and the partial pressure of the sulphur trioxide in the gases begins to increase rapidly. The determination of the partial pressures of sulphur dioxide and sulphur trioxide during the oxidation indicates that a persulphate is first formed; this then decomposes into ferric oxide and sulphur trioxide. At higher temperatures, the proportion of sulphur dioxide formed by direct combustion of part of the sulphur increases and at 430° ferrous sulphate is formed, thus:  $\text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3 = 2\text{FeSO}_4$ . At 525°, the ferrous sulphate begins to decompose again, whilst the sulphur trioxide thus liberated also decomposes into oxygen and sulphur dioxide. A. R. P.

**Comparison of the Atomic Weights of Terrestrial and Meteoric Cobalt.** V. Analysis of Cobaltous Chloride. G. P. BAXTER and M. J. DORCAS (*J. Amer. Chem. Soc.*, 1924, **46**, 357—366).—The atomic weights of cobalt of meteoric and terrestrial origin have been redetermined from the ratio  $2\text{Ag} : \text{CoCl}_2$ . Both varieties were found to give identical values, namely, 58·94 ( $\text{Ag} = 107·880$ ;  $\text{Cl} = 35·458$ ). This value is 0·03 unit lower than that

previously found by Richards and Baxter (A., 1900, ii, 78) and by Baxter and Coffin (A., 1906, ii, 858). H. T.

**Sulphito-cobaltammines.** E. H. RIESENFELD (*Z. anorg. Chem.*, 1924, **132**, 99—116).—An attempt is made to arrange systematically all the known sulphito-cobaltammines according to the number of sulphito groups present. With the exception of the complexes,  $[(\text{SO}_3)\text{Co}(\text{NH}_3)_3\text{H}_2\text{O}]^+$ ,  $[(\text{SO}_3)_2\text{Co}(\text{NH}_3)_2]^+$ ,  $[\text{Co}(\text{SO}_3)_3]^{3-}$ , the bivalent sulphito group fills only one co-ordination position (cf. Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3rd ed., 1913, 55). The sulphito group in these exceptional cases may occupy two positions, or the hexahedral arrangement of the groups about the central atom may pass into the tetrahedral arrangement. There is some experimental evidence in favour of the latter view.

New sulphito compounds having the following formulæ have been prepared and described :

$[\text{Co}(\text{NH}_3)_5\text{SO}_3]_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$ ;  $\text{NH}_4[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2]$ ,  
 $\text{NH}_4[\text{Co en}_2(\text{SO}_3)_2]$ ,  $\text{NH}_4[\text{Co pn}_2(\text{SO}_3)_2]$  (pn = propylenediamine),  
 $(\text{NH}_4)_3[\text{Co}(\text{NH}_3)_3(\text{SO}_3)_3]$ , and  $\text{Co}[\text{Co}(\text{NH}_3)_3(\text{SO}_3)_3]$ . H. T.

**Magnetisation of Nickel-Chromium Alloys above the Curie Point.** J. ŠAFRÁNEK (*Rev. Mét.*, 1924, **21**, 87—111).—The magnetic susceptibility of chromium prepared by electrolysis of chromium sulphate was found to be  $4.31 \times 10^{-6}$  between  $100^\circ$  and  $600^\circ$ ; that of pure nickel agreed with results obtained by earlier investigators. The specific magnetisation of nickel-chromium alloys was found by extrapolation to be zero for the alloy containing 13% Cr at absolute zero. This corresponds with the compound  $\text{CrNi}_6$ , but no confirmation of the existence of this compound could be obtained from micrographic examination. [Cf. B., 1924, 220, 385.] A. R. P.

**Electrolytic Production of Cobalt and Nickel Triacetates from the Diacetates, and of Nickel Trichloride.** C. SCHALL and H. MARKGRAF (*Trans. Amer. Electrochem. Soc.* [advance copy], 1924, **45**, 119—128).—Nickel and cobalt diacetates were dissolved in anhydrous acetic acid (specific conductivity  $0.6 \times 10^{-8}$  at  $18^\circ$  and  $1.1 \times 10^{-8}$  at  $25^\circ$ ), prepared by distilling 99.6% acid over triacetyl boride, and conductivity measurements made, a table of which is given; the results were compared with those obtained for lead (cf. Schall and Melzer, A., 1923, i, 87). Solutions were then made and electrolysed at  $65^\circ$  with platinum electrodes (96—99 volt, 0.007—0.009 amp. for six hours). The cobalt solution changed in colour from red to green and the nickel from light green to dark green. By evaporation, keeping the conditions anhydrous throughout, the two triacetates were isolated as well-defined green crystals. If the 99.6% acetic acid were used only green syrups were obtained. Conductivity data support the conclusion that the compounds have the simple formulæ  $\text{Co}(\text{CH}_3\text{CO}_2)_3$  and  $\text{Ni}(\text{CH}_3\text{CO}_2)_3$ , respectively. Nickel trichloride was obtained as green crystals either by

dissolving pure nickel trioxide in concentrated hydrochloric acid or by electrolysis a solution of nickel dichloride in the acid. W. A. S.

**Arc Spectrum of Chromium.** H. GIESELER.—(See ii, 285.)

**Absorption Spectrum of Chromium and Iron Vapours.** H. GIESELER and W. GROTRIAN.—(See ii, 287.)

**Germanium. VII. Hydrides of Germanium.** L. M. DENNIS, R. B. COREY, and R. W. MOORE (*J. Amer. Chem. Soc.*, 1924, **46**, 657—674).—The hydrides of germanium were prepared by decomposing magnesium germanide (obtained by heating 3 parts of germanium with 2 parts of arsenic-free magnesium) by slow addition of dilute hydrochloric acid in an atmosphere of hydrogen. The apparatus was similar to that used by Stock (A., 1916, ii, 319), and to test it some of the latter's work on mono- and di-silicane was repeated and confirmed. The subsequent fractionation of the condensed germanium hydrides yielded monogermene,  $\text{GeH}_4$ , digermene,  $\text{Ge}_2\text{H}_6$ , and trigermene,  $\text{Ge}_3\text{H}_8$ . A liquid residue remained, indicating the probable existence of higher hydrides. Only 22.7% of the germanium used was converted into hydrides, and of this 73.6% appeared as monogermene and 1% as trigermene.

*Digermene*,  $\text{Ge}_2\text{H}_6$ , is a colourless liquid, m. p.  $-109^\circ$ , b. p.  $29^\circ$ , and  $d_{-109}^{20} 1.98$ . In air, it turns yellow, then light brown and finally becomes a dark brown solid. On ignition, the vapour burns with explosive violence and the liquid burns with great rapidity, leaving a reddish-brown residue with black and white streaks. The hydride is not spontaneously inflammable, although one exception to this was noticed at reduced pressures. The action of oxygen on digermene produces a white solid which sublimes on to the walls of the containing vessel and after a time turns yellow. Liquid digermene reacts with water after a time to produce (in the water layer) a gelatinous substance which gradually turns yellow and then light brown; the liquids do not mix and a gas is evolved at the liquid interface. With 33% sodium hydroxide solution the liquid hydride reacts to produce a combustible gas which could not be recognised (distinction from monogermene). Liquid digermene mixes with carbon tetrachloride with evolution of heat, a clear solution being formed, depositing a white solid in air.

*Trigermene*,  $\text{Ge}_3\text{H}_8$ , is a liquid, m. p.  $-105.6^\circ$ , b. p.  $110.5^\circ$ , and  $d_{-105.6}^{20} 2.20$ . It burns readily in air, leaving a voluminous residue streaked with black, brown, and white. On exposure to air, it rapidly changes to a white solid. The behaviour towards oxygen and carbon tetrachloride resembles that of digermene, and with water a white oxidation product forms at the surface of the latter. No action occurred with 33% sodium hydroxide solution.

The dissociation temperature of digermene is  $218^\circ$  and of trigermene  $194^\circ$ , both at 200 mm. S. K. T.

**Preparation of the Double Fluorides of the Metals of the Platinum Group and Absorption Spectra of the Halogenoplatinates.** H. I. SCHLESINGER and M. W. TAPLEY (*J. Amer. Chem. Soc.*, 1924, **46**, 276—287).—By heating finely divided

platinum and iridium with the compound  $3\text{KF}\cdot\text{HF}\cdot\text{PbF}_4$ , the double fluoride of potassium and platinum,  $\text{K}_2\text{PtF}_6$ , and the double fluorides of iridium and lead and potassium,  $\text{K}_2\text{IrF}_6$  and  $\text{PbIrF}_6$ , were obtained in the crystalline condition. The absorption spectra of the double halides of platinum and potassium have been investigated and photographed.

H. T.

**Ruthenium Dichloride.** J. L. HOWE, J. L. HOWE, jun., and S. C. OGBURN, jun. (*J. Amer. Chem. Soc.*, 1924, **46**, 335—342).—By passing a mixture of chlorine and carbon monoxide over heated finely divided ruthenium, a brown powder consisting mainly of ruthenium dichloride was obtained. This dichloride is insoluble in most solvents, but readily dissolves in aqueous alcohol, giving a blue solution similar to that produced by the action of reducing agents on ruthenium trichloride; the solution is slightly ionised, but not colloidal.

H. T.

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### Analytical Chemistry.

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**A Simple Automatic Pipette.** G. A. HARRISON (*Biochem. J.*, 1924, **18**, 188—189).

**Modified Hempel Pipette.** A. HEFTER (*Chem.-Ztg.*, 1924, **48**, 142).—To avoid the difficulty and unpleasantness of filling a double Hempel pipette (with four bulbs), a T-piece is provided at the top of the third bulb, the upright arm being stoppered and the horizontal arm connecting with the second bulb.  
A. R. P.

**Burner for Elementary Micro-analysis.** E. APPELT and W. HOFFMEISTER (*Chem.-Ztg.*, 1924, **48**, 186).—By the employment of a burner which allows of the individual adjustment of a number of separate small flames, it is possible to regulate the heating in the same way as in ordinary analysis.  
S. I. L.

**Apparatus for the Determination of Melting and Freezing Points of Pure Substances and of Eutectic Mixtures.** E. W. WASHBURN (*Ind. Eng. Chem.*, 1924, **16**, 275).—The apparatus comprises a cylindrical Dewar flask with the inner wall narrowed down at the bottom so that a comparatively small amount of substance is sufficient completely to cover the bulb of a thermometer inserted in the flask. The walls of the flask are left unsilvered so that the thermometer can be read through them and no stem correction is necessary.  
H. C. R.

**Apparatus for the Analysis of "Oleum" and other Fuming Liquids.** E. BOSSHARD (*Helv. Chim. Acta*, 1924, **7**, 330—332).—The apparatus described is designed for weighing out and decomposing with water such liquids as fuming sulphuric acid (oleum), chlorosulphonic acid, phosphorus trichloride, etc., which, in the course of the operations, give off acid fumes. A 150 c.c. weighing

bottle, of quartz or Jena glass, has a glass stopper which may be replaced by two contrivances. The first is a stopper carrying two tubes so arranged that the liquid to be analysed can be sucked into the bottle. The second is a stopper on which is carried a bulb of 130 c.c. capacity delivering by a cock and glass tube to the bottle. Above this bulb is a second, communicating with the first by a tube descending nearly to the bottom of the latter; a return air-tube passes from the bottle to the first bulb. Water can be dropped slowly from the first bulb into the bottle, and air, carrying fumes, passes from the bottle into the first bulb, where it is trapped and forces water into the second bulb, which is filled with wet glass beads. Escape of acid fumes is thus prevented. When dilution of the acid is complete, the solution can be washed out of the apparatus and analysed. For analysing chlorosulphonic acid, the latter should be mixed in the weighing bottle with three times its weight of quartz sand before decomposing with water. E. H. R.

**Electrolytic Purification of Precipitates.** A. CHARRIOT (*Compt. rend.*, 1924, 178, 934—936).—When an insoluble substance, holding absorbed a soluble substance, is subjected to the influence of an electric current, the absorbed substance passes completely into solution and travels towards the electrode of opposite sign to that which it itself bears. By taking advantage of this phenomenon, it is possible to free precipitates from entrained soluble salts. Thus, precipitated aluminium hydroxide may be purified from chromic acid, permanganic acid, sulphuric acid, lime, or baryta, and ferric oxide from chromic acid. The precipitate may be filtered through a Gooch crucible and when it collects and prevents the liquid from passing through readily, two electrodes are placed, one beneath the bottom of the crucible and the other in the liquid in the crucible; passage of a direct current in one direction or the other then results in the elimination of the contaminating acid or base together with a few c.c. of water. In this manner, 3.7% of chromic acid was removed from a precipitate of 0.42 g. of aluminium hydroxide in 10 minutes, a current of 0.1 ampère being used. Another method of procedure consists in flattening the filter-paper containing the precipitate and placing it in a narrow cell between two sheet platinum electrodes. The above methods are applicable only to precipitates which are completely insoluble, slightly soluble precipitates like barium sulphate undergoing gradual dissociation and dissolution under the influence of the current. T. H. P.

**Arc Spectrum of Silicon in Relation to Spectrographic Analysis.** C. PORLEZZA (*Atti R. Accad. Lincei*, 1924, [v], 33, i, 193—197).—The results are given of measurements of about 70 lines comprising the silicon band  $\lambda = 2414.0$  (A., 1923, ii, 198, 448), and the appearances of the band spectrum of silicon in the spectrographs of various rocks with different contents of silica are described. For purposes of spectrographic analysis it may become necessary to eliminate the silica from minerals containing it in large proportion.

T. H. P.



**Determination of Hydrogen-ion Concentration by a Spectrophotometric Method and the Absorption Spectra of certain Indicators.** W. R. BRODE (*J. Amer. Chem. Soc.*, 1924, **46**, 581—596).—Change of hydrogen-ion concentration in a solution containing an indicator does not shift the absorption band as regards wave-length, but merely changes the height (intensity of absorption). By comparing the heights of the absorption bands in an unknown solution containing an indicator with those in a buffer containing the same indicator, the hydrogen-ion concentration of the solution is readily obtained. The most suitable general indicators covering the range  $p_H$  1 to 10 are thymol-blue ( $p_H$  1.0 to 3.5 and 7.5 to 10.0) and a mixture of methyl-red and bromothymol-blue, the latter covering the blank range of the former.

The results show definitely that whilst for phthalein- and azo-dyes the absorption band does not shift in wave-length, but simply changes in intensity as the hydrogen-ion concentration changes, this is not true for methyl-violet, a triphenylmethane dye (cf. Holmes, this vol., ii, 138). A secondary band also appears on the disappearance of the primary band, and at certain hydrogen-ion concentrations equilibrium exists between the heights of the two bands. These results confirm the theory that a definite configuration and frequency of vibration exist for each colour of a certain substance (cf. T., 1922, **121**, 1555) although they do not support the idea that intermediate coloured products exist between any two principal coloured modifications. For each indicator all the curves of various  $p_H$  values cross in a point about midway between the centres of the two bands in changing from one coloured form to another. The dissociation constants of the indicators studied, determined photo-metrically, are in good agreement with published values.

S. K. T.

**Spectrophotometric Determination of Hydrogen-ion Concentrations and of the Apparent Dissociation Constants of Indicators. I. Methods.** W. C. HOLMES (*J. Amer. Chem. Soc.*, 1924, **46**, 627—631).—The degree of transition of an indicator which is coloured in only one of its forms may be defined by a ratio  $R_1$ , which, for indicators behaving essentially as monobasic acids or monoacid bases, represents the percentage colour transformation. With two-colour indicators, two separate ratios of this type may be adopted or, alternatively, another ratio,  $R_2$ , that of the intensities of absorption at two wave-lengths selected at or near the respective maxima of the two absorption bands in question. Absorption curves obtained by preliminary determinations of  $R_2$  on two indicators are given, viz., sodium 1-naphthol-2-sulphonate indo-phenol ( $R_2$  = ratio of intensity of absorption at  $550\mu\mu$  to that at  $625\mu\mu$ ) and phenolsulphonephthalein ( $R_2$  = ratio of intensities of absorption at  $460\mu\mu$  and  $560\mu\mu$ , respectively). Regular variations between  $p_H$  and  $R_2$  are observed in each case. By determination of  $R_2$  in suitable buffers, this spectrophotometric method may be applied to the determination of hydrogen-ion concentrations, the most suitable indicators for this use being found among the

indophenols. This empirical calibration affords data which, for indicators behaving like monobasic acids, gives a method of determining the approximate form of the dissociation curves of the indicator (cf. A., 1920, ii, 382). S. K. T.

**Colorimetric Determination of Acidity of Soils.** R. M. BARNETTE, F. C. GERRETSEN, D. J. HISSINK, and J. VAN DER SPEK (*Chem. Weekblad*, 1924, 21, 145—147).—A comparison of the results obtained with 32 samples of soil, in which the acidity was determined both electrometrically and colorimetrically, gave satisfactory agreement, the average difference in the values for  $p_H$  by the two methods being 0.19. For the colorimetric determinations, the aqueous suspensions were separated by means of a centrifuge running at 8500 r.p.m.; the indicators used were methyl-red, bromophenol-blue, bromocresol-purple, and, in two cases only, phenol-red.

S. I. L.

**Solubility of Atmospheric Gases in Solutions of Ammonium Chloride.** J. H. COSTE and E. R. ANDREWS (*J. Physical Chem.*, 1924, 28, 285—286; cf. MacArthur, A., 1916, ii, 428).—Winkler's manganous method cannot be used for determining dissolved oxygen in the presence of ammonium salts. M. S. B.

**Determination of Chlorine by Volhard's Method in Presence of Colloids.** I. M. KOLTHOFF and O. TOMIČEK (*Chem. Weekblad*, 1924, 21, 106—107; 124—125).—The work of van der Burg and Koppejan (this vol., ii, 271) is contradicted. In presence of colloids, the end-point is vague and inaccurate if determined by the change of colour with ferric salts, although in no case was it found that all the silver chloride could be transformed into thiocyanate. In acid solution, however, the potentiometric method gives accurate results under all conditions. In the second paper, a curve previously omitted is included.

S. I. L.

**Influence of some Colloids on the Titration of Chlorides by Volhard's Method.** B. VAN DER BURG and C. A. KOPPEJAN (*Chem. Weekblad*, 1924, 21, 167).—A reply to the criticism of Kolthoff and Tomiček (preceding abstract) on an earlier paper of the authors (this vol., ii, 271). The colour alteration is gradual, and the end-point therefore arbitrary.

S. I. L.

**Potentiometric Determination of Chlorides in Presence of Colloids.** F. LIEBERT (*Chem. Weekblad*, 1924, 21, 167—169).—The statement of Kolthoff and Tomiček (above) that potentiometric determination is accurate in presence of colloids is true only in the case of soluble starch, the only colloid examined by these authors. In presence of proteins, the potential curves show very indefinite transitions, and end-points deduced from the middle points of the curves give inaccurate results.

S. I. L.

**Use of Amalgamated Zinc in the Evolution Method for the Determination of Sulphur in Iron and Steel.** T. ASHIDA (*J. Chem. Soc.*, 1924, 125, 665—668).—Trustworthy results for the

determination of sulphur in iron and steel by the evolution method are obtained by the use of hydrochloric acid, *d* 1.15—1.20, and amalgamated zinc, the hydrogen evolved preventing the oxidation of the hydrogen sulphide. Hydrogen chloride is removed from the gases by washing first with hot water and then with cold, and the hydrogen sulphide passed into an ammoniacal cadmium chloride solution, the sulphur being determined in the precipitated cadmium sulphide by titration with iodine and thiosulphate. The hydrogen sulphide in the cold water wash-bottle is determined separately.

J. W. B.

**Determination of Nitrogen in Cotton.** B. P. RIDGE (*J. Text. Inst.*, 1924, **15**, 94—103T).—Volumetric and colorimetric methods for the determination of nitrogen in cotton are described and data relating to the nitrogen contents of raw and bleached cotton obtained by these methods are discussed. The determination is carried out by a Kjeldahl process, the resulting ammonia being determined by direct titration with a standard acid or colorimetrically by means of a Nessler solution and a Kober-Klett colorimeter. The nitrogen content of Egyptian cottons is about 0.3%, and of American cotton about 0.2%, the proportional difference being less than that observed between their phosphorus contents (*infra*) and therefore not suitable for the differentiation of these two types of cotton. Immature cotton contains more nitrogen than mature cotton. [Cf. B., 1924, 371.]

A. J. H.

**[Determination of the] Phosphorus Content of Cotton.** A. GEAKE (*J. Text. Inst.*, 1924, **15**, 81—93T).—The ash of cotton is dissolved in sulphuric acid, the phosphorus precipitated as yellow strychnine phosphomolybdate by addition of a specially prepared solution of strychnine molybdate, the liquid centrifuged, and the volume of the precipitate compared with that produced under similar conditions from a standard phosphate solution. Strychnine molybdate is preferred to ammonium molybdate, since it gives a much more voluminous precipitate. The phosphorus content of raw cotton varies between 0.04% and 0.13% calculated as  $P_2O_5$ , and although the environment of the plant has a definite effect on the phosphorus content, it is not sufficient to prevent American and Egyptian cottons from being distinguished in this way. Immature cotton contains more phosphorus than mature cotton. [Cf. B., 1924, 371.]

A. J. H.

**Distillation of Arsenious, Antimonious, and Stannic Chlorides.** W. BÖTTGER.—(See ii, 333.)

**Volumetric Analysis of Sodium Hydrogen Carbonate containing Sodium Carbonate.** J. C. CHIARINO (*Anal. Fis. Quím.*, 1924, **22**, 69—71).—The method depends on the reaction between sodium hydroxide and sodium hydrogen carbonate, whereby sodium carbonate is formed, which can be precipitated by barium chloride. A determination of total alkalinity is followed by a determination of the change of alkalinity of a solution containing

sodium hydroxide and barium chloride, when added to the solution under examination.  
G. W. R.

**Volumetric Determination of Ammonium Salts.** V. AUGER (*Compt. rend.*, 1924, **178**, 1081—1082).—The determination depends on the fact that if sodium hydroxide is added to a solution of an ammonium salt to which Nessler's reagent has been added, no brown coloration is produced until sufficient alkali has been added to decompose the ammonium salt, but a slight excess gives a permanent brown coloration. The method gives excellent results within the usual limits of dilution provided sufficient reagent is added.  
A. B. H.

**Critical Studies on Methods of Analysis. IX. Calcium.** L. A. CONGDON, W. P. EDDY, jun., and E. S. MILLIGAN (*Chem. News*, 1924, **128**, 244—248).—Comparative analyses of pure calcium acetate by ten different methods showed that calcium may be determined with equal accuracy by precipitation and weighing as tungstate, carbonate, or sulphate or by precipitation as oxalate followed by ignition to, and weighing as, oxide. Conversion of calcium salts of volatile acids into sulphate by evaporation with a slight excess of sulphuric acid and gentle ignition invariably yields high results, whilst precipitation of the fluoride gives low results.  
A. R. P.

**Separation of Zinc from Iron and Aluminium.** E. G. R. ARDAGH and G. R. BONGARD (*Ind. Eng. Chem.*, 1924, **16**, 297—299).—The iron and aluminium are precipitated together by means of ammonia solution and ammonium chloride and the zinc is then titrated with standard ferrocyanide solution. The iron and aluminium hydroxides may be precipitated in a compact state by evaporating the original solution to a very small volume before adding ammonium chloride and ammonia.  
H. C. R.

**Determination of Lead in Potable Waters and in Urine.** J. C. THRESH (*Analyst*, 1924, **49**, 124—128).—In determining small quantities of lead in water by the author's method (A., 1921, ii, 551), the gelatin-acid solution is preferably made up by dissolving 0.1 g. of gelatin in 30 c.c. of acetic acid (B.P.) and 70 c.c. of water below the boiling point of the mixture. One c.c. of this reagent is used to 50 c.c. of the water to be examined. The presence of copper or iron reduces the sensitiveness of the test. For determining minute quantities of lead in urine, the urine is heated nearly to boiling and rendered alkaline with sodium carbonate. The precipitate is dissolved in dilute acetic acid and the solution is tested with gelatin-acetic acid and hydrogen sulphide, the colour produced being compared with a control.  
H. C. R.

**Critical Studies on Methods of Analysis. X. Cerium.** L. A. CONGDON and E. L. RAY (*Chem. News*, 1924, **128**, 233—236).—Cerium may be accurately determined by weighing cerous oxalate prepared by treating the hot, slightly acid solution of the nitrate with a slight excess of a hot dilute solution of oxalic acid, collecting

the precipitate on a Gooch crucible, and drying at  $100^{\circ}$  to constant weight. If desired, the dried precipitate may be ignited to ceric oxide before weighing. The purity of this oxide may be determined by heating it with strong hydrochloric acid and potassium iodide and titrating the evolved iodine with thiosulphate. Direct titration of cerous nitrate solutions with potassium permanganate with the addition of magnesia towards the end of the titration to neutralise the liberated acid yields slightly high results.

A. R. P.

**Soluble Aluminium and the Hæmatoxylin Test in Filtered Waters.** W. D. HATFIELD (*Ind. Eng. Chem.*, 1924, **16**, 233—234).—The range of minimum solubility of aluminium hydroxide in carbonate and hydrogen carbonate solutions extends approximately from  $p_H$  5.7 to  $p_H$  7.3. The gravimetric determination of aluminium in waterworks effluent is tedious and is complicated by the presence of aluminosilicates. Details are given of a modified colorimetric method depending on the coloration given in the presence of hæmatoxylin. The colour is formed in samples of water of which the hydrogen-ion concentration is adjusted to  $p_H$  8.2—8.3 by adding ammonium carbonate. The disturbing effect of the presence of magnesium, ferrous and ferric salts is nullified by acidifying with acetic acid before carrying out the colorimetric comparison. The method gives results accurate to 0.1 part per 1000 of aluminium.

H. C. R.

**Stability of Permanganate Solutions.** I. M. KOLTHOFF and N. SMIT (*Pharm. Weekblad*, 1924, **61**, 241—249).—A solution of the pure salt in ordinary distilled water is stable in 0.1*N*-concentration if kept in the dark, losing only 0.2 to 0.5% after 7 months. In 0.01*N*-concentration, the loss was 1.5 to 2.5% after 5 months. In daylight, the solutions lose strength more rapidly, and especially so when weak; a 0.01*N*-solution lost about 70% in daylight in 5 months. Decomposition is more rapid in alkaline solution, and very much more rapid in acid solution. Manganous salts and manganese dioxide act catalytically, accelerating decomposition, hence solutions should not be boiled, but should always be filtered through pure asbestos, and kept in absolutely clean vessels.

S. I. L.

**Spontaneous Decomposition of Permanganate under Various Conditions.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1924, **61**, 337—343; cf. preceding abstract).—The increase of the velocity of decomposition with concentration of acid in hot solutions is explained as a consequence of the increasing solubility of manganese dioxide, which dissolves and behaves as hydrogen peroxide, and is regenerated by the reaction between the manganous salt formed and the permanganate. The reaction of manganous salts with permanganate introduces errors in the titrations in which excess of permanganate is used in hot acid solutions. In neutral solutions, the decomposition is very slight, and in the cold it is very slight, even if acid solutions are employed. Titrations should therefore be carried out at ordinary temperatures.

S. I. L.

**Diphenylamine as Indicator in the Titration of Iron with Dichromate Solution.** J. KNOP (*J. Amer. Chem. Soc.*, 1924, **46**, 263—269).—When a drop of 0.1*N*-potassium dichromate solution is added to an acidified solution of diphenylamine sulphate containing ferric salts, an intense blue colour is produced. The use of diphenylamine as an internal indicator in the titration of ferrous iron with dichromate gives satisfactory results with dilute solutions; with more concentrated solutions, preliminary addition of sulphuric and phosphoric acids is necessary, in order to avoid interference by the yellow ferric ion. Back titration with this indicator is possible; hence it can be used in determining the chromium content of chrome-steels. It gives very accurate results when stannous chloride is used as the reducing agent for ferric salts. H. T.

**Use of Hexamminenickelous Perchlorate in Analysis.** E. NEUSSER (*Oesterr. Chem.-Ztg.*, 1924, **27**, 54—55).—As the solubility of hexamminenickelous perchlorate in ammoniacal solutions of ammonium perchlorate is appreciable, and as the salt is decomposed by washing either with alcohol or water, the use of this substance in the qualitative or quantitative analysis of solutions containing nickel gives untrustworthy results. As a qualitative test for nickel, the formation of this compound in 10% ammonia will detect 1 part of nickel in only 7700 parts of solution, whereas dimethylglyoxime gives a distinct precipitate in solutions containing 1 part of nickel in 360,000 parts and a red colour with solutions containing 1 part of the metal in 13,000,000 parts.

A. R. P.

**Determination of Chromium.** H. T. S. BRITTON (*Analyst*, 1924, **49**, 130—133).—The gravimetric determination of chromium by precipitation as the hydroxide and subsequent ignition gives results that are up to 2% too high, owing to the presence of some chromium chromate. The author prefers the iodometric method after oxidation with aqueous sodium peroxide; 10 minutes' boiling is sufficient to remove the excess.

H. C. R.

**Volumetric Determination of Titanium.** A. M. MORLEY and J. K. WOOD (*J. Chem. Soc.*, 1924, **125**, 518—520).—By using aluminium foil in place of zinc, the reduction of titanium to the titanous condition can be completed in 9 minutes in solutions containing hydrochloric acid. Reduction is allowed to proceed in the cold for about 5 minutes; after regulated heating to boiling, and cooling in a stream of carbon dioxide, a solution of ammonium thiocyanate is added and the liquid is titrated with a standard solution of iron alum, carbon dioxide being passed continuously. A blank determination is necessary. The iron alum solution is standardised against a solution of titanium of known concentration. The method gives results accurate to 1%.

J. W. B.

**Determination of Naphthenes in Petroleum Spirits.** W. R. ORMANDY and E. C. CRAVEN (*J. Inst. Petrol. Tech.*, 1924, **10**, 101—104).—A discussion of three methods for determining the percentage of naphthenes in mixtures of these with paraffins:

Tizard and Marshall's aniline-point method (A., 1921, ii, 280), and methods assuming rectilinear relationship between the naphthene content of mixtures and their densities and specific refractivities, respectively. The following specific refractivities, calculated from actual measurements on samples of known purity, were taken as typical of the paraffins and naphthenes respectively: heptane, 0.5672; cyclohexane, 0.5479. There appears to be little to choose between the three methods, but in several cases one or other of them gave anomalous results. [Cf. B., 1924, 363.] L. A. C.

**Colour Test for Chloroform and Chloral Hydrate.** J. H. Ross (*J. Biol. Chem.*, 1923, 58, 641—642).—When substances containing the group  $\cdot CX_3$  ( $X = Cl, Br, \text{ or } I$ ) are heated with sodium hydroxide (17—25%) and pyridine, a red coloration is produced which passes into the pyridine layer. This reaction may be used to detect chloroform or chloral hydrate in amounts less than 0.005 mg. The reaction does not take place when piperidine or quinoline is substituted for pyridine. E. S.

**Glycerol as a Disturbing Factor in Testing for Methyl Alcohol in Ethyl Alcohol.** C. H. LA WALL (*Amer. J. Pharm.*, 1924, 96, 226—227).—One part of glycerol in 500 parts gave a reaction at least equal in intensity to the presence of 1% of methyl alcohol in ethyl alcohol and 1 part in 2000 parts gave a distinctly positive reaction in the test previously described (this vol., ii, 279). No glycerol comes over on distilling mixtures of glycerol, alcohol, and water until the glycerol in the distilling flask reaches a concentration of about 50% by volume. Before testing for methyl alcohol, distillation must therefore always be resorted to with liquids which leave any residue on evaporation, and the distillation must be so conducted that the concentration of the residue in the distilling flask is not too great. H. C. R.

**Determination of Formaldehyde in the Presence of Acetone and Acetaldehyde and of Formaldehyde and Acetone in the Presence of Each Other.** F. MACH and R. HERRMANN (*Z. anal. Chem.*, 1923, 63, 417—438).—The substance in solution is treated with methyl alcohol (if acetaldehyde is present), potassium hydroxide, and iodine solutions, and the mixture shaken and then set aside. Sulphuric acid is added, and the excess of iodine is titrated with thiosulphate. The liquid is then distilled for 10 minutes in a current of steam to expel the iodoform formed from the acetaldehyde or acetone. The distillate is boiled under a reflux condenser with an excess of standard silver nitrate solution, alcohol, and nitric acid. After 90 minutes, the iodoform is decomposed, yielding silver iodide, and the excess of silver nitrate determined by titration with thiocyanate. In the original iodine treatment, the following reactions take place with formaldehyde and acetone, respectively:  $H \cdot CHO + I_2 + 3NaOH = H \cdot CO_2Na + 2NaI + 2H_2O$  and  $(CH_3)_2CO + 3I_2 + 4NaOH = CHI_3 + CH_3 \cdot CO_2Na + 3NaI + 3H_2O$ , so that from these results the proportions of acetone and formaldehyde may be calculated. In the presence of methyl or ethyl alcohol or of acetaldehyde, the

formation of iodoform is not quantitative, so that the process gives accurate figures only for the formaldehyde. A. R. P.

**Micro-analytical Methods for the Examination of Small Quantities of Waxes, in particular Cotton Wax.** R. G. FARGHER and L. HIGGINBOTHAM (*J. Text. Inst.*, 1924, **15**, 75—80T).—Methods for the determination of the acid, saponification, unsaponifiable, acetyl, and iodine values of waxes such as may be extracted from cotton by means of organic solvents are described, such methods being particularly suitable when the amount of wax available is not greater than 0.3 g. The methods were checked by examination of many substances, including carnauba wax, spermaceti, beeswax, wool wax; gossypyl, montanyl, and ceryl acetates; carnaubic, montanic, and isobehenic acids; methyl montanate and methyl gossypate, and the results thus obtained are tabulated. [Cf. *B.*, 1924, 370.] A. J. H.

**Distinction between Citric and Tartaric Acids.** H. STEVENS (*Ind. Eng. Chem.*, 1924, **16**, 155).—About 0.2 g. of the sample is placed on a spatula and held in a flame until it ignites, when the spatula is removed. In the case of tartaric acid, the burning mass draws up into a dry ball and burns with a blue flame, the ball shrinking until only a small residue of carbon is left. Citric acid, when ignited, spreads out on the spatula, remaining in the liquid state while burning with a yellow flame. The burning is accompanied by considerable spattering. H. C. R.

**Determination of the Hydrogen Cyanide Content of Amygdalin by the Aëration Method.** J. H. ROE (*J. Biol. Chem.*, 1924, **58**, 667—669; cf. *A.*, 1923, ii, 702).—The aëration method previously described is applied to the determination of the hydrogen cyanide liberated, during the analysis, from amygdalin by emulsin. G. M. B.

**Determination of Ferrocyanides.** W. M. CUMMING (*J. Chem. Soc.*, 1924, **125**, 240—243).—The method is based on the fact that sodium, potassium, and calcium ferrocyanides precipitate from a neutral solution of a benzidine salt the same benzidine hydroferrocyanide,  $(C_{12}H_{12}N_2)_3 \cdot H_4Fe(CN)_6 \cdot H_2O$ . To a cold neutral solution of the ferrocyanide excess of benzidine hydrochloride is added. The white precipitate is filtered, washed, dried, and ignited, the percentage of ferrocyanide being calculated from the weight of ferric oxide found. Accurate results are obtained for sodium, potassium, and calcium ferrocyanides by this method. A volumetric method is also described, based on the same reaction, in which a solution of sodium hypobromite is used as external indicator.

The formula of crystalline calcium ferrocyanide is found to be  $Ca_2Fe(CN)_6 \cdot 11H_2O$ . When heated at  $100^\circ$ , it loses  $10.5H_2O$ ; above  $100^\circ$ , hydrogen cyanide is evolved. When heated in an oxygen-free atmosphere above  $100^\circ$ , the decomposition is represented by the equation:  $2Ca_2Fe(CN)_6 \cdot 11H_2O = Ca_4Fe_2(CN)_{11} \cdot OH + 21H_2O + HCN$ . J. B. F.



**Detection and Determination of Thiocyanates in presence of Ferrocyanides.** F. PERCIABOSCO (*Annali Chim. Appl.*, 1923, 13, 346—348).—Treatment of the solution of a commercial ferrocyanide with a greater amount of a ferric salt than is required to precipitate the whole of the ferrocyanide, followed by filtration, yields a blood-red filtrate if thiocyanate is present. A method for determining the proportion of thiocyanate contained in a commercial ferrocyanide is based on this reaction. [Cf. *B.*, 1924, 253.] T. H. P.

**Transposition of Insoluble Substances by means of a Sodium Carbonate Solution. I. Oxalates.** L. J. CURTMAN and D. HART (*Chem. News*, 1924, 128, 248—251).—In the examination of insoluble substances for acid radicals, such a quantity of the substance as will yield 0.5 g. of the acid is digested with 50 c.c. of 3*N*-sodium carbonate solution for 5 minutes and the resulting solution examined for acid radicals. Under these conditions, barium, aluminium, nickel, manganese, bismuth, copper, and stannous oxalates are completely decomposed, whilst more than 90% of the oxalate radical passes into solution in the case of the iron, cobalt, zinc, lead, cadmium, strontium, calcium, and magnesium salts, and only 77% in the case of the silver salt. The oxalic acid content of all the above salts except the ferrous, cobalt, lead, and stannous oxalates may be determined by direct solution in sulphuric acid and titration with permanganate. Ferrous and cobalt oxalates are dissolved in sulphuric acid, and the metal is separated by ammonia and ammonium sulphide; lead oxalate is dissolved in sodium hydroxide solution, and the lead removed with sodium sulphide, and stannous oxalate is heated with concentrated hydrochloric acid, the tin removed by passing hydrogen sulphide through the diluted solution, the oxalic acid precipitated by ammonia and calcium chloride, and the calcium oxalate dissolved in sulphuric acid for titration as usual. A. R. P.

**Effect of Sodium Trichloroacetate on the Reduction of Copper Solutions by Dextrose.** D. STEVEN (*Biochem. J.*, 1924, 18, 19—21).—Trichloroacetic acid forms an unstable compound with copper which is not reducible. Its presence therefore vitiates dextrose determinations by reduction methods after its use as a precipitant for proteins. S. S. Z.

**Determination of Pentosans (Furfuraldehyde) in Wood Cellulose.** W. J. POWELL and H. WHITTAKER (*J. Soc. Chem. Ind.*, 1924, 43, 35—36r).—The substance (0.5 to 0.8 g.) is distilled with 12% hydrochloric acid until the distillate ceases to give a reaction with aniline acetate, and the distillate is diluted with 12% hydrochloric acid to 500 cc. Part of this solution, with 0.1*N*-sodium bromide-bromate solution, is kept in a stoppered bottle in the dark for 1 hour, a control being performed with 12% hydrochloric acid. To each bottle is added 10 c.c. of 10% potassium iodide solution and the mixtures are titrated with 0.1*N*-thiosulphate solution. The difference between the two titrations, multiplied by 0.0024, gives the quantity of furfuraldehyde present. W. P. S.

**Behaviour of Formaldehyde.** N. TARUGI (*Boll. Chim. Farm.*, 1924, 63, 97—102, 129—133).—The behaviour of formaldehyde towards amino compounds is discussed in its relationship towards the formaldehyde titration method, the work of Clementi (A., 1915, ii, 382; 1917, ii, 344) in particular being considered. The results obtained vary considerably with the indicator employed, and show that the indicator most suited to titration of the acidity of an amino-acid in presence of formaldehyde is phenolphthalein used as paper outside the liquid. Addition of dextrose to a concentrated solution of an amino-acid results in the manifestation of a large part of the acid function of the amino-acid, the action of the dextrose being similar to that of formaldehyde. This result is in disagreement with Maillard's views (A., 1912, i, 169). T. H. P.

**The Titration of Amino- and Carboxyl-groups in Amino-acids, Polypeptides, etc. IV—VI. Determinations in Presence of Formaldehyde and Alcohol.** L. J. HARRIS (*Proc. Roy. Soc.*, 1924, B, 95, 500—522).—It is suggested that Sørensen's method for determining the carboxyl group in a solution of amino-acids, which consists in adding neutralised formaldehyde and then titrating with potassium hydroxide solution until a red colour is obtained with phenolphthalein as indicator, depends on the formation of methyleneamino-acid compounds having an acid dissociation constant,  $K_a$ , about 1000 times as great as that of the original amino-acids. Foreman's method (titration in presence of alcohol) would also appear to depend on a similar increase of  $K_a$ . Certain amino-acids give a low titration value according to these methods, and the two following modifications are suggested. Titration with 0.1N- or N-sodium hydroxide solution may be carried out in 80% aqueous alcoholic solution, to which 5% of the total volume of neutralised formaldehyde solution has been added, using phenolphthalein as indicator, or preferably without the addition of formaldehyde but using thymolphthalein as indicator. Under these latter conditions, 24% of the hydroxyl group in tyrosine also reacts. Titrations of alcoholic solutions according to Foreman's method, but heated, give values nearer to the theoretical than titrations of cold solutions. As heating is known to increase  $K_w$ , this bears out the view that the basis of Sørensen's and Foreman's methods is the increase of  $K_a$ .

In order to titrate the amino groups, methyl-red is added to the solution, neutralised to phenolphthalein, and it is then titrated with hydrochloric acid. The amount of acid required corresponds approximately with the total amino groups present. In arginine one of the two amino groups and the carboxyl group fail to react. Blank corrections should be applied to the titrations.

W. O. K.

**Determination of Amino-acids in the Presence of Ammonium Salts.** O. FERNÁNDEZ and T. GARMÉNDIA (*Anal. Fís. Quím.*, 1924, 22, 103—114).—Ammonium salts interfere with the determination of amino-acids by the formaldehyde titration method (cf. A., 1923, i, 881).

G. W. R.

**Reaction of Aromatic Polynitro Compounds with Alkali Alkyloxides, and its Application.** H. W. VAN URK (*Chem. Weekblad*, 1924, 21, 169—171).—A review of the literature on the subject. By addition of solid potassium hydroxide to an alcoholic solution of the nitro compound, it is possible to detect thiophene and toluene in benzene, and di- and tri-nitrobenzenes in nitrobenzene. Vitali's colour test for atropine is probably due to the presence of the benzene ring; similar colours are obtained with veratrine, strychnine, and other alkaloids. S. I. L.

**Naphthalenedisulphonic Acids. V. Determination of Naphthalene-2 : 6- and -2 : 7-disulphonic Acids.** H. L. HALLER and D. F. J. LYNCH (*Ind. Eng. Chem.*, 1924, 16, 273—275).—The solubilities of the lead salts of naphthalene-2 : 6- and -2 : 7-disulphonic acids in 100 g. of water at 25° are respectively 0.19 g. and 8.2 g. The proportions of the two acids in a mixture may be determined by the preparation of the lead salts and the determination of the solubility of the mixture. A curve showing the total solubility of mixtures of the lead salts is given. [Cf. *B.*, 1924, 367.] C. I.

**Reaction of Resorcinol and its Application to the Detection of Nitroprussides and Ammonia.** CASENEUVE (*Ann. Chim. analyt.*, 1924, [ii], 6, 43—44).—Dilute resorcinol solutions yield a bluish-green coloration when treated with a mixture consisting of 10 c.c. of 10% sodium nitroprusside solution, 5 c.c. of saturated sodium acetate solution, and 10 c.c. of ammonia; the test will detect as little as 0.5 mg. of resorcinol, and the coloration is not obtained with other phenols. A 10% resorcinol solution in ammonia gives a blue coloration with nitroprussides; the coloration changes to yellow on the addition of an excess of sodium hydroxide. Ammoniacal resorcinol solution also yields colour reactions with zinc, cadmium, nickel, and copper salts, but in this case the colours are destroyed by alkali hydroxides. When a drop of a solution containing sodium nitroprusside and resorcinol is exposed to an atmosphere containing ammonia or a volatile amine a blue colour develops in the drop. W. P. S.

**Osmium Tetroxide as a Reagent for the Determination of Tannins and their Derivatives.** C. A. MITCHELL (*Analyst*, 1924, 49, 162—169).—A dilute "osmic acid" solution is used as a reagent for the colorimetric determination of pyrocatechol, pyrogallol, gallic acid, and the corresponding tannins. It is successfully applied to a number of tannin-bearing substances. A. G. P.

**Determination of Eugenol in Clove Oil.** J. A. L. BOUMA (*Pharm. Weekblad*, 1924, 61, 249—250).—Van Eck's method (*A.*, 1923, ii, 702) is criticised on the ground that the factor silver/eugenol given does not correspond with any definite molecular ratio. Thus the amount of silver salt reduced should depend on the time of boiling and the quantities and concentrations of the

reagents; the method is unsuitable, since very wide differences were found.

S. I. L.

**Determination of Pyridine, especially in the Presence of Nicotine, by means of Silicotungstic Acid.** F. MACH and F. SINDLINGER (*Z. angew. Chem.*, 1924, **37**, 89—92).—Pyridine silicotungstate separates from neutral solutions as an amorphous precipitate, and from feebly acid solutions as lustrous, white needles. When heated it decomposes, without melting, into pyridine and silicic and tungstic acids. The substance, after being dried at  $120^{\circ}$ , has the composition  $4C_5H_5N, SiO_2, 12WO_3, 4H_2O$ , and yields 88·15% of residue on incineration. To the cold pyridine solution to be examined (85—100 c.c.), which has been brought to an acidity of 0·5% by addition of hydrochloric acid and water, is added 10% silicotungstic acid (10 c.c. per 50 mg. of pyridine). The mixture is stirred for 15 minutes, kept for 18 hours, and filtered through a Gooch crucible. The precipitate is washed in the filter with exactly 10 c.c. of 0·5% hydrochloric acid, in quantities of 2—3 c.c. at a time. The crucible is dried over a small flame, then strongly heated with a Teclu burner for 10 minutes, cooled, and weighed. Owing to the solubility of the precipitate, it is necessary to add to the weight of the incinerated residue, 6 mg. per 10 c.c. of wash acid (up to 20 c.c.), and 105 mg. per 100 c.c. of reaction liquid. The solubility in hydrochloric acid increases with increasing strength of the latter, so that the salt will remain completely dissolved, under the above conditions, in a 5% solution of the acid. Mixtures of pyridine and nicotine may be roughly determined by precipitating with silicotungstic acid in 0·5% hydrochloric acid, heating the reaction mixture to boiling (whereby the pyridine salt is dissolved), and filtering. The pyridine salt separates from the cold filtrate, and the nicotine silicotungstate precipitate is determined as above. Working with 100 c.c. of solution it is found that 2·9 mg. of nicotine are dissolved by the boiling acid; of this only 2·32 mg. are reprecipitated on cooling, so that 2·32 mg. must be subtracted from the quantity of pyridine found and 2·9 mg. added to that of nicotine. Alternatively, the precipitation may be carried out in the cold in a sufficient volume of 0·5% hydrochloric acid completely to dissolve the pyridine salt. After determining approximately the quantities of pyridine and nicotine in the mixture, as above, the exact determination is best carried out as follows. Glacial acetic acid is added to the mixture and the pyridine separated from it by distillation with steam, the quantity of acetic acid in the flask being kept constant by continuous addition through a dropping funnel, and the pyridine being absorbed in hydrochloric acid. It is advisable to pass the vapour through a wash-bottle containing a further quantity of boiling acetic acid. The distillate is made strongly alkaline with sodium hydroxide and again distilled, the quantities being adjusted so that 100 c.c. of the second distillate contain 50—100 mg. of pyridine. The residue from the distillation with steam, containing the nicotine, is likewise made alkaline and distilled with steam. Finally, the pyridine and nicotine are separately determined by precipitation with silico-

tungstic acid, as described above. The quantities of pyridine and nicotine are respectively equal to 0.1119 and 0.1139 times the weight of the incinerated precipitates. W. T. K. B.

**Determination of Purine Bases of Foodstuffs.** G. KOLLMANN (*Biochem. Z.*, 1924, **144**, 219—223).—Hydrolysis of pure yeast nucleic acid by sulphuric acid and precipitation of the purine bases by copper hydrogen sulphite and ammoniacal silver solution followed by a careful recovery, does not yield more than 70—80% of the theoretical quantity of the bases estimated on Levene's formula. It is concluded that the values for the purine base content of a dietary, as determined by this method, are too low and should be revised. J. P.

**Nephelometry of Protein Solutions.** S. RUSZNYÁK (*Biochem. Z.*, 1924, **144**, 147—148).—A reply to the criticisms by Rona and Kleinmann (*A.*, 1923, ii, 890) of the method employed by the author for determining albumin-globulin quotients (*Biochem. Z.*, 1923, **133**, 370). [Cf. also Rusznyák, *A.*, 1923, ii, 891.] J. P.

**Analysis of Proteins. II. Action of Nitrous Acid on the Hexone Bases.** R. H. A. PLIMMER (*Biochem. J.*, 1924, **18**, 105—109).—In determining lysine, histidine, and arginine by Van Slyke's method, it is sufficient to allow the hexone bases to react with the nitrous acid at 14—17° for 1 hour. If a longer time is taken, an excess of nitrogen is liberated from the guanidine residue of arginine. S. S. Z.

**Determination of the Tryptophan Content of Caseinogen, based on Determinations of Nitrogen Values of the Mercuric Sulphate Precipitate.** H. ONSLOW (*Biochem. J.*, 1924, **18**, 63—83).—The caseinogen is digested with trypsin and the product is treated with acid mercuric sulphate which precipitates free tryptophan, polypeptide of tryptophan, free tyrosine, histidine, and probably small quantities of other amino-acids. The precipitate is washed with 7% sulphuric acid containing 2—3% of mercuric sulphate to remove the tyrosine. The precipitates are then decomposed by hydrogen sulphide, and in the filtrate containing tryptophan, histidine, etc., the total nitrogen and amino nitrogen is determined. The histidine is determined by Koessler and Hanke's method. Three portions of the original solution are hydrolysed with hydrochloric acid in an autoclave and then evaporated to dryness in a vacuum. The residue is distilled with calcium hydroxide and the ammonium-nitrogen determined. The total nitrogen is determined in the melanin which is filtered off and the amino-nitrogen and the total nitrogen are also determined in the filtrate. The tryptophan is calculated from the following equations:  

$$\text{Total N} = \text{Tryptophan N} + \text{Histidine N} + \text{Monoamino N} + \text{Peptide N}$$

$$\text{Amino N} = \text{Tryptophan N}/2 + \text{Histidine N}/3 + \text{Peptide amino N} + \text{Monoamino N}$$

$$\text{Tryptophan N} = 2 [\text{Non-amino N} - (\text{Histidine } 2\text{N}/3 + \text{Peptide non-amino N})]$$
 Acid hydrolysis of tryptophan does not alter the ratio of the amino-nitrogen to the total nitrogen. S. S. Z.

**Determination by Distillation of Volatile Constituents in Blood, especially Alcohol.** H. W. SOUTHGATE (*Biochem. J.*, 1924, **18**, 101—104).—A still-head is described which entirely prevents frothing fluids from reaching the receiver. Pringsheim's method for the determination of alcohol in blood is modified.

S. S. Z.

**Determination of Carotene by means of the Spectrophotometer and the Colorimeter.** F. M. SCHERTZ (*J. Agric. Res.*, 1923, **26**, 383—400).—Carotene, in alcoholic or light petroleum solution, was determined by measurement of the transmissive index, using the spectrophotometer. The mercury line 435·8 was used in the determination. Carotene solutions in alcohol and light petroleum were found to have the same transmittancy, which was slightly greater than the figure for ethereal solutions. The specific transmissive index (extinction coefficient) for alcoholic solutions was 1·91 and in ether 1·986. Transmittancy was shown to depend on the physical properties of the material used and was unaffected by the variability of light, physiological factors, or abnormalities of the observer's colour vision. The colorimeter method introduced difficulties in the manner of matching the tints of the solutions.

A. G. P.

**Determination of Sugar in Blood.** R. V. STANFORD and A. H. M. WHEATLEY (*Biochem. J.*, 1924, **18**, 22—28).—The blue coloration obtained by the action of phosphomolybdic acid on cuprous oxide in acid solution fades with time and therefore the colorimetric measurements in sugar determinations must be made within an hour. The temperature at which the blue coloration is produced must be the same for the standard and other solutions. The comparisons must be made in a dilution colorimeter. The concentrations of the reacting substances must not fall below those given by Folin. Calvert's method is criticised.

S. S. Z.

**Determination of Urea in 0·1 c.c. of Blood.** H. M. HINDMARSH and H. PRIESTLEY (*Biochem. J.*, 1924, **18**, 252—254).—The blood is collected in a solution of urease and is incubated. A saturated solution of borax is then added and the ammonia driven by an impinging current of air into 0·05*N*-sulphuric acid and determined by Nessler's method. This method is as accurate as that of Folin and Wu.

S. S. Z.

**Ivar Bang's Micro-chemical Method for Determining Fat and Cholesterol.** J. MAAS (*Biochem. Z.*, 1924, **144**, 379—382).—Blank determinations and controls on pure triolein and cholesterol do not give satisfactory results with Bang's micro-method for determining the fat and cholesterol content of blood (cf. Szent-Györgyi, A., 1923, ii, 344).

J. P.

**Determination of Bile Acids in Urine.** C. L. A. SCHMIDT and J. A. MERRILL (*J. Biol. Chem.*, 1923, **58**, 601—609).—The method of Foster and Hooper (A., 1919, ii, 377) as modified by

Schmidt and Dart (A., 1920, ii, 284) is employed after removing the bile acids from interfering substances present in urine. This is accomplished by evaporating the urine to dryness, extracting the bile acids with alcohol, and finally precipitating them from aqueous solution by saturation with magnesium sulphate. Application of the method to several cases of jaundice indicated that only small amounts of the bile acids are excreted in the urine, the value, calculated as glycocholic acid, usually being about 100 mg. per day; in one case, however, about 600 mg. were excreted in 24 hours.

E. S.

**Determination of Tannin in Plant Tissue.** P. MENAUL (*J. Agric. Res.*, 1923, 26, 257—258).—The ground material (20 g.) is extracted in a 300 c.c. Erlenmeyer flask with 100 c.c. of light petroleum, the flask being shaken occasionally and allowed to remain over-night. The residue is collected on a dry paper, washed with 100 c.c. of light petroleum in 20 c.c. portions, and dried. The dried material is returned to the flask and extracted for about sixteen hours with 200 c.c. of 95% alcohol. After filtering through a dry filter, 10 c.c. of the filtrate are placed in a urine centrifuge tube, and after the addition of 2 c.c. of 10% lead acetate solution are heated in a water-bath at 75° until the precipitate coagulates. The liquid is centrifuged for three minutes, the supernatant liquid decanted, and the residue allowed to drain as completely as possible; 5—10 drops of 5% sulphuric acid are added (sufficient to dissolve the lead tannate and to precipitate all the lead). Water is added until the tube is nearly full, and after centrifuging for three minutes the clear liquid is transferred to a graduated flask. A standard solution of gallotannic acid (from which gallic acid has been removed by ether) is prepared in a similar flask. Two c.c. of the reagent (see below) are added to each, followed by 10 c.c. of a 20% sodium carbonate solution. After dilution, the colours are compared at the end of five minutes and the tannin content is calculated. The reagent is prepared by boiling 100 g. of sodium tungstate and 30 g. of arsenic acid ( $\text{As}_2\text{O}_5$ ) with 300 c.c. of water and 50 c.c. of concentrated hydrochloric acid for two to three hours under a reflux condenser and diluting to 1 litre. Phenols, proteins, and dextrose do not affect the reagent, which must, however, be kept out of contact with reducing agents. The coloration produced with tannic acid is stable for an hour.

A. G. P.

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## General and Physical Chemistry.

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**Theory of the Helium Atom.** F. J. v. WISNIEWSKI (*Physikal. Z.*, 1924, **25**, 135—137).—An attempt is made to obtain the terms of the neutral helium spectrum, on the basis of classical mechanics. The subject is attacked as a special case of the three-body problem, by assuming the nucleus to be at rest, with the first electron moving round it at a constant angular velocity. The terms obtained agree with the experimental values for parhelium. S. B.

**Model of the Helium Atom.** R. DE L. KRONIG (*Science*, 1923, **58**, 537).—The assumption that the moving electrons of atomic systems containing more than one electron interchange energy and momentum in a sudden discrete manner leads, when applied to the crossed orbit configuration of the helium atom, to a model of the same general character as the classical one, and having an ionisation potential of  $5.799W$ , where  $W$  is the energy of the hydrogen atom in its normal state. The best experimental value is  $5.807W$ , whereas that computed from classical dynamics is  $5.5235W$  (cf. Kramers, A., 1923, ii, 479). A. A. E.

**The Rydberg Correction and the Radius of Ions.** F. HUND (*Z. Physik*, 1924, **22**, 405—415).—The problem is discussed whether the azimuthal quantum numbers of the stationary states, corresponding with optical spectra, take whole- or half-number values. The effective size of the atomic ion is calculated, assuming first whole-number, and then half-number values, from the magnitude of the orbit at which the transition from the "hydrogen-like" to the disturbed type of orbit occurs. The values so obtained are compared with independent estimates of ionic radii (from viscosity of inert gases, and from space-lattice distances). Agreement is obtained only when half-number values are assigned to the azimuthal quantum numbers. S. B.

**Relation between Inner Quantum Numbers and Intensity of [Components of] Multiplets.** H. C. BURGER and H. B. DORGELO (*Z. Physik*, 1924, **23**, 258—266).

**Determination of the Relative Values of the Terms of a Spectrum. Application to the Spectrum of Neutral Vanadium.** M. A. CATALÁN (*Anal. Fis. Quím.*, 1924, **22**, 72—83).—For the partial interpretation of complex spectra containing large numbers of lines, the spectrum is first searched for its multiplets, each of which is formed of two multiple levels or terms recognisable by their respective set of separations. The repeated appearance of a certain set of separations shows that its corresponding term is combined in various multiplets. By giving an arbitrary value to one of the terms, especially that term giving multiplets with



reversed lines, the other terms may be derived. The calculated values of the terms may be checked by those multiplets resulting from the combination of terms already determined. The values obtained are purely relative, but may assist in elucidating the structure of the spectrum and those relations involved in the differences of energy between various levels of the atom. Values for maximal multiplicity,  $r$ , azimuthal quantum number,  $k$ , and internal quantum number,  $j$ , may be obtained from the relations between the separations of the terms and of the intensities and Zeeman effects of the lines forming the multiplets. The method is applied to the analysis of the spectrum of neutral vanadium and gives a satisfactory explanation of its multiplets. G. W. R.

**Interaction between Radiation and Free Electrons.** W. BOTHE (*Z. Physik*, 1924, **23**, 214—224).—The conception that radiation consists of molecules of radiation, *i.e.*, of energy complexes carrying multiple quanta, is applied to the interaction of radiation and free electrons (cf. Pauli, *ibid.*, 1923, **18**, 272, for discussion on thermal equilibrium between radiation and free electrons).

S. T. B.

**Estimation of the Average Life of Excited Mercury Atoms.** L. A. TURNER (*Physical Rev.*, 1924, **23**, 464—471).—A mathematical paper in which the average life of excited mercury atoms in mixtures with hydrogen and air, respectively, is calculated from the data of Cario and Franck (*A.*, 1922, ii, 809) and of Wood (*Phil. Mag.*, 1912, **23**, 689);  $\tau$  is found to be of the order  $10^{-7}$  sec.

L. J. H.

**Light Period of Atoms and the Damping of Spectral Lines.** W. WIEN (*Ann. Physik*, 1924, [iv], **73**, 483—504).—The period of light emission of atoms in a positive ray stream has been determined by observing photographically the intensity of the radiation of a given wave-length at different distances from the cathode (cf. *ibid.*, 1921, **66**, 232). The periods observed were independent of the *E.M.F.* imposed, in contradiction to the results of Dempster. The periods for the Balmer series, He 4478, and Hg 4358 Å. are very close to the value deduced from the classical theory,  $5.35 \times 10^7$  sec.<sup>-1</sup>. In accordance with the views of Sommerfeld and Heisenberg, the period for Hg 2536, the resonance line, is different,  $1.02 \times 10^7$  sec.<sup>-1</sup>. The methods of ultra-violet photometry are shortly discussed.

S. B.

**Duration of Molecules in Upper Quantum States.** R. C. TOLMAN (*Proc. Nat. Acad. Sci.*, 1924, **10**, 85—87).—The author has shown from data on the intensity of absorption lines that the mean life,  $\tau$ , of atoms and molecules in excited quantum states and the specific rate,  $A_{2,1}$ , at which they spontaneously leave the excited state, 2, to return to the lower state, 1, is given by  $1/\tau = A_{2,1} = (8\pi\nu^2 p_1 / c^2 N_1 p_2) \int_0^\infty \alpha d\nu$ , where  $A_{2,1}$  is the chance per unit time that a molecule in quantum state 2 will spontaneously jump to quantum state 1 in the absence of exciting radiation,  $\nu$  is the frequency of the light emitted in such a jump, and  $p_1$  and  $p_2$

are the *a priori* probabilities of states 1 and 2, whilst  $N_1$  and  $\alpha$  are data obtained in some particular absorption experiment,  $N_1$  being the number of molecules per unit volume in the lower quantum state, and  $\alpha$  the absorption coefficient for light producing the quantum jump. The mean life of the excited atom or molecule has been calculated from the data available in the literature for certain lines in the spectra of mercury, sodium, caesium, iodine, and hydrochloric and hydrofluoric acids. It is found that the mean life may vary over at least the range 1 to  $10^{-8}$  second, and that the rate of decay is not a simple function of the frequency of the emitted light.

S. S.

**Interferential Methods for Determining the Duration of and the Law of Emission of Light by Atoms.** E. BAUER (*Compt. rend.*, 1924, **178**, 1268—1270).—The author proposes to obtain information as to the law of emission of light as predicted by the quantum theory by measuring the length of the wave trains emitted by atoms in canal rays by an interferential method. The Doppler effect due to the thermic movements of the molecules and the disturbances due to collisions is to be eliminated by causing the gas, *e.g.*, mercury vapour, to behave as if it were unidimensional. On theoretical grounds, it is regarded as impossible to utilise X-rays for the measurements.

A. B. H.

**Broadening of Spectral Lines. II.** J. HOLTSMARK (*Physikal. Z.*, 1924, **25**, 73—84).—A mathematical paper in which the theory (*Ann. Physik*, 1919, **58**, 577) which assumed that the ionised atoms could be regarded as point sources is extended to cover the case of ions of finite magnitude. The new theory is used to calculate the breadth of the  $H_\alpha$  line at different pressures with results in satisfactory agreement with the observations of Michelson.

S. S.

**A Photographic Method in the Infra-red.** A. TERENCE (*Z. Physik*, 1924, **28**, 294—297).—The author gives an account of experiments in the registration of infra-red spectra. The chief experimental method discussed depends on the fact that, if a sensitive photographic plate is first exposed to ordinary light and then to infra-red radiation, a positive image of the infra-red is obtained. The action of various dyes on the process is discussed and details of the method found most satisfactory are given. By this means, wave-lengths up to  $1.18 \mu$  can be measured.

G. S.

**Lyman "Ghosts" and Measurements in the Infra-red Spectrum of Neon.** K. W. MEISSNER (*Ann. Physik*, 1924, [iv], **73**, 643—646).—"Ghosts" of the type described by Lyman and by Meggers and Kiess (*J. Opt. Soc. Amer.*, 1922, **6**, 417) have been found in the spectra from a concave Anderson grating of 15,000 lines to the inch. They occur at positions given by  $\lambda_{\text{ghost}} = \lambda(n/5 \pm p/1500)$ , where the values of  $n$  are whole numbers between 1 and 12, and  $p$  varies from  $-1$  to  $+5$ . Twelve of the lines in the wave-length range 9840—7528 Å. previously attributed by the author to neon (*A.*, 1919, ii, 206) must now be recognised as ghosts.

S. B.

**Spectrum of Iron.** O. LAPORTE (*Z. Physik*, 1924, **23**, 135—175).—The 20 multiplets in the spectrum of iron recorded by Walters (cf. A., 1923, ii, 519) have been increased to 30. Their interpretation by the quantum theory is supported by their Zeeman effects. The fundamental term of the iron spectrum is found to be a *d*-term in agreement with Angerer and Joos (cf. *Naturwiss.*, 1924, **12**, 140). This is the first time the *d*-orbit appears as the normal state. The ionisation potential is  $5.9 \pm 0.1$  volts, and the first excitation potential 3.20 volts. A table gives all the classified lines (321), including all the strong lines, of the iron spectrum in order of wave-length. S. T. B.

**Spectrum of Iron.** S. GOUDSMIT (*Nature*, 1924, **113**, 604).—Absolute values for the “inner” quantum numbers *J* have been obtained, and the results show that the 20 iron multiplets belong to a triplet and a quintuplet system. Two of the 13 different terms are irregular. A. A. E.

**Spectra of Arcs between Metal Poles in Various Media and in *Vacuo*.** S. PROCOPIU (*Ann. Physique*, 1924, [x], **1**, 89—133).—The spectra of arcs between poles of copper, gold, magnesium, calcium, zinc, cadmium, mercury, aluminium, and thallium, in air, hydrogen, nitrogen, coal-gas, water, and *in vacuo* are described. In water, coal-gas, and hydrogen, the arc spectra are reduced in intensity and the higher members of the series disappear; on the other hand, the spark spectra become more intense. In nitrogen, the higher members of the arc spectra are augmented and the spark spectra disappear. *In vacuo*, the lines of the arc spectra are narrow and intense, including the higher members of the series, and a larger number are reversed than in air. The arc across a flame gives spectra similar to those *in vacuo*, but some lines show “double reversal.” The potential across the arc changes sharply according to whether the anode is within or beyond the region of the cathode glow (about 5 mm.), but otherwise is almost independent of the length of the arc. Across portions of the length of the arc *in vacuo*, a continuous spectrum may be produced which is sufficiently intense in the ultra-violet to serve as a source for absorption measurements. The effect of striking the arc between poles of different metals indicates the predominant rôle of the cathode. These results and the variation in intensity of the lines along the arc support the view that the lines of the arc spectrum originate from the neutral atoms, those of the spark spectrum from the ions, the band-spectra from the atom ion, and the continuous spectrum from the neutralisation of the positive ion. L. J. H.

**Ultimate Lines in the Spectra of the Electric Arc.** S. PROCOPIU (*Compt. rend.*, 1924, **178**, 1368—1369).—A study of the conditions under which “ultimate” lines due to metallic impurities appear in the arc or spark spectra of metals. In the case of impurities of a low ionisation potential, the “ultimate” lines are scarcely visible at low pressures, but intense in air at atmospheric pressure. In the case of impurities of a higher ionisation potential

than that of the metal itself, the lines due to the impurity are invisible at low pressures. It is concluded that the emission of the "ultimate" lines is a thermal phenomenon. A. B. H.

**The Series of Triplets of the Arc Spectrum of Mercury.** H. BUISSON (*Compt. rend.*, 1924, **178**, 1270—1272).—Measurements have been made of the wave-lengths of the members of the first and second subordinate series of triplets in the arc spectrum of mercury which have not previously been measured. The wave-lengths were found by interpolation from known values for copper. The measurements, in the case of both series of triplets, confirm the existence of constant differences between the frequencies of the three members of each triplet. A. B. H.

**Vanadium Multiplets and the Zeeman Effect.** F. MEGGERS (*J. Washington Acad. Sci.*, 1924, **14**, 151—159).—A number of multiplets has previously been detected in the arc spectrum of vanadium. The observed Zeeman patterns for the lines of these multiplets are tabulated with the corresponding values calculated according to Landé's scheme for multiplets (*Z. Physik*, 1923, **15**, 189). The agreement is fairly satisfactory. S. B.

**Arc and Spark Spectra of Aluminium, Zinc, and Carbon in the Extreme Ultra-violet.** R. O. HUTCHINSON (*Astrophys. J.*, 1923, **58**, 280—293).—By the use of a vacuum grating spectrograph, the arc spectra of aluminium, zinc, and carbon have been extended to 696.2, 768.1, and 595.5 Å., and the spark spectra to 678.0, 467.5, and 460.1 Å., respectively. A. A. E.

**Evidence of a Spark Line in the Lithium Spectrum.** F. L. MOHLER (*Science*, 1923, **58**, 468—469).—Excitation of spark lines by thermionic discharge in gas at low pressure, when applied to lithium vapour between 500° and 600°, causes the appearance, near 50 volts, of a line  $2934.15 \pm 0.1$  Å. Removal of the valency electron of lithium requires 5.3 volts, and the potential for removal of one of the K electrons is estimated to be about  $50 \pm 5$  volts. In the spectrum of the thermionic discharge in lithium the subordinate series are developed to an unusual extent. A. A. E.

**Cosmic Clouds of Calcium and Sodium.** B. GERASIMOVICH.—(See ii, 335.)

**Spectrum of Glow of Phosphorus.** W. E. DOWNEY.—(See ii, 250.)

**Quantum Theory of Molecules.** M. BORN and W. HEISENBERG (*Ann. Physik*, 1924, [iv], **74**, 1—31).—A theory for band spectra is developed from consideration of the molecule as a mechanical system consisting of a nucleus and electrons by developing the energy function in powers of  $\lambda$ , where  $\lambda^2$  is of the same order of magnitude as the ratio of the masses of the electrons and the nucleus. S. P. B.

**New Hydrocarbon Band.** R. FORTRAT (*Compt. rend.*, 1924, **178**, 1272—1275).—A new band in the ultra-violet of the spectrum emitted by the blue cone of the hydrocarbon flame is described.

Its origin is  $3143 \text{ \AA}$ . and it has the theoretical structure of a hydrocarbon band. It is considered possible that the band is related to the bands  $4320 \text{ \AA}$ . and  $3889 \text{ \AA}$ ., and that the three bands may be emitted by the same molecule but under very different conditions. This supposition is confirmed by calculations of the moments of inertia, before and after emission, and the fundamental frequency  $\nu_0$  of the molecule concerned.

A. B. H.

**Behaviour of the Oxygen Band  $3064 \text{ \AA}$ . in a Magnetic Field.**

R. FORTRAT (*J. Phys. Radium*, 1924, [vi], 5, 20—32).—Heurlinger resolved this band (often known as an "OH" band) into a system of eleven simple band series. The author has observed the Zeeman effects of the lines of this spectrum, using the oxyacetylene flame as his source. He concludes that the lines in any one of the simple bands picked out by Heurlinger have Zeeman patterns of the same type, but of progressively varying separations. No marked analogies were found between the effects in the different simple bands.

S. B.

**Formulation of Absorption Bands in the near Infra-red.**

W. F. COLBY (*Astrophys. J.*, 1923, 58, 303—306).—The fundamental band of hydrogen chloride, and that at  $1.7\mu$ , are re-formulated with half-parameter numbers. The combination band corresponding with a vibrational quantum change  $1 \rightarrow 2$  is calculated and found to agree with the faint absorption band already observed

A. A. E.

**Band Spectrum of Boron Nitride.**

W. JEVONS (*Nature*, 1924, 113, 744—745).—A criticism of Mulliken's view (this vol., ii, 3, 294, 295) that the bands in question should be ascribed to an oxide rather than to a nitride of boron. The greater intensity of the bands in presence of a trace of oxygen is not conclusive proof of the correctness of this view, since the spectrum of any nitride, produced by the action of active nitrogen on a suitable substance, would presumably be intensified by the admission of a trace of oxygen, in view of Rayleigh's observations on the influence of foreign gases on the production of active nitrogen. Other gases may produce the same effect as oxygen and, further, if the spectrum is due to an oxide it should be easy to produce it in the absence of nitrogen (the author has, however, failed to do so), and it should be given by the uncondensed discharge through a mixture of boron trichloride vapour and oxygen.

A. A. E.

**Terms of the (C+H) Band Spectra.**

A. KRATZER (*Z. Physik*, 1924, 23, 298—332).—A detailed discussion of the structure of the bands at  $4300$  and  $3900 \text{ \AA}$ . is given. The (C + H) band at  $4200$  can be represented as combinations from four initial electronic states to one final state. The final state is determined by means of the formulæ of Kramers and Pauli for diatomic molecules. The moment of momentum about the line joining the atoms is  $\hbar/2\pi$ . The initial states can be represented by the same formulæ. The corresponding moment of momentum is less than  $\hbar/2\pi$  and approximately  $\frac{1}{2}\hbar/2\pi$ .

Combinations between the bands at 4300 and 3900 show that both correspond with the same final state of the molecule. The absence of certain possible combinations of these two is explained by a selection rule. The experiments are not sufficient to decide the question as to whether it is CH or CH<sub>2</sub> which gives rise to these bands.

G. S.

**Ultra-violet Absorption Spectrum of Furfuraldehyde.**

F. H. GETMAN (*J. Physical Chem.*, 1924, **28**, 397—401).—Contrary to the conclusions of Hartley and Dobbie (T., 1898, **73**, 598), but in agreement with those of Purvis (T., 1910, **97**, 1655), both alcoholic and aqueous solutions of furfuraldehyde are found to exhibit a strong absorption band the head of which is at  $\lambda = 270\mu\mu$ , in addition to general absorption beginning at about  $\lambda = 300\mu\mu$  for a layer of N/100-solution 1 mm. thick. Furfuraldehyde which has been darkened by exposure to light shows a tendency to increased absorption for ultra-violet light of longer wave-length. The structure of furfuraldehyde is discussed on the assumption that no organic compound shows an absorption band unless the possibility of tautomerism exists. A condensed spark, between two electrodes of alloys of ferro-vanadium and ferro-chromium, respectively, was used as a source of ultra-violet radiation.

M. S. B.

**Ultra-violet Absorption Spectrum of Naphthalene Vapour. Molecular Activation and Structure.**

V. HENRI and H. DE LÁSZLÓ (*Compt. rend.*, 1924, **178**, 1004—1006).—A series of bands without fine structure is exhibited when the pressure is not greater than 0.22 mm.; above this value, more than 400 fine bands in 18 series were observed. For wave-lengths less than 2820 Å., there is a sharp change in the spectrum, which it is suggested corresponds with an abrupt increase in the internal energy of the molecule of more than 101,000 cal./mol. The authors draw conclusions regarding the structure and moment of inertia of the naphthalene molecule which indicate that the carbon atoms are nearer each other than those in diamond or graphite.

H. J. E.

**Absorption Spectra of certain Derivatives of *p*-Cymene.**

W. C. HOLMES.—(See i, 576.)

**Continuous Spectrum of Hydrogen.**

H. B. LEMON (*Nature*, 1924, **113**, 570; cf. Horton and Davies, A., 1923, ii, 820; this vol., ii, 217).—Priority for the description of the visible continuous spectrum of hydrogen is accorded to Horton and Davies, with whose conclusions the author agrees in so far as they concern the voltage condition for its production, but not as regards its origin. The persistence of the lines 6032 and 6021 Å. after the rest of the secondary spectrum has been virtually eliminated is noted.

A. A. E.

**Light Radiation and Total Radiation of Tungsten.**

E. LAX and M. PIRANI (*Z. Physik*, 1924, **22**, 275—285).—The relation between the visible and total radiation of a material would appear to offer a very simple method of temperature determination. The use of the tungsten filament lamp for this purpose is hampered by

variations in the absorptive power of the metal. These variations are due, it is suggested, to different surface conditions of the metal filaments; this view is supported by comparison of the absorptive powers of tungsten filaments of which the component crystals were very different in size. S. B.

**Soft X-Rays.** P. LUKIRSKY (*Z. Physik*, 1924, **22**, 351—367; cf. this vol., ii, 215).—A method is described for the study of radiation in the region between ruled grating and crystal grating spectra. The radiation is generated in a Coolidge X-ray tube which is directly attached to a spherical condenser. The anticathode of the tube is so arranged that the rays fall, through a hole in the outer spherical cover, on the inner sphere of the condenser, where they generate secondary electrons. The velocity of these electrons is determined from the minimum retarding field that must be applied to the condenser to prevent the electrons reaching the outer cover. The wave-length of the radiation liberating the electrons can then be calculated. The following wave-lengths have been obtained by this method. *K* line of carbon, 48.9 Å.; *L* line of aluminium, 154 Å.; *M* line of zinc, 112 Å., with a probable error of 1%. S. B.

**Important Conclusion from the Compton Effect.** L. MEITNER (*Z. Physik*, 1924, **22**, 334—342).—When X-rays or  $\gamma$ -rays are absorbed by matter, electrons may be ejected by either of two principal processes. One is the normal photo-effect, the other the Compton effect (*Physical Rev.*, 1923, **21**, 483), in which part of the absorbed energy reappears as light energy. The detection of the Compton effect by the continuous X-ray spectrum it produces is hampered by secondary effects producing similar spectra. It is suggested that the distribution of the ejected electrons can be used to decide the extent of the Compton effect. The normal photo-electron velocities should be distributed symmetrically about an axis perpendicular to the exciting rays, but the Compton effect electrons should all have a forward component. Old data are examined in the light of this suggestion, and it is concluded that the Compton effect is more marked with a target of light than of heavy atoms. S. B.

**Spark Lines in X-Ray Spectra.** G. WENTZEL (*Ann. Physik*, 1924, [iv], **73**, 647—650).—In a previous paper (*A.*, 1922, ii, 249), lines which appear as short wave-length satellites to certain series lines in X-ray spectra were attributed to the radiation of ionised atoms. Quantitative evidence in favour of this view is afforded by the relations between frequency differences in the spectra of elements of successive atomic number. Contrary to the statement in the previous paper, it is necessary to assume that a multiple-charged atom loses its electrons simultaneously. S. B.

**Secondary and Tertiary Rays from Chemical Elements of Small Atomic Number Due to Primary X-Rays from a Molybdenum Target.** G. L. CLARK, W. DUANE, and W. W. STIFLER (*Proc. Nat. Acad. Sci.*, 1924, **10**, 148—152).—A continuation

of previous work (*ibid.*, 1923, **9**, 413, 419; 1924, **10**, 41, 92). In the present case, primary rays from a water-cooled molybdenum target tube were employed, the radiators consisting of chemical elements of low atomic number, lithium, graphite, rock-salt, aluminium, and sulphur. It is shown that the displacement of the modified peaks increases and their intensities decrease with increase in atomic number; also, the position of the short wave-length limit of the modified peak is in approximate agreement with that calculated for tertiary radiation. This supports the view that the rays with wave-lengths shifted towards the larger values should be ascribed to tertiary radiation produced by the impacts of photo-electrons.

L. J. H.

### Secondary and Tertiary X-Rays from Germanium etc.

G. L. CLARK and W. DUANE (*Proc. Nat. Acad. Sci.*, 1924, **10**, 92—96).—In previous notes (*ibid.*, 1923, **9**, 413, 419; 1924, **10**, 41, 47; this vol., ii, 299) it has been shown that the X-rays emerging from a secondary radiator at right angles to the primary beam contain (a) scattered primary rays, (b) fluorescent secondary rays characteristic of the radiator, and (c) tertiary rays produced by the impact of secondary photo-electrons on atoms in the radiator. The short wave limit of these tertiary rays is given by  $\lambda = \lambda_1 \lambda_2 / (\lambda_2 - \lambda_1)$ , where  $\lambda_1$  denotes a primary wave-length and  $\lambda_2$  is a critical absorption wave-length of the chemical element in the radiator (cf. this vol., ii, 300). The shift from the wave-length of the unmodified ray in the scattered beam is  $\Delta\lambda = \lambda_1^2 / (\lambda_2 - \lambda_1)$ . Further data have been obtained for silver, molybdenum, and germanium which demonstrate the existence of tertiary radiations. With a molybdenum radiator and a primary tungsten beam, it is found, in accordance with the theory, that the short wave limit of the tertiary rays is independent of the angle between the primary beam and the measured radiation. With a radiator of germanium, the tertiary rays due to tungsten  $K_\alpha$  and  $K_\beta$  were observed in both first and second order spectra. An experiment with a block of paraffin wax gave the same result as that found previously for graphite (*loc. cit.*), hence the failure to obtain the shifted rays predicted by Compton's theory is not due to the crystalline nature of graphite.

S. S.

### X-Ray Spectra and Atomic Structure.

L. DE BROGLIE and A. DAUVILLIER (*J. Phys. Radium*, 1924, [vi], **5**, 1—19).—A general review, with bibliography, of the theoretical and experimental work of the authors on the system of X-ray spectra and its relation to atomic structure. The authors have been led independently to a theory of X-ray spectra which is broadly in agreement with that of Bohr, with some important differences.

S. B.

**Interference Phenomena during the Passage of Röntgen Rays through a Diatomic Gas.** P. EHRENFEST (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 479—485).—Reference is made to observations of Friedrich (*Physikal. Z.*, 1913, **14**, 317), that a bundle of Röntgen rays passing through yellow wax, other amorphous solids, and liquid paraffin give interference rings on a photographic plate



placed behind them. The author favours one of the explanations advanced by Friedrich, namely, that the disposition of particles in amorphous solids and more so in liquids is quite irregular; the phenomenon observed during the passage of Röntgen rays is analogous to that taking place during the passage of rays of light through a glass plate sprinkled with lycopodium powder. To simplify the problem, the author calculated the effect of Röntgen rays passing through a diatomic gas. Assuming that  $a$  is the distance between the atoms (regarded as points),  $\lambda$  the wave-length of the rays which are assumed to be perpendicular to the plate, and  $\phi$  the angle formed by the rays with a line joining a point on the photographic plate and a molecule, then with the increase of  $\phi$  the mean intensity varies as  $1 + \sin 2\pi\rho/2\pi\rho$ . By solving the problem geometrically, the same result is obtained, the formula  $M_2(1 + \sin 2\pi\rho/2\pi\rho)$  giving an expression for the dark rings.  
S. P. S.

**Scattering of Röntgen Rays.** W. FRIEDRICH and M. BENDER (*Ann. Physik*, 1924, [iv], **73**, 505—553).—Measurements were made of the scattering coefficients for lithium, sodium, potassium, water, and alcohol, and the results compared with those calculated from the atomic numbers of the atoms.  
W. E. G.

**Radiation Produced by Intensive Bombardment of Oxides with Cathode Rays.** K. TEUCKE (*Physikal. Z.*, 1924, **25**, 115—119).—Thorium oxide and Auer's mixture (rare earths) were bombarded with cathode rays using 300 watts, and the radiation produced was compared with that given by the same substances when heated in a gas flame to the same brightness and general appearance. The distribution of energy through the spectrum, measured for the infra-red from 0.5 to 4.115 $\mu$ , for the visible region from 450 to 715 $\mu\mu$ , and for the ultra-violet from 241 to 525 $\mu\mu$ , was the same in both cases. The variation of the total energy emitted with temperature, measured in the first case pyrometrically, was also the same. The radiation produced by the bombardment is therefore purely thermal. The effect of varying the pressure in the exhausted tube was also studied, and it was found that with constant bombardment energy (140 watts) an optimum of luminosity was obtained at 0.45 mm. The luminosity was found to be proportional to the energy of bombardment, and a curve for the variation of efficiency (luminosity to bombardment energy) with bombardment energy is given.  
L. J. H.

**Fluorescence.** J. TRÖGER and O. GRÜNTAL.—(See i, 540.)

**Fluorescent Powers of Cellulose and its Derivatives.** S. J. LEWIS.—(See i, 374.)

**Fluorescence of Æsculin Solutions.** M. B. KEARNEY (*Phil. Mag.*, 1924, [vi], **47**, 648—656).—An extension of the work of McLennan and Cale (*Proc. Roy. Soc.*, 1922, **A**, **102**, 256), using the same methods. Solutions of æsculin in water, ethyl alcohol, methyl alcohol, acetone, and glycerol have been subjected to the action of ultra-violet light and ozone, and the rate of decay of fluorescent inten-

sity has been examined. The initial fluorescent intensity is greater, and the initial rate of transformation by ultra-violet light and by ozone less, for aqueous than for organic solutions. Unexposed ethyl alcohol and glycerol solutions have an absorption band with a maximum at  $3400 \text{ \AA}$ . This and a band at  $2700 \text{ \AA}$ . (in aqueous solutions) are active in exciting fluorescence. Solutions jacketed with transformed solutions continue to fluoresce without transformation when exposed to ultra-violet light, showing that the decay of fluorescent intensity is due to wave-lengths in the extreme ultra-violet, and verifying the result of McLennan and Cale (*loc. cit.*) that *æsculin* solutions are not transformed if exposed to radiation of appropriate wave-length. Neither ultra-violet light nor ozone affects solid *æsculin*.  
A. E. M.

**Optical Properties of Fluorescent Rhodamine-B.** A. PORITSKY (*J. Franklin Inst.*, 1924, **197**, 527—539).—Measurements made with a contrast Lummer-Brodhun spectrophotometer, on aqueous and alcoholic solutions of rhodamine, show that the coefficient of absorption for any wave-length is the same whether the transmitted light is monochromatic or comes from an undispersed source. Lambert's law holds strictly, and for ranges of concentration of  $1 \times 10^{-3}$ — $5 \times 10^{-6}$  g./c.c. there is direct proportionality between concentration and absorption. Increasing the concentration from  $1 \times 10^{-6}$  to  $1 \times 10^{-4}$  g./c.c. caused a gradual shift of maximum of the energy distribution of the fluorescent band from  $568$  to  $583 \text{ \AA}$ . with no further shift even up to  $1 \times 10^{-2}$  g./c.c. A solution of concentration  $1 \times 10^{-4}$  g./c.c. when heated or exposed to intense illumination showed a shift of maximum fluorescent intensity from  $573$  to  $564 \text{ \AA}$ . A film of solid rhodamine shows the same absorption band as the solution from which it is deposited. The film possesses an intense metallic reflection not present in the solution.  
A. E. M.

**Photoluminescence of Flames.** E. L. NICHOLS and H. L. HOWES (*Physical Rev.*, 1924, **23**, 472—477).—A continuation of previous work (*ibid.*, 1923, **22**, 425). A flat hydrogen flame, well salted, was exposed to the excitation influence of an "amalgam arc" in quartz, and it was found that the sensitiveness to excitation is confined chiefly to the boundary between the oxidising and reducing regions. The width of the bands is decreased and the sharpness and intensity of the maxima are increased, without shift, for barium, strontium, and calcium. With thallium, great increase in brightness was obtained owing to the presence of thallium in the arc. By dispersing the exciting light, it was found that the thallium lines  $5351$ ,  $3776$ , and  $3519 \text{ \AA}$ . are effective whilst the neighbouring mercury lines are inactive. The luminescence is thus shown to be selective and to be closely analogous to the resonance radiation of vapours.  
L. J. H.

**Mesomorphic State and Magnetic Birefringence.** L. ROYER (*Compt. rend.*, 1924, **178**, 1066—1068).—An attempt to apply certain quantitative laws relative to magnetic birefringence to the

birefringence of mesomorphic substances. If  $n_0$  is a fictitious refractive index for a temperature in the mesomorphic region, calculated from the temperature coefficient of the refractive index in the isotropic region, and  $n_1$  and  $n_2$  are the actual ordinary and extraordinary indices at the temperature considered,  $a=(n_1-n_0)/(n_2-n_0)=-2$ , independent of wave-length. Also, Havelock's expression connecting  $n_1$  and  $n_2$  is applicable to certain classes of liquid crystals. Magnetic birefringence and the birefringence of liquid crystals decrease in a similar manner with increase in temperature.

It is concluded that magnetic birefringence is due to the orientation of anisotropic molecules by an external magnetic field, whilst that of the mesomorphic state is caused by a spontaneous orientation of the molecules by the molecular field. A. B. H.

**Relation between the Refractivities and the Sizes of the Atoms of certain Elements.** J. E. CALTHROP (*Phil. Mag.*, 1924, [vi], 47, 772—779).—The refractivities of 15 elements of groups V, VI, VII, and O of the periodic table, for the sodium  $D$  line, have been compared with the corresponding atomic volumes, derived from the results of W. L. Bragg (*ibid.*, 1920, 40, 169). For the elements of a vertical column, the refractivity is proportional to the atomic volume. The ratio of refractivity to atomic volume decreases with decreasing valency. The ratios of the refractivities in a vertical column are approximately the same for the last four groups and correspond with those found by Cuthbertson (A., 1909, ii, 105). It is suggested that this is due to the approach of the atomic radii to a constant value towards the end of a period. With the exception of the values for xenon, iodine, tellurium, and arsenic, for which the discrepancies are large, the results agree among themselves to about 5%, which is in accordance with the order of discrepancy found in the estimates of atomic radii by different workers. A. E. M.

**Molecular Refraction of Ions and Molecules and Atomic Structure.** K. FAJANS and G. JOOS (*Z. Physik*, 1924, 23, 1—46).—A discussion of the molecular refraction of ions and molecules in the solid state and in solution. The assumption is made that molecular refraction is a measure of the elasticity of the electron envelopes of the atoms or ions, and that changes in its value indicate deformations of the electron systems.

Such deformations produced by cations are considerably greater than those produced by anions. This is due to the relatively weak electrostatic field of the anions, which for the most part occupy a much larger volume than the cations. S. B.

**Optical Constants of Metallic Films obtained by Cathodic Sputtering.** K. LAUCH (*Ann. Physik*, 1924, [iv], 74, 55—78).—The refractive index, extinction coefficient, coefficient of reflection, and the angles of principal incidence and azimuth have been determined with light from 5460 Å. to 5780 Å. for opaque films of silver, gold,

platinum, copper, and nickel obtained by cathodic sputtering. For various grades of purity there is a relation between the constants and the principal angles; the lowest refractive index is given by the purest film. The values of the constants found with the maximum absorption coefficient are very nearly equal to the optical parameters of the metal in bulk. S. P. B.

**Refractive Indices of Calcite and Aragonite.** W. L. BRAGG (*Proc. Roy. Soc.*, 1924, **A**, 105, 370—386).—The refractive indices of calcite and aragonite have been calculated from a knowledge of the relative positions of the atoms of calcium, carbon, and oxygen given by X-ray analysis, and of the extent to which the atoms become polarised under a given electric field, as deduced from the atomic refractivities. These values are in fair agreement with the values observed by experiment when the possible errors in calculation are taken into consideration.

The strong double refraction of calcite and aragonite is attributed to the structure of the  $\text{CO}_3$  group. X-Ray analysis shows that it consists of three oxygen atoms grouped round a central carbon atom and lying in one plane. These oxygen atoms, owing to their position, must be strongly polarised, and more so by an electric field parallel to the plane of the group than by one perpendicular to it. Hence the refractive index of the crystal is greater when the electric vector is perpendicular to the trigonal axis than when it is parallel. A similar structure probably accounts for the strong birefringence of sodium nitrate.

An arrangement of the oxygen atoms in the  $\text{SO}_4$  group which would account for the weak birefringence of the sulphates is suggested, but these crystals have not yet been satisfactorily examined by X-rays. M. S. B.

**Rotatory Dispersion of Tartaric Acid.** L. LONGCHAMON (*Compt. rend.*, 1924, **178**, 951—953).—A section of a tartaric acid crystal cut normally to the optic axis exhibits rotatory dispersion which follows a normal course but is of considerable magnitude, the ratio between the rotations for the indigo and yellow mercury rays being 2.14, whereas for tartrates this ratio does not exceed 1.8. Examination of the curves representing the dispersion of solutions of tartaric acid in water and in salt solutions shows that the dispersion of the laevorotatory component assumed to exist in such solutions lies between 2 and 2.2 and is thus nearly identical with that of crystallised tartaric acid. Further, the dispersion 2.14 corresponds with the rotatory power  $-70^\circ$ , which may be regarded as the specific rotation of the laevorotatory component. Hence the latter is neither an anhydride nor an internal ether, but ordinary tartaric acid, as it exists in the crystals; the author suggests for it the name  $\alpha$ -tartaric acid and for the dextrorotatory compound the name  $\beta$ -tartaric acid. T. H. P.

**Induced Asymmetry of Unsaturated Radicals in Optically Active Compounds.** T. M. LOWRY and E. E. WALKER (*Nature*, 1924, **113**, 565—566).—The authors have independently concluded that, instead of the asymmetric centres of a molecule being made

to adopt the absorption frequencies of the chromophoric groups, the latter exhibit "induced asymmetry," themselves becoming optically active when coupled sufficiently closely to an asymmetric complex. Thus the chromophoric groups will contribute directly to the optical rotatory power of the molecule, as represented in the equations of rotatory dispersion, instead of indirectly as a substituent. The inequality of the two linkings of a double bond (as evidenced in the camphor series) is quoted in support, as also is the polar view that activation of a double bond leads ultimately to a complete rupture or ionisation of one of the two linkings, and therefore to a disappearance of symmetry. Bohr's atom provides possibilities for the development of asymmetry, *e.g.*, in saturated groups,  $\text{:CH}_2$ ,  $\text{:CMe}_2$ ,  $\text{:CBr}_2$ , and in unsaturated groups,  $\text{:CO}$ ,  $\text{:C:C}$ , if placed in an asymmetric environment, optical activity appearing only under conditions which would lead to the production of unequal quantities of the two enantiomorphous forms. Induced asymmetry can give rise to important developments of rotatory power only when applied to unsaturated or chromophoric groups, and need not lead to an optical rotation of the same sign as that of the fixed asymmetric groups by which it is controlled. A. A. E.

**Production of a Luminous Discharge in a Gas by very small Differences of Potential.** S. BOROVIC and W. PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 486—496).—The method employed combined the methods of Wehnelt (*Ann. Physik*, 1904, **14**, 425), and of J. J. Thomson ("Conduction of Electricity through Gases," 1906, 599). The apparatus used had a cathode covered with barium oxide and the anode with sodium phosphate. These could be heated independently. The simultaneous heating of the electrodes considerably lowers the difference of potential necessary to maintain the luminosity of the discharge. Under favourable conditions, the luminosity of hydrogen was observed at a difference of potential equal to 18 volts. Since a connexion between luminosity and the ionisation of a gas doubtless exists and the ionisation potential of hydrogen is equal to 11 volts, it is very likely that under suitable conditions it will be possible to bring the potential required for the luminosity of hydrogen still nearer to the ionisation potential, *i.e.*, 11 volts. S. P. S.

**Behaviour of Low Velocity Electrons in Methane.** G. GLOCKLER (*Proc. Nat. Acad. Sci.*, 1924, **10**, 155—159).—Electrons moving under the influence of a low potential gradient (up to 20 volts) were passed through argon, helium, hydrogen, methane, and nitrogen, respectively, in the usual 3-electrode apparatus, and the current-potential curves obtained. Well-defined maxima were given by argon, methane, and nitrogen between 0 and 1 volt, but not by hydrogen or helium. In the case of methane, it is shown that the maximum is not due to its dissociation or to its thermal decomposition by the hot filament, but it may be due to a low radiation potential of the gas or to its transparency for slow electrons. By analogy with argon (*cf.* Minkowski and Sponer, *Z. Physik*, 1923, **15**, 403), the latter is considered more probable. L. J. H.

**Ionisation of Gases as a Function of the Energy of Electron Impacts.** A. L. HUGHES and E. KLEIN (*Physical Rev.*, 1924, **23**, 450—463).—Helium, neon, argon, hydrogen, nitrogen, and methane, respectively, were exposed at low pressure to the bombardment of electrons and the fraction of the total number of collisions  $f(V')$  which resulted in ionisation was determined as a function of the maximum energy of impact, over a range from the ionisation potential to 300 volts. Owing to the conflicting experimental data on the subject, the total number of collisions was calculated from the kinetic theory. The absolute values may be in error from this cause, but the relative values are unaffected.  $f(V')$  was found to increase very rapidly to a maximum, beyond which there was a less rapid, although marked, decrease. The maxima occur at 147, 157, 80, 74, 101, and 80 volts for the gases in the order named, the maximum fractional ionisation being respectively 0.11, 0.14, 0.35, 0.21, 0.32, and 0.28. A break in the argon curve suggests  $L$  radiation for argon at 250 volts impact energy, and a break in the methane curve indicates possible  $K$  radiation for carbon at 248 volts (cf. following abstract). L. J. H.

**Effective Radii of Gas Molecules.** L. L. NETTLETON (*Proc. Nat. Acad. Sci.*, 1924, **10**, 140—145).—The effective radius of a gas molecule is defined as the radius of a sphere about the molecular centre within which (on an average) an electron must pass to ionise a gas molecule. When the gas pressure, number of electrons passing through the gas, and the distance through which the electron travels are kept constant, the number of ions produced decreases with increasing velocity of the electrons. This may be interpreted as a decrease in the effective molecular radius. The relationship was studied for air, hydrogen, and mercury vapour for electron velocities ranging from  $6 \times 10^8$  to  $30 \times 10^8$  cm./sec. The results are in accordance with Rutherford's formula  $I = K/E^{\frac{1}{2}}$ , where  $I$  is the ionisation,  $E$  the energy of the electron, and  $K$  a constant. The data of other workers were reduced to the same basis and give general agreement (cf. preceding abstract). L. J. H.

**Electrical Properties of Helium.** J. S. TOWNSEND and S. P. McCALLUM (*Phil. Mag.*, 1924, [vi], **47**, 737—753).—Experiments on photoelectric currents in helium gas, placed between charged parallel plate electrodes, indicate that the electrons set free from the negative electrode by ultra-violet light acquire sufficient energy to ionise molecules by collision before any other process of ionisation can occur to an appreciable extent. A constant electric force of 120 volts/cm. was maintained between the plates, and for a certain range of plate distances, with constant gas pressure, the currents are given by the formula  $n = n_0 e^{ax}$ . Above this range, the rate of increase of current is greater and an additional ionisation process must occur, the nature of which is discussed. The positive and negative currents from a filament for pressures of helium of 4—20 mm. increase rapidly above a filament potential of 20 volts. There is no effect due to electrons set free from the negative electrode by radiation

from activated helium comparable with that due to direct ionisation by electron collision with molecules, nor do positive ions make any appreciable contribution. These results are not in agreement with the properties of atomic models as indicated by the quantum theory nor with the theory of ionisation potentials. It is concluded that the additional ionising agency is direct ionisation by electron collision and that the action is essentially the same either in the presence or absence of ultra-violet light. A. E. M.

**Emission from an Incandescent Platinum Wire in Air.** A. M. TYNDALL and G. C. GRINDLEY (*Phil. Mag.*, 1924, [vi], 47, 689—702).—When removed from the vicinity of the particles, the electrons from an incandescent platinum wire attach themselves to molecules and give rise to normal ions of the same mobility as those produced by polonium. The positive emission is complex, and although the greater number have mobility of 1.4 cm./sec./volt/cm. the mean value is of the order of 1.1. It is concluded that positive ions are emitted either as small metallic clusters or as atoms, many of which cluster before reaching the observation chamber, and that the uncharged particles are metallic clusters ranging from atomic size to metallic dust. Their growth and subsequent coagulation are held responsible for the blackening of filament lamps. A. E. M.

**Electron Stream Generated by Ionic Impacts on Platinum in a High Vacuum.** E. BADAREU (*Physikal. Z.*, 1924, 25, 137—140).—Experiments on a 3-electrode vacuum tube with a hot platinum anode indicate that there is no definite energy minimum which cations must possess in order to eject electrons from the cathode, although such a minimum has been postulated in explanation of the cathode fall. Within the range of the experiments (cathode fall of 75—400 volts) the number of electrons ejected was proportional to the energy of the ions at impact. It is suggested that the normal cathode fall is determined by the minimum number of electrons which must be ejected from the cathode to stabilise the discharge. S. B.

**Thermodynamics of Electron Emission.** O. W. RICHARDSON (*Proc. Roy. Soc.*, 1924, A, 105, 387—405).—A mathematical paper in which the sudden reversible changes in thermionic emission at transition points are considered thermodynamically. The relation of thermionic emission to the kinetic electron theory of metallic conduction is also discussed. The author considers that the experiments of Davisson and Germer (*Physical Rev.*, 1922, 20, 300) on the latent heat of electron emission, definitely contradict the kinetic theory of metallic conduction in favour of a theory according to which the kinetic energy of the internal electrons is either zero or practically independent of temperature. This is not inconsistent with Bohr's theory of electron orbits, because the electrons might be handed on from one orbit to another, possibly through intersection or coalescence of neighbouring orbits at certain points. M. S. B.

**Emission of Electrons under the Influence of Chemical Action.** M. BROTHERTON (*Proc. Roy. Soc.*, 1924, **A**, 105, 468—480).—A continuation of previous work by Richardson (*A.*, 1921, ii, 422). The emission of electrons from liquid alloys of sodium and potassium when acted on by carbonyl chloride has been examined at both low and high pressures. The saturation current may be as large as  $3.8 \times 10^{-8}$  amp. where the rate of the drops is 54 per minute and the average pressure 0.027 mm., and as small as  $2.0 \times 10^{-11}$  amp. for a rate of drops of 2 per minute and a pressure as large as 0.21 mm. The shape of the current-potential curve is dependent mainly on the pressure of the gas and is independent of the composition of the alloy.

An important factor in the emission is the accumulation of the products of reaction on the surface of the drops. Exceptional results, not yet explained, are obtained for very slow and very fast rates of fall of the drops.

M. S. B.

**[Effect of Gas Evolution on] the Photoelectric Effect.** R. DÜMPELMANN and W. HEIN (*Z. Physik*, 1924, **22**, 368—383).—Oxygen and hydrogen, generated either chemically or electrolytically, on one side of an iron plate, greatly increase the photoelectric effect from the other, when the latter is illuminated by ultra-violet light. It is concluded that this phenomenon is connected with the occlusion of gas by the metal plate, as evolution of gas has very little or no effect on the electron emission from copper, which occludes very little gas in comparison with iron. The recovery from "fatigue" in photoelectric emission is also much more rapid with an iron plate highly charged with occluded gas than with one nearly free from it.

S. B.

**Photoelectric and Selenium Cells.** RESEARCH STAFF OF THE GENERAL ELECTRIC CO. (*Nature*, 1924, **113**, 606).—Photoelectric cells prepared with untreated surfaces of the alkali metals in a high vacuum are trustworthy, and of sufficiently great sensitivity for ordinary photometric purposes.

A. A. E.

**Mobility of Radioactive Ions in the Bunsen Flame.** E. N. DA C. ANDRADE (*Z. Physik*, 1924, **22**, 345—346).—An answer to criticism by Schönborn (*ibid.*, 1921, **4**, 118) of a previous paper (*Phil. Mag.*, 1912, [vi], **23**, 865) on the mobility of ions in flames.

S. B.

**Variations of the Thermo-electric Power of Iron with its Structure.** W. HERAEUS (*Ann. Physik*, 1924, [iv], **73**, 554—576).—The experiments of Borelius and Gunneson (*ibid.*, 1922, **67**, 227) are criticised. A new method of observing the thermo-*E.M.F.* between annealed and unannealed iron is described. One part of a long rod of iron was heated to a temperature between 70° and 950° and then quenched. The *E.M.F.* between this part and the adjoining unaltered part of the rod depends on the time of heating, and on the temperature attained before the quenching. The curves connecting the *E.M.F.* with the quenching temperature



have a sharp maximum at  $490^{\circ}$ , and a minimum at  $790^{\circ}$ . With a longer heating period, the *E.M.F.* rises more regularly with the temperature. S. B.

**Hall Effect and Thermo-electric Power.** P. RAETHJEN (*Physikal. Z.*, 1924, 25, 84—89).—The constant for the Hall effect for a number of metals at a magnetic field strength of 10,500 gauss,  $R \times 10^4$ , is for silver, 9.44; gold, 7.36; platinum, 2.30; copper, 6.09; aluminium, 3.43; tin, 0.41; palladium, 7.60. The constant for palladium is practically unaffected by saturating the metal with hydrogen when a correction is applied for the expansion of the metal. The thermo-electric force against silver of these metals was also determined. According to Lorentz's theory of metallic conduction, the thermo-electric force between two metals should be proportional to the logarithm of the ratio of the Hall constants of the metals. If  $E$  is the thermo-electric force between the metal and silver in microvolts per degree, and  $K$  is the logarithm of the ratio of the Hall constant of silver to that of the metal measured, the data found may be summarised as follows. Gold,  $E = -0.26$ ,  $K = 0.247$ ; platinum,  $E = -2.94$ ,  $K = 1.410$ ; aluminium,  $E = -3.30$ ,  $K = 1.010$ ; copper,  $E = -1.78$ ,  $K = 0.439$ ; tin,  $E = -2.57$ ,  $K = 3.130$ ; palladium,  $E = -11.50$ ,  $K = 0.149$ ; palladium saturated with hydrogen,  $E = -5.30$ ,  $K = 0.122$ ; there is no simple relationship between the two series of numbers, as would be expected from the theory. Palladium and palladium saturated with hydrogen have nearly the same value for the Hall constant, and should therefore develop only a small thermo-electric force; it is found, however, that this couple gives the large figure of 16.8 microvolts per degree. The results of this investigation are therefore directly opposed to the usual electronic theory of metallic conduction which assumes that only one kind of charged particle is in motion.

S. S.

**Paramagnetism of Iron in Potassium Ferricyanide.** P. COLLET (*Compt. rend.*, 1924, 178, 937).—The value of the molecular susceptibility of potassium ferricyanide in aqueous solutions containing from 1.127 g. to 20.27 g. per 100 g. of solution varies from  $1960 \times 10^{-6}$  to  $2258 \times 10^{-6}$ , the relative accuracy being 1 in 36 in the former case and 1 in 720 in the latter. The diamagnetism of the residue,  $[\text{K}_3(\text{CN})_6]$ , was found by Pascal to be  $118 \times 10^{-6}$ . Calculation in accordance with Curie's law gives for the magnetic moment of the iron atom the values 11.40 and 10.91 for high and low concentrations of the salt, respectively. These values, like the value 13 deduced by Weiss from Honda's measurements on the solid ferricyanide, are greatly inferior to the number of magnetons, namely, 26, 27, and 29, found in normal ferric salts. T. H. P.

**Magnetothermal Phenomenon and the Specific Heat of Nickel.** P. WEISS and R. FORRER (*Compt. rend.*, 1924, 178, 1347—1351).—The rise of temperature due to the liberation of heat on magnetisation is a linear function of the strength  $H$

of the magnetic field between  $20^\circ$  and  $277.5^\circ$ , whilst the curves are concave towards the axis of  $H$  between  $277.5^\circ$  and  $357^\circ$ . The theoretical interpretation of the observations is discussed.

A. B. H.

**Magnetic Isothermals of Nickel.** P. WEISS and R. FORRER (*Compt. rend.*, 1924, **178**, 1046—1049).—Curves have been drawn representing the specific magnetisation of nickel as a function of the field, from  $H=0$  to  $H=17,000$  gauss, and for temperatures from  $20^\circ$  to  $405.7^\circ$ . Below the saturation point (about 5000 gauss) and at temperatures below  $357^\circ$ , a hyperbolic curve is obtained. For fields above 5000, the magnetisation is proportional to the field. At temperatures above  $357^\circ$ , the rate of increase of the magnetisation for fields of feeble intensity diminishes, and the rectilinear portion of the curve becomes hyperbolic. At still higher temperatures, the magnetisation is proportional to the field over the whole range.

A. B. H.

**Transformation of Atoms and Researches on the Chemical Elements.** O. HAHN (*Z. angew. Chem.*, 1924, **37**, 153—158).—A general account of radioactivity, isotopes, and atomic structure.

S. K. T.

**Effect of Temperature on the Luminosity of Radium Compounds.** J. A. RODMAN (*Physical Rev.*, 1924, **23**, 478—487).—Tubes containing radium bromide, pure or mixed with barium bromide, were sealed under reduced pressure, heated to various temperatures, and then cooled to some fixed temperature. The initial luminosity (after cooling) was almost directly proportional to the proportion of radium present and was the greater the more sudden the cooling. It increased exponentially with the temperature of pre-heating. The rate of decay of the luminosity was far greater with radium bromide than with the mixtures, but was similar in form in all cases. After the first hour it may be represented by the equation  $I_t = I_\infty + I_0 e^{-\Delta t^b}$ . The final (equilibrium) luminosity  $I_\infty$  depends only on the composition and temperature, and not on the previous treatment. The results support Rutherford's theory of "active centres," but suggest that these are produced at all temperatures at rates dependent on the temperature.

**Apparatus for Purification of Radium Emanation.** V. F. HESS (*Phil. Mag.*, 1924, [vi], **47**, 713—721).—An apparatus is described giving quick and efficient purification of radium emanations from other gases such as hydrogen, oxygen, carbon dioxide, etc. The equivalent amounts of hydrogen and oxygen are recombined by an electric spark, and water vapour and carbon dioxide absorbed. The process of purification occupies about 15 minutes and gives a final concentration of about 1 millicurie per c.mm. To produce higher concentrations, the emanation tube is cooled with liquid air before sealing off.

A. E. M.

**Long-range Particles from Radium-active Deposit.** D. PETTERSSON (*Nature*, 1924, **113**, 641—642).—The results of Bates and Rogers (A., 1923, ii, 720) are criticised in that the existence of long-range particles from radium-*C* would involve invalidity of the Geiger-Nuttall equation; the observed heterogeneity of velocity is, however, a familiar feature with particles of secondary origin. New experiments indicate that it is extremely doubtful whether any hydrogen- or  $\alpha$ -particles of a range exceeding 7.5 cm. of air are discharged from radium-*C*; in any case, their number cannot be more than a few % of the number given by Bates and Rogers.

A. A. E.

**Brightness of Scintillations from H-Particles and from  $\alpha$ -Particles.** E. KARA-MICHAILOVA and H. PETTERSSON (*Nature*, 1924, **113**, 715).—A method has been developed whereby the surface-brightness of two kinds of scintillations can be compared. Such comparison, first of hydrogen- and  $\alpha$ -particles, and then of  $\alpha$ -particles with the particles expelled from quartz, indicates that the latter are hydrogen nuclei expelled from the silicon atoms (cf. Bates and Rogers, A., 1923, ii, 720; Kirsch and Pettersson, A., 1923, ii, 675, 819; Rutherford and Chadwick, this vol., ii, 296).

A. A. E.

**Artificial Disintegration of Atoms.** G. KIRSCH and H. PETTERSSON (*Nature*, 1924, **113**, 603; cf. A., 1923, ii, 819).—By means of a method similar to that employed by Rutherford and Chadwick (this vol., ii, 296), experiments carried out in helium indicate that carbon gives hydrogen particles of about 6 cm. range; previous results with silicon and beryllium were confirmed. Oxygen appears to give  $\alpha$ -particles of 9 cm. range in the forward direction (cf. Bates and Rogers, A., 1923, ii, 720). The results support the "explosion" as against the "satellite" hypothesis for the mechanism of atomic disintegration.

A. A. E.

**Structure of the Atomic Nucleus and the Mechanism of its Disintegration.** H. PETTERSSON (*Proc. Physical Soc.*, 1924, **36**, 194—202).—As an alternative to the view that the H-particle which is expelled from certain atoms as the result of bombardment by  $\alpha$ -particles, is a satellite of the nucleus and is removed from it owing to a transfer of the momentum of the  $\alpha$ -particle to the H-particle, the author suggests that the  $\alpha$ -particle transfers its momentum to the nucleus as a whole and that subsequently an explosion takes place during which the H-particle is emitted. Approximate calculations are made of the velocities to be expected for the H-particles from various nuclei and the results compared with experiment. In four of the six elements considered, the agreement is good, but the observed velocities for particles from boron and fluorine are much less than those calculated. The law of force between electrical charges in the neighbourhood of the nucleus is discussed, and it is claimed that the hypothesis put forward removes the necessity of postulating a change from a repulsive to an attractive force. The data at present available are too limited to decide definitely in favour of either mechanism,

and the author concludes by suggesting lines of further research work.  
G. S.

**Structure of Sulphur.** H. COLLINS (*Chem. News*, 1924, **128**, 289—291).—From the relative volumes and heats of formation of sulphur compounds, it is deduced that the atom of sulphur is constituted thus:  $\text{Na}-\text{H}-\text{H}_3-\text{H}-\text{H}_3-\text{H}$ . The heat of formation of an element expressed as large calories is frequently equal to a relative volume of the element or to a relative volume multiplied by a valency of the element.  
A. R. P.

**Binding of Electrons in the Nucleus of the Mercury Atom.** H. NAGAOKA, Y. SUGIURA, and T. MISHIMA (*Nature*, 1924, **113**, 567—568).—In order to explain the fact that the structure of the line 3131.84 Å. does not satisfy the relation previously given (this vol., ii, 295), it is assumed that in atoms of elements consisting of several isotopes, the binding of positive and negative protons is not simple; it is conceived that a mass of electrons may make coupled vibrations with a mass of protons. Further, it is supposed that the quantum relation still holds in the neighbourhood of the nucleus, so that the particle can move in stationary orbits. The hypothesis that, at distances of nuclear dimensions, there is attraction between like electrical charges, and repulsion among unlike, would thereby be supported.  
A. A. E.

**Magneton Number and Atomic Structure.** J. DORFMANN (*Z. Physik*, 1924, **23**, 286—293).—An attempt is made with the help of the Bohr theory to explain the observed magneton numbers of the various ions in the paramagnetic groups. The fundamental assumptions made are (1) that the ion is paramagnetic if the number of electrons in one or more of the groups with similar ( $n_k$ ) orbits is odd; (2) that it is only one electron in any such odd group which contributes to the effect: its moment is  $k$  Bohr magnetons; (3) the moments of these special electrons are additive if they belong to groups with the same total quant number ( $n$ ) and act independently if they belong to different groups. With the help of these assumptions, the author calculates the magneton numbers of various ions and compares them with the experimental results. It is shown that a satisfactory agreement is obtained, not only for the iron group, but also for the rare earths. Tables of the proposed electron distributions in the different ions are given, and other evidence is quoted in support of the structure suggested by the magnetic properties.  
G. S.

**X-Ray Examination of Metal Films.** (SIR) W. H. BRAGG (*Nature*, 1924, **113**, 639).—Examination of films of gold, silver, aluminium, and copper suggests that beating puts some strain into a crystal, although it increases the amount of arrangement, whereas heating relieves the strain, allowing surface tension to come into play. The greater strain is also the cause of the greater response to chemical action which is found in the beaten state.  
A. A. E.

**Crystalline Structure of Succinic Acid, Succinic Anhydride, and Succinimide.** K. YARDLEY (*Proc. Roy. Soc.*, 1924, **A**, 105, 451—467).—Crystals of succinic acid and its derivatives have been examined by  $X$ -ray methods. The monoclinic holohedral crystal of succinic acid possesses two molecules per unit cell. The structure is based on the Bravais lattice,  $\Gamma_m$ , and belongs to the space-group,  $C_{2h}^2$ . The arrangement suggested gives an explanation of cleavage and twinning. It has not been found possible to determine with certainty the space-group to which the orthorhombic crystals of succinic anhydride belong. They are based, however, on the lattice  $\Gamma_o$  and have four molecules in each cell. The orthorhombic holohedral crystal of succinimide belongs to the space-group  $Q_h$ ; the unit cell contains eight asymmetric molecules, and the lattice is  $\Gamma_o$ . The different atomic dimensions have also been deduced. M. S. B.

**Crystal Structure of Metallic Arsenic.** A. J. BRADLEY (*Phil. Mag.*, 1924, [vi], 47, 657—671).— $X$ -Ray examination by the powder method shows that the structure of arsenic is very similar to those of antimony and bismuth in that it consists of two interpenetrating face-centred rhombohedral lattices forming a Sohncke point system. The unit rhomb contains eight atoms. The length of the edge of the unit rhomb is 5.60 Å., the longer atomic distance 3.15 Å., and the shorter atomic distance 2.51 Å. A. E. M.

**Crystal Structure of Bismuth.** O. HASSEL and H. MARK (*Z. Physik*, 1924, 23, 269—277).—The crystal structure of bismuth has been re-determined by means of  $X$ -rays, using the rotating crystal with photographic registration. The results confirm the structure proposed by Ogg and James. Bismuth crystallises in the ditrigonal scalenohedral class. It belongs to the point group  $D_{3d}^6$ , the dimensions of the cell being given by  $a=6.57$  Å.,  $\alpha=87^\circ 34'$ . The arrangement of the atoms is that of two interpenetrating face-centred rhombohedra. From a discussion of the intensities, the authors conclude that the co-ordinates of the corners of the two rhombohedra are 0, 0, 0 and  $\frac{1}{2}+x, x, x$ , etc., where the value of  $x$  lies between 0.022 and 0.035. G. S.

**Structure of Sodium Chlorate and Rock Salt Crystals.** C. HERMAN (*Z. Physik*, 1924, 22, 416).—An answer to criticism by Beckenkamp (this vol., ii, 143) of the model proposed by Kiby (A., 1923, ii, 687) for sodium chlorate crystals. S. B.

**Metastability of the Elements and Chemical Compounds in Consequence of Enantiotropy or Monotropy.** V. E. COHEN and A. L. T. MOESVELD (*Proc. K. Akad. Wetensch.*, 1924, 27, 81—82).—The discrepancy between the results obtained for the structure of silver iodide on the basis of  $X$ -ray observations (cf. Wyckoff, A., 1923, ii, 300; Wilsey, A., 1921, ii, 548) is attributed to the dimorphism of the substance and the variation in the proportions of the two forms in different samples. T. H. P.

**Metastability of the Elements and Chemical Compounds in Consequence of Enantiotropy or Monotropy.** IV. E. COHEN and J. KOOY (*Proc. K. Akad. Wetensch.*, 1924, **27**, 65—80; cf. A., 1920, ii, 620, 625).—In consequence of the reluctance exhibited by the  $\beta$ -rhombohedral modification (III) of ammonium nitrate to undergo transformation into the  $\alpha$ -rhombohedral modification (IV), the values given by Bridgman (*Proc. Amer. Acad. Arts and Sci.*, 1916, **51**, 581) for the change in volume accompanying this transformation are erroneous. By two different methods, the authors find that the change occurs at  $32.3^\circ$ , which is considered to be more accurate than the value,  $32.1^\circ$ , obtained by Early and Lowry (T., 1919, **115**, 1387). The decrease in volume per gram is 0.0221 c.c. T. H. P.

**Compressibility of the Alkali Halides.** J. C. SLATER (*Physical Rev.*, 1924, **23**, 488—500).—The compressibility of eleven alkali halides and its variation with pressure has been determined up to 12,000 atm. for both  $30^\circ$  and  $75^\circ$ , the samples being single crystals. Approximate values for the compressibilities at zero pressure and temperature are obtained by extrapolation. The crystal potential energy as a function of volume, at absolute zero, is determined from the experimental results, and an empirical expression for it is developed which, at large volumes, is found to be approximately equal to the expression derived by Madelung on the assumptions that the potential energy is due to electrostatic action and that each atom is singly charged. For smaller volumes, the potential energy is partly associated with the repulsive forces, and, with the assumption that the attractive forces are solely electrostatic, a series development is obtained for the repulsion between atoms. This is found not to vary as any single inverse power of the grating space, nor is there any discontinuity between lithium and the other metals, as demanded by the theory of Born. Values for the energy of dissociation of the crystals into ions are given.

The compressibilities and their coefficients with pressure (at the absolute zero) are plotted against the alkali ion for a series of salts with the same halogen ion, and *vice versa*. The curves break sharply at the ion similar to argon ( $K^+$  or  $Cl^-$ ), the rate of increase suddenly decreasing. This is in accordance with Bohr's theory of atomic structure. L. J. H.

**Compressibility of Alkali Salts.** E. SAERENS.—(See ii, 334.)

**Extension of Zinc Crystals.** E. N. DA C. ANDRADE (*Z. Physik*, 1924, **22**, 343—344).—A priority claim in observations on the extension of metallic crystals, over the work of Mark, Póányi, and Schmid (*ibid.*, 1922, **12**, 58). S. B.

**Etching of Hollow Metallic Crystals.** R. GROSS, F. KOREF, and K. MOERS (*Z. Physik*, 1924, **22**, 317—321).—A hollow tungsten cylinder, in which the direction of the crystallographic axes was constant throughout, was etched with alkaline potassium ferri-cyanide solution. Six equal faces were developed by this treat-

ment on the interior, and six on the exterior of the cylinder. The interior faces were set at  $30^\circ$  to the adjacent exterior faces. This relative position is in accordance with the rule that the exterior faces developed on an etched cylinder are the planes of maximum solution velocity, those on the interior the planes of minimum velocity.

S. B.

**Deformation and Strength of Crystals.** A. JOFFÉ, M. W. KIRPITSCHewa, and M. A. LEWITZKY (*Z. Physik*, 1924, **22**, 286—302).—The elastic constants of rock-salt have been determined approximately by examination of the Laue X-ray patterns from crystals under strain. The "elastic limit" of a crystal is defined as the minimum strain producing distortion of the Laue pattern. It is a well-defined constant for a given material and temperature, and decreases to zero at the melting point. The plastic deformation of rock-salt above this elastic limit consists of movements along the (110) glide planes, as is shown by the points on the patterns, which correspond with these planes, alone remaining sharp. The plastic deformation increases its tensile strength about twelve times. The discrepancy between the theoretical and experimental values of the tensile strength of rock-salt is explained by surface cracking. Crystals immersed in water have a greatly increased strength, which may be due to the healing of these superficial cracks.

S. B.

**The Valency Bond. Electrovalence and Covalence.** S. H. C. BRIGGS (*Phil. Mag.*, 1924, [vi], **47**, 702—713).—A theoretical discussion in which it is shown that electrovalence entails unequal electron sharing and covalence equal sharing. In the case of ethylene, the ideas of Langmuir and Lowry are reconciled by considering Lowry's formula (T., 1923, **123**, 866) as a distorted case of Langmuir's model and representing an active form present in small amount.

A. E. M.

**Secondary Valency of the Hydroxyl Group. III. Polynuclear Chain forming Complex Salts of Protocatechualdehyde.** H. REIHLEN and A. SAPPER (*Z. anorg. Chem.*, 1924, **132**, 54—64; cf. A., 1922, i, 1146, 1147).—On treating alkaline protocatechualdehyde with nickel and other salt solutions, polynuclear complex derivatives are obtained, containing five metal atoms in the molecule. Their formation is taken as evidence that in the compounds of phenolic derivatives with bivalent and trivalent heavy metals, the hydroxyl group does not exert a secondary valency to the nuclear atom.

H. T.

**Supposed Limitation of the Second Law of Thermodynamics.** J. W. FISHER (*Phil. Mag.*, 1924, [vi], **47**, 779—781).—A verification, by a generalised treatment, of the fallacy shown by Witmer (*ibid.*, 1924, [vi], **47**, 152) in Fairbourn's proof of a limitation of the second law of thermodynamics (*ibid.*, 1922, [vi], **43**, 1047).

A. E. M.

**Wohl's Equation of Condition, especially with Reference to Certain Thermal Values for Water Vapour.** K. NESSELMANN (*Z. physikal. Chem.*, 1924, **108**, 309—340).—In a mathematical paper the advantages and limitations of Wohl's equation of condition (A., 1914, ii, 430; 1922, ii, 117) are discussed. M. S. B.

**Thermal Emission and Evaporation from Water.** M. ALLEN (*Proc. Nat. Acad. Sci.*, 1924, **10**, 88—92).—A quantity termed the thermal emission from a water surface, consisting of radiation, convection, and conduction, has been determined by evaporating water from an electrically heated vessel into an enclosure maintained at a constant temperature of 20.5°, the rate of evaporation being measured at the same time by the loss in weight of the vessel. The thermal emission is defined as the quantity of energy given up per second by unit area of water surface per unit difference of temperature between the surface and surrounding bodies. The experimental data cover a range of 40° and are reproduced by the equation  $10^6 Q = 215 + 4.87(t - t_0) - 0.022(t - t_0)^2$ . The thermal emission of a water surface is greater than that for polished copper and, when the temperature difference is more than 10°, exceeds the emission from blackened copper. The rate of evaporation in inches lowering of the water surface per hour is given by  $10^3 W = 13(p - p_0) + 1.03(p - p_0)^2$ , where  $p - p_0$  is the difference between the vapour pressures of water at the temperatures of the vessel and its environment. The values found are in approximate agreement with those obtained by Fitzgerald (*Trans. Amer. Soc. Civ. Eng.*, 1886, **15**, 581). S. S.

**Isotherms of Gases at 400°, and their Importance for the Gas Thermometer.** L. HOLBORN and J. OTTO (*Z. Physik*, 1924, **23**, 77—94).—Previous measurements of gas isotherms (A., 1922, ii, 737) have been extended to 400°. The corresponding corrections of the gas thermometer to the thermodynamic scale have been calculated. S. B.

**Density and Diffusion of Gases Measured by Displacement Interferometry.** C. BARUS (*Proc. Nat. Acad. Sci.*, 1924, **10**, 153—155).—A simple apparatus is described which virtually gives a comparison, by means of an interferometer, of the pressure of a rather long column of gas with that of an identical column of air. It may be employed to determine both the density and the coefficient of diffusion. The data and calculation for the case of coal gas are given. L. J. H.

**Determination of the Boiling Points of Permanent Gases.** F. HENNING and W. HEUSE (*Z. Physik*, 1924, **23**, 105—116).—The temperatures recorded are: oxygen, — 183.00°; nitrogen, — 195.81°; hydrogen, — 252.78°. The probable error is given as  $\pm 0.02^\circ$  for each constant. S. B.

**Alternation in the Heats of Crystallisation of the Normal Monobasic Fatty Acids.** I. W. E. GARNER and F. C. RANDALL (*J. Chem. Soc.*, 1924, **125**, 881—896).—The molar heats of crystallis-



ation of the acids from octoic to lauric alternate in value, the odd acids having heats of crystallisation which are less than the means of those of their neighbours. The molar heat capacities of the liquid acids show only slight alternation, the odd members possessing the higher value.

The heats of crystallisation of the  $\beta$ -forms of undecolic and nonoic acids fall just above the curve for the even acids. The observed differences between the odd and even acids are attributed to differences in the mode of attachment of the carboxyl groups in the crystal molecule (cf. T., 1923, 123, 2043, 3152). S. K. T.

**Boiling Point of Bromine.** A. BOUZAT and G. LELUAN.—(See ii, 247.)

**Vapour-pressure Measurements for Ozone.** E. H. RIESENFELD and M. BEJA.—(See ii, 248.)

**Vapour Pressure of Carbon.** A. THIEL and F. RITTER.—(See ii, 253.)

**Osmotic Pressure of certain Electrolytes of High Molecular Weight.** E. and H. HAMMARSTEN (*Ark. Kemi, Min., Geol.*, 1923, 8, No. 27, 1—16).—Thymus-nucleic acid, which is a fairly strong tetra-basic acid, and its sodium salt exhibit abnormal osmotic properties similar to those shown by Congo-red. Aqueous solutions of the acid contain numerous colloidal particles, some of them aggregated, and their osmotic pressures are about 70% of the values calculated for the undissociated compound. The pressures calculated from the observed hydrogen-ion concentration are also higher than the observed values. The sodium salt is considerably hydrated in aqueous solution and thus shows no ultramicroscopic particles, but the osmotic pressures of its solutions are 78% of the values calculated for the undissociated state.

In explanation of these abnormal results it is suggested that the molecular volume plays a part and that two ions forming a salt give rise to an osmotic pressure double that of the undissociated compound only when the smallest distance between these ions never falls below a certain magnitude.

Measurements of the osmotic pressures and conductivities of solutions of guanylic acid and its disodium salt, thymus-nucleic acid and its sodium salt, sodium glycocholate, taurocholic acid and its sodium salt, protamine chloride, and histone chloride are recorded. These are compared with data for brilliant-Congo, Congo-blue, and Chicago-blue. The results suggest that when ions of small volume combine with ions of large volume to form salts the number of the ions which are osmotically inactive increases with the size of the large ion. T. H. P.

**Osmotic Equation of State and Activity of Dilute Strong Electrolytes.** P. DEBYE (*Physikal. Z.*, 1924, 25, 97—107).—A theoretical paper in continuation of previous work (A., 1923, ii, 459, 617, 729). It is assumed that strong electrolytes are

completely dissociated and that in great dilution their osmotic pressure,  $P$ , is the same as that of an ideal solution,  $\bar{P}$ , modified by their mutual electrical action. By considering the thermodynamical process of concentrating such a solution (*a*) by means of a semipermeable membrane and (*b*) by first reversibly removing the charge to infinity, concentrating the residual ideal solution by a semipermeable membrane, and then restoring the charge, the expression  $P = \bar{P} - \delta W / \delta V$  is deduced, where  $W$  is the electrical work involved. The discussion is limited to the case of solutions so dilute that the dielectric constant of the solution is sensibly the same as that of the pure solvent. A theoretical value for the activity coefficient is derived from this, and the empirical law of Lewis that "in dilute solutions the activity coefficient of a given strong electrolyte depends only on the total ionic strength of the solution" receives a theoretical interpretation as a limiting law for infinite dilution. On applying the expression obtained, which contains no arbitrary constant, to solutions of finite concentration, the activity coefficients at 20° of univalent electrolytes in solutions of ionic strength 0.001 and 0.1 are calculated to be 0.89 and 0.70, respectively, whilst the experimental values of Lewis vary between 0.92 and 0.85 for the former and between 0.84 and 0.61 for the latter value. Somewhat similar agreement is found for bivalent electrolytes, and, considering the deliberate neglect of specific factors, this is considered very satisfactory.

L. J. H.

**Calculation of the Limiting Value  $\lambda_\infty$  of the Equivalent Conductivity of Uni-univalent and Uni-*n*-valent Salts in Aqueous and Non-aqueous Solutions.** P. WALDEN (*Z. physikal. Chem.*, 1924, **108**, 341—386).—The author shows that the behaviour of different electrolytes, on dilution in a given medium, can be very simply represented by the equation  $\lambda_\infty = \lambda_v(1 + n_1 n_2 K_1 / v^{0.5})$ , in which  $n_1$  is the valency of the cation,  $n_2$  that of the anion, and  $K_1$  is a constant which depends only on the dielectric constant of the solvent. The value of  $K_1$  between 0° and 25° is taken as 0.692 and at 100° as 0.818.

On putting  $a = \lambda_v / \lambda_\infty$  the dissociation constant  $K_2 = a / [(1 - a)v^{0.5}] = 1/0.692n_1 n_2$  is obtained.

These equations have been applied to the experimental data, for a very large number of electrolytes of various types, and they are found to hold down to dilutions as low as  $v = 32$  in some cases. That is, all salts of the same type, at the same dilution in the same solvent, have the same ionisation constant,  $K_2$ , or the same value for  $a$ , this expression being interpreted simply as a conductivity ratio.

Similar equations have also been found to apply to non-aqueous solvents, in so far as they have been tested using data for uni-univalent salts. For these, in solvents with a dielectric constant lying between 42 and 12.4,  $K_1$  at 18—25° is given by the expression  $K_1 = 1/0.00872\epsilon$ , where  $\epsilon$  is the dielectric constant. The lower limit of dilution to which the expressions are valid depends on the

dielectric constant, being lower the larger the value of  $\epsilon$ . For example, the limiting dilution for furfuraldehyde,  $\epsilon = 42$ , is 100—200, and for pyridine,  $\epsilon = 12.4$ , it is 5000. M. S. B.

**Electrolytic Dissociation, Temperature, and the Solvent.** A. BRODSKY (*Z. physikal. Chem.*, 1924, **108**, 293—297).—The author shows that Walden's rules (A., 1906, ii, 527; 1920, ii, 599) connecting dielectric constant, dilution, and equivalent conductivity ratio, as well as Abegg's formula (A., 1897, ii, 240) for the dependence of dielectric constant on temperature, are in agreement with Ghosh's ionisation theory (T., 1918, **113**, 449, 627, 707, 790; A., 1922, ii, 125). M. S. B.

**Electrical Conductivity of Flames containing Salts of the Alkali Metals.** A. PONTREMOLI (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 223—227).—On the assumption (Wilson, A., 1916, ii, 72) that the conductivity of a flame containing a salt of an alkali metal is due to ionisation of the alkali metal and of a moderately readily ionisable combustion product present in the flame, the author has derived a value for the electrical conductivity, in the region in which Ohm's law is valid, in terms of the temperature and of universal and atomic constants. (Cf. Noyes and Wilson, A., 1923, ii, 112.) T. H. P.

**Dual Ion of Helianthin and the Dielectric Behaviour of its Solutions.** A. THIEL and A. DASSLER (*Z. physikal. Chem.*, 1924, **108**, 298—302; cf. A., 1923, i, 937, 1109).—The authors discuss the experiments of Blüh (A., 1923, ii, 823) on the dielectric constant of helianthin solutions. On the basis of their own previous determinations of the "apparent" acid and basic constants, they disagree with his conclusions relative to the behaviour of helianthin in solution. They explain Blüh's results by supposing that he used methyl-orange instead of helianthin, and that the water employed was not free from dissolved carbon dioxide. M. S. B.

**Solubility Curves Relating to the Decomposition of Double Salts.** S. M. LEVI (*Z. physikal. Chem.*, 1924, **108**, 411—430).—It is shown that, in a system consisting of water and two salts with a common ion which combine to form a double salt, interesting relationships are found by extrapolating the solubility curves on one side of the temperature axis, until they meet either in the labile or stable region. In addition to the transition temperatures, three other temperatures are thus marked out as characteristic for the system.

A graphical method of representing such systems by plotting the solubility of each solid phase in the presence of one of the other phases is indicated, and several examples of decomposition have been considered.

Evidence is also given to show the incorrectness of Meyerhoffer's rule (A., 1890, 564), according to which the abrupt change of solubility, due to a transition is only shown by the disappearing phase. M. S. B.

**Aqueous Pressure of Hydrated Crystals. II. Oxalic Acid, Sodium Sulphate, Sodium Acetate, Sodium Carbonate, Disodium Phosphate, Barium Chloride.** G. P. BAXTER and W. C. COOPER, jun. (*J. Amer. Chem. Soc.*, 1924, **46**, 923—933).—The air-current method has been used to determine the vapour pressures at different temperatures of the salts mentioned above. Identical results are obtained whether equilibrium is reached from the side of under-saturation or over-saturation of the air current. The results are expressed by the equation  $\log p = a - b/(T + c)$ , where  $a$ ,  $b$ ,  $c$  are constants. The heats of hydration of the dehydrated salts calculated by means of the Clausius-Clapeyron equation, and by a method suggested by van't Hoff (cf. Frowein, *Z. physikal. Chem.*, 1887, **1**, 362) agree fairly well with one another, but do not always agree with those found experimentally by Thomsen ("Thermochem. Unters.," ii, 293; iii, 119 *et seq.*). W. H.-R.

**Law of Solubility of Salts.** P. MONDAIN-MONVAL (*Compt. rend.*, 1924, **178**, 1164—1166).—Measurements of the vapour pressures of solutions of ammonium nitrate between 32.6° and 47.8° agree fairly well with the theoretical values. H. J. E.

**Properties of Mixtures of Aniline, Water, and some Fatty Acids.** J. R. POUND and R. S. RUSSELL (*J. Chem. Soc.*, 1924, **125**, 769—780).—The densities, contractions, and viscosities of mixtures of aniline and water with formic, acetic, and *n*-butyric acids are tabulated for 30° or 30.4°. The mixtures of maximum density are in no case identical with those of maximum contraction or maximum viscosity. The ternary mixtures of aniline, acetic acid, and water with maximum contraction are produced by addition of water to aniline-acetic acid mixtures of maximum contraction. Various complexes appear to be formed in binary mixtures of the above acids with water or with aniline, but, excepting when formic acid is present, there is no evidence of further complex formation in the ternary mixtures. S. K. T.

**Non-, Uni-, and Multi-variant Equilibria. XXIV. XXV.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch.*, 1924, **26**, 719—726; **27**, 57—64).—Theoretical (cf. A., 1923, ii, 137, 546). T. H. P.

**Unimolecular Films of Sodium Ricinoleate in Emulsions.** P. A. VAN DER MEULEN and W. RIEMAN 3rd (*J. Amer. Chem. Soc.*, 1924, **46**, 876—881).—In emulsions of the oil-in-water type, containing a solution of phenol in toluene as the oil phase and sodium ricinoleate as the emulsifying agent, the average size of the globules, determined by counting the number in a given volume by a modification of the hæmacytometer method, and also by measuring individual globules microscopically, indicates that the average area of interface covered by a molecule of sodium ricinoleate is a function of the concentration of soap in the external phase, and varies from 39 to 106 square Å. These figures are not in disagreement with the view that a unimolecular soap film is formed. The amount of soap in the interface is determined, with a probable error of 10%, by

centrifuging the original emulsion so that it is divided into two layers, one practically free from oil globules, and the other containing twice as many globules as the original emulsion; by analysing the two layers as well as the original emulsion, the amount of soap in the interface can be estimated.

W. H.-R.

**Superficial Solutions and the Law of Gases.** A. MARCELIN (*Compt. rend.*, 1924, **178**, 1079—1081).—A continuation of previous work (A., 1923, i, 881; this vol., i, 353). Films of oleic acid on the surface of water consist of a superficial solution analogous to a two-dimensional gas. The product of the area occupied by a given quantity of oleic acid and the superficial pressure exerted by the film remains constant when the occupied area varies from 2 to 9 times the area of the saturated surface. At low pressures, the measurements are complicated by the disturbing effects of surface tension.

A. B. H.

**Effect of a Magnetic Field on the Surface Tension of a Liquid of High Susceptibility.** (MISS) W. L. ROLTON and R. S. TROOP (*Proc. Physical Soc.*, 1924, **36**, 205—207).—A small quantity of the liquid (aqueous solution of ferric chloride or manganous chloride) was placed in a capillary tube and the pressure necessary to flatten the meniscus measured. The capillary tube was placed between the poles of an electromagnet and the effect of the magnetic field on the meniscus was observed. Within the limit of error, there was no change of surface tension for a field of 16,000 gauss. A change of 0.04% could have been detected.

G. S.

**Dimensions of the Molecules of certain Colloidal Substances.** P. LECOMTE DU NOÛY (*Compt. rend.*, 1924, **178**, 1102—1104).—The sharp minimum in the value of the surface tension of certain colloidal solutions at a particular concentration is attributed to the formation of an orientated unimolecular layer of the disperse phase at the surface of the liquid. The supposition is confirmed by the slowness of evaporation at the same concentration. For solutions of pure sodium oleate, allowed to stand for 2 hours in watch glasses, the minimum occurs at a concentration of 1/750,000, and has a value of 56.0 dynes per sq. cm. The calculated thickness of the unimolecular layer is  $12.6 \times 10^{-8}$  cm., and the width of the molecule  $6.8 \times 10^{-8}$  cm., in agreement with Langmuir's results for oleic acid. The increase in length ( $1.4 \times 10^{-8}$  cm.) due to the sodium atom is close to Langmuir's value for that due to the carbon atom ( $1.3 \times 10^{-8}$  cm.). The probable length of a molecule of crystallisable egg-albumin is  $52.8 \times 10^{-8}$  cm., and the width  $29.2 \times 10^{-8}$  cm.

A. B. H.

**Interpretation of Surface Energy Data.** G. M. BENNETT (*J. Chem. Soc.*, 1924, **125**, 958—959).—The high values found by Schenck and Kintzinger (A., 1923, ii, 614) for the Eötvös coefficient of *n*-hexacosane, *n*-myricyl alcohol, and *n*-hexacontane are not abnormal, since they give values for the total molecular surface energy which are approximately independent of temperature.

S. K. T.

**Freezing of Water in Capillary Systems.** E. A. FISHER (*J. Physical Chem.*, 1924, **28**, 360—367).—This is a criticism of the conclusions of Bouyoucos and his co-workers (A., 1917, i, 510; 1919, i, 115), and of Foote and Saxton (A., 1916, ii, 230; 1917, ii, 241, 364), that much of the water of soils and inorganic gels fails to freeze, even at temperatures as low as  $-78^{\circ}$ , because it is physically adsorbed, chemically combined, or in solid solution. The author points out that water present in very fine capillary tubes or pores must be under considerable tension, and so the density may not necessarily be the same as that of water in bulk, but probably less. Hence the expansion on freezing will probably be less, and since the amount of water which fails to freeze is determined by dilatometric measurements, false conclusions may thus be drawn. M. S. B.

**Structure and Composition of Soap Gels.** R. ZSIGMONDY (*Z. physikal. Chem.*, 1924, **108**, 303—308).—Fischer (A., 1922, ii, 430), from a study of the water taken up by fatty acids, drew the conclusion that the water in the soap gel or curd is in solution. The author, on the basis of the vapour pressure-concentration diagram, contends, however, that the water is neither in solution nor present as water of crystallisation, but is enclosed in capillaries formed by the framework of fine needle-like crystals of the soap, ultra-microscopic in two dimensions, which are known to compose the curd (Zsigmondy and Bachmann, A., 1912, ii, 1149; McBain and Laing, T., 1919, **115**, 1279; 1920, **117**, 1506). M. S. B.

**Theory of Ionic Adsorption.** A. GYEMANT (*Z. physikal. Chem.*, 1924, **108**, 387—405).—The author explains the difference between the electrokinetic potential  $\zeta$  and the thermodynamic potential  $\epsilon$  at the surface of contact of two different phases, namely an aqueous solution and an adsorbent, as due to the presence of a boundary phase between the two. This boundary phase is supposed to consist of a mixture of the adsorbent and water, the concentration of the electrolyte characteristic of the adsorbent being constant. The total thermodynamic potential is then conceived as the sum of two terms,  $\epsilon'$  referring to the surface of contact between the water and the boundary phase and equal to  $\zeta$ , and  $\epsilon''$  at the surface between the boundary phase and the adsorbent.

Electrolytic adsorption is then regarded as the taking up of the electrolyte by the boundary phase. Each ion has a special distribution coefficient between water and the boundary phase, and this is really a measure of the adsorbability of the ion. As the adsorbent itself is usually an electrolyte, or contains an electrolyte, exchange between the cation of this characteristic electrolyte and that of the adsorbed electrolyte may take place also.

On the basis of these views, equations developed thermodynamically, showing the dependence of the electrokinetic potential  $\zeta$  on the different ions brought into play, give results in agreement with the experimental facts, except where the concentrations in the aqueous phase become very small, that is, below  $10^{-3}$ — $10^{-4}$  molar.

M. S. B.

**Chemical Sorption.** V. MORÁVEK (*Ark. Kemi, Min., Geol.*, 1923, **8**, No. 30, 1—18).—Measurements have been made of the sorption of brucine by *d*-tartaric acid with benzene or toluene as solvent, of barium hydroxide by abietic acid with water as solvent, and of gaseous ammonia by silver chloride. The sorbent was prepared by fusion, the dimensions of the surface being thus rendered measurable and the influence of orientating crystallisation forces made negligible. From the maximum amounts of adsorbed substance per sq. metre, the values of the radii of the ions have been calculated on the assumption that the sorption leads to the formation of a single layer. In the case of tartaric acid, for which approximately the same ionic magnitude may be assumed as for silver chloride, the extent of the sorption is tenfold that which corresponds with the unimolecular layer hypothesis. The results obtained for the ionic radius with abietic acid are, however, in good agreement with the values given by various authors. In the case of silver chloride also, satisfactory agreement is attained.

T. H. P.

**Hydrolysis in Stages and Adsorption Equilibrium.** P. P. KOSAKIEWITSCH (*Z. physikal. Chem.*, 1924, **108**, 281—292).—When a solid reacts with a dissolved substance to form a solid compound, the equation for the equilibrium state is not in agreement with the adsorption isotherm. In the equilibrium between a solid base and a soluble acid, it is suggested that a series of basic salts may be formed. As the concentration of the acid solution increases, these basic salts will contain an increasing quantity of acid, until finally the neutral salt is obtained. If, in such a system, the concentrations in the solid phase are plotted against the concentrations of the acid in the liquid phase, a succession of straight lines is obtained, forming a series of steps. A smooth curve drawn through these steps simulates an adsorption isotherm.

To support these views, the author has carried out experiments on the action of oxalic acid solution on lead oxide, and of arsenic acid on mercuric oxide and on copper oxide.

M. S. B.

**Behaviour of Gases in Contact with Glass Surfaces.** D. H. BANGHAM and F. P. BURT (*Proc. Roy. Soc.*, 1924, **A**, **105**, 481—488).—The rates of adsorption and desorption of gases by a glass surface, and the conditions of equilibrium, have been studied. The volumes of gas taken up, after different times, and under different pressures, by glass wool which had been previously exhausted by heating electrically *in vacuo* for several days at a temperature of about 200°, have been measured. By plotting the logarithm of the amount adsorbed,  $s$ , against the logarithm of the time,  $t$ , a straight line is obtained, so that the process may be expressed by the equation  $s^m = kt$ . The index  $m$  is a function of the pressure, the value for carbon dioxide increasing from 10.1 to 13.9 for pressures varying from 17.2 to 655 mm. Similar values of  $m$  have been obtained for other gases. No limit to the amount of gas which may be taken up is indicated. In all cases, sorption values were observed greatly exceeding those required for the formation of a unimolecular film.

The results of desorption experiments, in which the pressures were approximately halved at successive intervals of 24 hours, may be represented by the equation  $r \log \zeta = \log t + \text{constant}$ , where  $\zeta$  is the quantity desorbed in any given step at time  $t$  after the reduction of pressure. The constant quantities of gas remaining after each period of 24 hours were found to be related to the corresponding pressures by the Freundlich equation,  $s^n = k'p$ . The values of  $n$  observed are  $\text{CO}_2$ , 4.2;  $\text{N}_2\text{O}$ , 3.2;  $\text{SO}_2$ , 10.7; and  $\text{C}_2\text{H}_2$ , 3.7. The sorption values for ammonia appear to be much greater than for the above gases, and there is a rough parallelism, but no direct proportionality, between the activity of the different gases and their solubility in water, great solubility being associated with high sorption values and large values of  $n$ . M. S. B.

**Adsorptive Capacity of Wood Charcoal for Dissolved Substances, in Relation to the Temperature of Carbonisation.** J. C. PHILIP and J. JARMAN (*J. Physical Chem.*, 1924, 28, 346—350).—The effect of time and temperature on the carbonising of birch wood has been examined. The temperature at which maximum adsorptive power is reached depends on the substance to be adsorbed. The adsorptive power is increased by allowing freer access of air during carbonisation. Samples prepared by the same method are found to be very similar in properties. [Cf. *B.*, 1924, 499.] M. S. B.

**Relation between the Hydrogen Content of certain Charcoals and some other Properties.** H. H. LOWRY (*J. Amer. Chem. Soc.*, 1924, 46, 824—846).—Measurements of chemical composition, apparent density in air and in different liquids, sorptive capacity, and porosity as determined by the sorption of water vapour, have been made on 23 samples of non-activated charcoal prepared from anthracite coal. The charcoals retained from 0.21 to 0.53% of chemically combined hydrogen, the amount decreasing as the temperature at which the specimen was heated was raised. Hydrogen was still retained, however, at  $1200^\circ$ , and the experiments indicate that pure carbon would not be obtained below the temperature at which graphitisation occurs. The apparent densities of the charcoals, which are practically independent of the immersion fluid, are incompatible with the views of Harkins and Ewing (A., 1922, ii, 123), and of Cude and Hulett (A., 1920, ii, 309). It is suggested that the density is affected by the degree of wetting of the charcoal by the various liquids. The pore volumes decreased with decreasing hydrogen content, probably owing to the shrinkage of the charcoals at the higher temperatures. The apparent densities of the charcoals give an S-shaped curve when plotted against the hydrogen content, increasing with hydrogen content to a maximum value. This maximum is reached at a temperature below that at which shrinkage begins. When shrinkage occurs, the volume impenetrable by the liquid becomes relatively larger, resulting in a lower apparent density. The sorptive capacity increases with increasing hydrogen content, in agreement with the view that "amorphous carbons" are hydrocarbons of low hydrogen



content built up from polymerised residues resulting from the decomposition of hydrocarbons richer in hydrogen. Any treatment tending to increase the unsaturation of these residues increases the sorptive capacity of the charcoal. A description is given of an apparatus for the accurate determination of the very small amounts of gases contained in non-activated charcoals. W. H.-R.

**Adsorption. V.** K. C. SEN, P. B. GANGULY, and N. R. DHAR (*J. Physical Chem.*, 1924, **28**, 313—332).—The coagulation of negatively and positively charged ferric hydroxide sols, and of negatively charged antimony sulphide sols of different concentrations, by a large number of different electrolytes, has been studied, the coagulating powers of the salts being measured by Picton and Linder's titration method. In general, although there are exceptional cases, the greater the concentration of the sol the greater is the amount of electrolyte necessary to coagulate it, irrespective of the nature of the sol and of the valency of the precipitating ion. This is not in accordance with the generalisation put forward by Burton (A., 1921, ii, 176). The Schulze-Hardy law is obeyed, but the ratio between the coagulating powers of ions of different valency does not conform to the quantitative relationship suggested by Whetham (A., 1900, ii, 62). M. S. B.

**Influence of Stirring on the Formation of Precipitates.** VOLMAR and STAHL (*Compt. rend.*, 1924, **178**, 1169—1171).—Mechanical stirring (250 r.p.m.) during the precipitation of barium sulphate in the presence of nitrate ions prevents adsorption, although hand stirring produces little effect. Similar results were obtained in the determination of strontium as oxalate in presence of magnesium ions. The authors regard their work as confirmatory of that of Dutoit (A., 1922, ii, 550). H. J. E.

**Purification of Insulin and Similar Substances by Sorption on Charcoal and Subsequent Recovery.** P. J. MOLONEY and D. M. FINDLAY (*J. Physical Chem.*, 1924, **28**, 402—406).—The possibility of using an adsorbing agent for the purification of chemically ill-defined substances, such as dyes and toxins, has been considered by the authors with special reference to the purification of insulin. The four methods suggested depend essentially on the selective adsorption of the substance to be purified and its subsequent removal from the adsorbent. The most effective method of removing insulin previously adsorbed by charcoal, is by treatment with a solution of a substance which is more strongly adsorbed than the insulin. Benzoic acid is satisfactory, but other reagents, such as the higher fatty acids, are possible. By treating pancreas with an alcoholic solution of benzoic acid, instead of sulphuric acid, the yield is increased from 100—300 units of insulin per pound to 2000 units. [Cf. B., 1924, 507.] M. S. B.

**Physical Chemistry of Dyeing: Substantive Dyes.** J. R. BRIGGS (*J. Physical Chem.*, 1924, **28**, 368—386).—The process of substantive dyeing is regarded as due to the tendency of the colloid to collect at the interface between the liquid and solid phases, that

is, between the aqueous colloidal solution of dye and the fibre. Anything which increases the stability of the colloidal solution should check this tendency. On the other hand, the addition of a coagulating agent, by decreasing the stability and the dispersion, should increase adsorption, provided insufficient for actual coagulation is added, maximum adsorption being obtained at a certain optimum concentration. An electrolyte will thus assist adsorption. This theory has been confirmed by experiments with a number of dyes in the presence of different coagulating agents at varying concentrations. The restraining effect of stabilising colloids has also been noted. The interfacial effect may equally well be observed by using two liquid phases, for example, an aqueous solution of the dye and an immiscible liquid in which it is completely insoluble. [Cf. *B.*, 1924, 507.] M. S. B.

**Kinetics of the Process of Coagulation of Colloids in the Light of Smoluchowski's Theory.** J. N. MUKHERJEE and S. K. MAJUMDAR (*J. Chem. Soc.*, 1924, **125**, 785—794).—Observations on the rate of coagulation of arsenious sulphide sols in presence of inorganic salts confirm generally the results previously obtained (*A.*, 1922, ii, 694) in support of Smoluchowski's theory (*A.*, 1917, ii, 297). In the region of "slow coagulation," the rate is, however, not constant as it should be according to Smoluchowski's theory, and the suggestion is made that coalescence is reversible or irreversible according to the potential of the double layer, the limiting condition corresponding with the attainment of equilibrium between the rates of coalescence and the breaking up of the aggregates due to fluctuations in thermal energy. S. K. T.

**Influence of Anions on the Coagulation of Negatively Charged Suspensoids.** J. N. MUKHERJEE and S. G. CHAUDHURI (*J. Chem. Soc.*, 1924, **125**, 794—802).—Solutions of chlorides, bromides, iodides, and nitrates show the same coagulating power towards arsenious sulphide sols when the cations are of the same concentration. The same relation obtains for the corresponding free acids and holds in this case for gold sols also. To obtain the same effect with benzoates, ferrocyanides, oxalates, etc. (*i.e.*, fairly complex anions) a higher cation concentration is required. The characteristic influence of the valency and mobility of the ions is only observed when their charge is opposite to that on the colloid. The coagulating powers of the alkali-metal sulphates are in the order  $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$ . S. K. T.

**Mechanical Condition of Coagula and its Bearing on the Theory of Complete Coagulation.** S. S. BHATNAGAR, K. K. MATHUR, and D. L. SHRIVASTAVA (*J. Physical Chem.*, 1924, **28**, 387—396).—The coagula obtained by precipitating various sols have been examined in order to compare the sizes of the particles. Oden's method (*Trans. Faraday Soc.*, 1922, **17**, 335) of calculation from the "accumulation curve" did not yield satisfactory results, and was replaced by an elutriation method which gave concordant values. Colloidal solutions containing one size of

particle, obtained by ultra-filtration, form a coagulum in which the particles are also of uniform size. The largest elutriation velocities required to separate the final size of particles from the coagula obtained by precipitating the colloidal solution by uni-, bi-, and ter-valent ions are approximately in the ratio 1 : 2 : 3, respectively, which favours the electrical adsorption theory of coagulation. The sols used were arsenic and antimony sulphides, manganese dioxide, and copper ferrocyanide. M. S. B.

**Absorption of Light by Finely Divided Gold in Fused Borax.** A. EHRLINGHAUS and R. WINTGEN (*Z. physikal. Chem.*, 1924, **108**, 406—410; cf. A., 1923, ii, 390).—By means of a photometer, the authors have determined the amount of absorption which takes place when monochromatic light is transmitted through gold suspensions of different concentrations in fused borax. The proportion of incident light absorbed increases as the size of the particle diminishes, in agreement with Mie's conclusion (*Ann. Physik*, 1908, **25**, 377) deduced from the electromagnetic theory of light. The observed results agree substantially with those calculated from the ordinary absorption formula. The absorption coefficient for massive gold, calculated from the authors' results, is of the same order of magnitude as that given by Hagen and Rubens (*Ann. Physik*, 1903, **8**, 1, 432). M. S. B.

**Contact Potential.** S. TAKEGAMI (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 45—67).—With reference to the elimination of diffusion potentials, the author has investigated the element,  $\text{Hg} | \text{Hg}_2\text{Cl}_2 | N\text{-KCl} - N\text{-HCl} | \text{Hg}_2\text{Cl}_2 | \text{Hg}$ . The connecting solutions employed contained mixtures of (1) potassium chloride (81.87 mols.) and nitrate (18.13 mols.), and (2) ammonium nitrate (89.93 mols.) and lithium chloride (10.07 mols.), these proportions being those for which, at 25°, the average mobility of the anions is equal to the average mobility of the cations.

The effect of adding potassium nitrate to potassium chloride is almost negligible, and the concentrations of these solutions are insufficient for elimination of the diffusion potential. Connecting solutions of the second type and of relatively higher concentration give, however, satisfactory results. On the assumption that, when the diffusion potential has been eliminated at a certain concentration, no change will take place in the *E.M.F.* of the cell when the concentration is further increased, the *E.M.F.* of the above element in the absence of diffusion potential is  $-0.0025$  to  $-0.0030$  volt. Fales and Vosburgh (A., 1918, ii, 424) obtained 0.0081 volt, but the accuracy of this result depends on the assumption that the contact potential at the junction,  $4.1N\text{-KCl} - N\text{-HCl}$  is zero and also on the values adopted for the *E.M.F.* of the calomel cells by these authors. Consideration of Nernst's theory of diffusion potential leads the author to question the validity of these premises. T. H. P.

**Mechanism of Oxidation-Reduction Processes Manifest in Biochemical Processes.** P. GIRARD and M. PLATARD (*Compt. rend.*, 1924, **178**, 1212—1215).—Some reactions involving oxidation and reduction processes are not brought about by the intervention

of a catalyst, but are due to the selective permeability to ions of a parchment septum. Experiments cited in support of this view include the formation of metallic copper, cuprous chloride, amorphous sulphur, and sodium polysulphide from cupric chloride and sodium sulphide; amorphous sulphur, succinic acid, and sodium polysulphide from fumaric acid and sodium sulphide; ferrous sulphate and tartaric acid from ferric sulphate and alkaline sodium fumarate. Such results may afford an explanation of many reactions taking place in living organisms, as cell-walls exhibit a high degree of selective permeability.

H. J. E.

**Oxidation-Reduction Mechanism without Catalysts.** P. GIRARD and M. PLATARD (*Compt. rend.*, 1924, 178, 1393—1395; cf. preceding abstract).—The authors discuss the interaction between two electrolytes separated by a membrane exhibiting selective permeability. The introduction of a membrane, such as animal parchment, between solutions of ferric sulphate and potassium ferricyanide prevents the formation of ferric ferricyanide. In the ferricyanide solution, Pelouze's insoluble ferro-ferric complex,  $\text{Fe}_3(\text{CN})_8$ , is formed, whilst Turnbull's blue and what seems to be an unstable ferrous cyanide,  $\text{Fe}_2(\text{CN})_4$ , make their appearance at the membrane. These effects are due to the passage of the  $\text{SO}_4^{--}$  ions through the membrane and the impermeability of the latter to the  $\text{Fe}(\text{CN})_6^{--}$  and the  $\text{Fe}^{+++}$  ions. Some of the  $\text{Fe}(\text{CN})_6^{--}$  ions, in dissociating to form new saturated groupings such as  $\text{Fe}_3(\text{CN})_8$ , give up their valency electrons, which convert the ferric ions into the ferrous state. The electrostatic equilibrium is thus re-established.

Such reactions as these, occurring without the intervention of a catalyst, indicate the possibility that some reactions formerly regarded as enzymic may be due to the selective permeability of the cell-walls of the tissues. It is suggested that ions  $(\text{H}_2\text{O})^+$  may play a part in the phenomena.

T. H. P.

**Rate of Oxidation of certain Charcoals.** H. H. LOWRY and S. O. MORGAN (*J. Amer. Chem. Soc.*, 1924, 46, 846—852).—Non-activated charcoals prepared from anthracite were heated before use at  $1030^\circ$  in hydrogen in order to drive off absorbed gases and water. The rate of oxidation at  $450^\circ$  was roughly proportional to the amount of chemically combined hydrogen and to the extent of surface, as calculated from observations on the absorption of water vapour. It diminished as the period of preheating in hydrogen was lengthened, and as the temperature of preheating was raised. This is attributed to an increase in the resistance of the carbon atoms to oxidation, and to a decrease in the available surface owing to the shrinkage of the charcoal and the clogging of the capillaries by the products of decomposition of methane formed by the direct action of hydrogen on carbon.

W. H.-R.

**Maximum Temperatures and Pressures attainable in the Combustion of Gaseous and Liquid Fuels.** G. A. GOODENOUGH and G. T. FELBECK (*Univ. Illinois Bull.*, 1924, 21, 158 pages).—The values of the equilibrium constant  $K_p$  in its dependence on the

temperature  $T^\circ$  (Fahr. abs.) have been calculated for certain gaseous reactions. For  $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$  the connexion is given by  $4.571 \log_{10} K_p = 102,820/T - 2.6135 \log_{10} T - 0.4713 \times 10^{-3}T + 0.0605 \times 10^{-6} T^2 - 2.3$ ; for  $\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$  by  $4.571 \log_{10} K_p = 120,930/T - 7.4719 \log_{10} T + 1.95 \times 10^{-3} T - 0.13 \times 10^{-6} T^2 + 0.6$ , for  $T < 2900^\circ$ , and by  $4.571 \log_{10} K_p = 125,810/T + 4.147 \log_{10} T + 0.21 \times 10^{-3} T - 0.03 \times 10^{-6} T^2 - 37.107$ , for  $T > 2900^\circ$ . The values of  $K_p$  for the water-gas reaction  $\text{H}_2 + \text{CO}_2 = \text{H}_2\text{O} + \text{CO}$  are obtained by subtraction of the respective values given by the second from those given by the first equation. By combination of the energy equation, deduced thermodynamically, with the equilibrium equations, the temperatures attained by the combustion of various fuels and the composition of the resulting products have been calculated. The results are in fair agreement with experimental data for mixtures of coal gas, hydrogen, carbon monoxide, benzene, gasoline, and kerosene, respectively, with air.

J. S. G. T.

**Gaseous Combustion at High Pressures. III. Energy-absorbing Function and Activation of Nitrogen in the Combustion of Carbon Monoxide.** W. A. BONE, D. M. NEWITT, and D. T. A. TOWNEND (*Proc. Roy. Soc.*, 1923, **A**, 103, 205—232).—The authors have studied the rate of combustion, in the explosion bomb at an initial pressure of 50 atm., of various mixtures of carbon monoxide and oxygen, both alone and in presence of nitrogen or argon, with a view to explain the previously observed "slow-burning" of carbon monoxide mixed with air, as contrasted with the "quick-burning" of hydrogen under similar conditions (cf. Bone and Haward, *A.*, 1921, ii, 628).

In the absence of nitrogen, the time-pressure curve for carbon monoxide is very similar in form to that obtained with hydrogen, so that the slow development of the maximum pressure in nitrogen, and the subsequent slow fall in pressure, is not due simply to the diluent action of nitrogen. Nitrogen oxides, in quite appreciable quantity, are formed in the explosion of carbon monoxide-air mixtures, but only the faintest trace in the explosion of hydrogen-air mixtures.

To explain these phenomena, it is suggested that the nitrogen is able to absorb energy during the combustion of carbon monoxide at high pressures and become chemically "activated." The absorbed energy is afterwards evolved again as heat. The various ways in which this "activation" may take place are discussed.

M. S. B.

**Gaseous Combustion at High Pressures. IV. Influence of Varying Initial Pressures upon the Rate of Pressure Development and the Activation of Nitrogen in Carbon Monoxide-Air Explosions.** W. A. BONE, D. M. NEWITT, and D. T. A. TOWNEND (*Proc. Roy. Soc.*, 1924, **A**, 105, 406—433; cf. preceding abstract).—Experiments have been carried out on the explosion of mixtures of carbon monoxide and oxygen with nitrogen and argon, using different initial pressures, and also of mixtures of hydrogen and oxygen under similar conditions, with a view to determine the

part played by nitric oxide in the phenomena previously noticed. In the case of hydrogen-air and carbon monoxide-oxygen mixtures, an increase in the initial pressure shortens the time required for the attainment of the maximum pressure; but in carbon monoxide-air mixtures the time interval before maximum pressure is reached progressively increases from 0.07 sec., when the initial pressure,  $P$ , is 3 atm., to 0.45 sec. when  $P=100$  atm. At  $P=3$  atm. nitrogen has merely the same diluting effect as an excess of oxygen, but even at  $P=10$  atm. the curve begins to take on the characteristic form observed at 50 atm. No comparable effect is observed in mixtures of hydrogen, oxygen, and nitrogen, at any rate up to 75 atm.

The amount of nitric oxide surviving in the exploded gases after cooling is very small at low pressures. In the mixture of optimum composition for nitric oxide formation,  $2\text{CO}+3\text{O}_2+2\text{N}_2$ , the amount in the cooled products for  $P=3$  atm. is 0.3%, but for  $P=75$  atm. it is 3%. Practically no nitric oxide appears to be formed in mixtures containing excess of carbon monoxide. The time-pressure curve, however, still retains its characteristic form. Only 0.07% of nitric oxide is found in the cooled gases after the explosion of a mixture of composition  $2\text{H}_2+3\text{O}_2+2\text{N}_2$  at  $P=75$  atm.

These results confirm the previous conclusion as to the energy-absorbing function of nitrogen in the combustion of carbon monoxide. This behaviour is probably the result of the similar electronic structure which has been postulated for the carbon monoxide and nitrogen molecules. The formation of nitric oxide is a secondary reaction following on the activation of the nitrogen and is not responsible for the peculiar form of the time-pressure curve.

M. S. B.

**Mechanism of the Explosive Reaction.** AUDIBERT (*Compt. rend.*, 1924, 178, 1275—1277).—Explosive mixtures of gases were ignited at one end of a tube composed of two sections of glass united by one of rubber and the course of the explosion wave was recorded photographically on a revolving drum. For the mixture,  $\text{CH}_4+2\text{O}_2$ , the rate of propagation is changed during the passage of the wave through the rubber portion of the tube. This is not the case for the mixture  $2\text{H}_2+\text{O}_2$  unless nitrogen is added. The change in velocity produced by the presence of nitrogen is attributed to the formation of nitrous oxide.

A. B. H.

**Propagation of the Detonation Wave.** P. LAFFITTE (*Compt. rend.*, 1924, 178, 1277—1279).—Solid explosives were placed at one end of a glass tube filled with various gases. Detonation was effected by means of mercury fulminate and the propagation of the explosion wave in the solid, and of the detonation wave in the gas, was followed photographically by means of a revolving drum. In general, the initial velocity of propagation of the detonation wave is greater than that of the explosion wave, but its speed subsequently decreases.

A. B. H.

**Evaporation Rate of some Solutions.** L. S. BAGSTER (*J. Soc. Chem. Ind.*, 1924, 43, 61—65r).—The rate of evaporation of

solutions of glycerol, sucrose, sodium nitrate, and sodium sulphate in tube evaporators depends on the surface tension, volume percentage of water, and viscosity of the solution. A. R. P.

**Leucoplasts : Living, Reproducing, Perfect Chemical Catalysts.** E. J. WITZEMANN (*J. Physical Chem.*, 1924, 28, 305—312).—The author visualises the action of the leucoplast *in situ* as that of a perfect chemical catalyst. This action is not attained with the usual enzyme preparations in artificial surroundings. The leucoplast, in a dilute sugar solution, is able to secrete starch in its interior as a condensation product on account of the property, often characteristic of a catalyst, of concentrating a component of the surrounding medium at its surface. When the sugar concentration outside the leucoplast is below a certain critical level the reverse reaction takes place, and the starch grains are broken up.

Other problems are discussed, for instance, the relation of the leucoplast to the protoplasm of which it forms a part, the influence of other conditions on the activity of the leucoplast, the different views as to its manner of reproduction, and, by analogy, the possibility of the existence of a "glycogen leucoplast." The relation of the sugar concentration to the behaviour of the enzyme is an illustration of Le Chatelier's principle. M. S. B.

**Catalytic Actions of Nickelised Aluminium Hydroxide.** N. ZELNSKY and W. KOMMAREWSKY (*Ber.*, 1924, 57, [B], 667—669).—The catalyst is prepared by the addition of a solution of aluminium nitrate in the requisite quantity of sodium hydroxide to an aqueous solution of nickel nitrate and saturation of the product with carbon dioxide. After addition of pure aluminium oxide which has not been ignited, the material is thoroughly washed, dried at 120°, and reduced by hydrogen at 300—330°; it is regarded as nickel deposited on aluminium hydroxide of the approximate composition  $\text{Al}_2\text{O}_2(\text{OH})_2$ . In an atmosphere of hydrogen it does not cause the production of methane from benzene or cyclohexane, whereas this decomposition has been observed by Sabatier and Senderens in the presence of pure nickel. It is a powerful hydrogenating agent which at a higher temperature induces the reverse processes of dehydrogenation; in the latter respect, its behaviour is in striking contrast to that of the catalyst prepared under closely similar conditions by Pfaff and Brunck (this vol., i, 129). The hexahydroaromatic components of the benzene hydrocarbons are readily dehydrogenated to aromatic compounds. The action of the catalyst is milder than that of pure nickel and resembles that of platinum and palladium catalysts, which it can replace for these purposes. Very little carbon is deposited on it. H. W.

**Catalytic Effects of the Oxides of Cerium and Thorium, and their Bearing on the Theory of the Welsbach Mantle.** R. L. SWAN (*J. Chem. Soc.*, 1924, 125, 780—785).—The catalytic activity of mixtures of ceria and thoria on the combination of hydrogen

and oxygen at  $450^{\circ}$  reaches a maximum when the mixture contains 1% of ceria (Welsbach mixture). The activity of pure thoria is the same as that of a mixture containing 9% ceria. The light-giving powers of these are also equal. The author considers that the Welsbach mixture represents the most efficient illuminant obtainable from the two oxides in question. The ceria may act as a carrier of oxygen (cf. A., 1907, ii, 557) or as a promoter of the electronic emission from the thoria. S. K. T.

**Chemical Dynamics of Auto-catalysed Reactions. V. Velocity of Isomeric Change of the Alkyl Phosphites.** J. ZAWIDZKI (*Bull. Acad. Polonaise*, 1920, [A], 111—134).—The experimental data of Arbusov (A., 1910, i, 802) for the rate of isomeric change of the trialkyl phosphites under the catalytic influence of the halogen alkyls are found to agree with the equation  $dx/dt = (k_1 + k_2x)(1-x)$ , indicating that the isomeric change is auto-catalysed by the product of the reaction. The temperature coefficients of the velocity of the reaction are 3.32, 1.97, and 1.82 for the trimethyl, triethyl, and tripropyl esters, respectively. The dependence of the reaction velocity on the nature of the alkyl group in the ester is discussed. S. T. B.

**Chemical Dynamics of Auto-catalysed Reactions. VI. Velocity of Saponification of Potassium Alkylsulphates.** J. ZAWIDZKI and J. ZAYKOWSKI (*Bull. Acad. Polonaise*, 1920, [A], 135—166).—The velocity of the spontaneous saponification of potassium ethylsulphate, potassium and sodium propylsulphates, and potassium butylsulphate may be represented with fair accuracy by the equation  $dx/dt = k_2\sqrt{x(a-x)}$ . The acid salt which is formed acts as an autocatalyst in the reaction. The relative values of the velocity coefficients for potassium methyl-, ethyl-, propyl-, and butyl-sulphates are 1, 2.30, 1.47, and 1.58. The replacement of potassium by sodium in the case of the propyl salt increases the velocity coefficient in the ratio 1 to 1.40. S. T. B.

**Behaviour of Silver Iodide in the Photo-voltaic Cell.** A. GARRISON (*J. Physical Chem.*, 1924, 28, 333—345).—The effect of light on the potential of an electrode, formed by coating silver with silver iodide and dipping in a solution of potassium iodide or silver nitrate saturated with silver iodide, has been examined. The phenomena observed are similar to those previously described for cuprous oxide electrodes (cf. A., 1923, ii, 728). The initial potential in the dark is negative to the calomel electrode. With a polished silver electrode in 0.1N-potassium iodide solution, practically no effect is noticed on illumination. With a very thin coating of silver iodide on the electrode a small positive change of potential (2—3 millivolts) is observed in the light, and in the dark the electrode takes up a slightly larger negative potential than initially. As the thickness of the layer of iodide is increased, the initial dark potential becomes less negative, and ultimately a small negative potential change is first observed in the light, but this is quickly superseded by a positive one.



By decreasing the concentration of the iodide ions the negative light effect becomes larger and less transient, but by increasing it a point may be reached when the positive light effect only is obtained. The positive light effect is attributed to the greater solubility of silver iodide in the light, and the negative effect to the photochemical decomposition of the silver iodide with the separation of silver, since darkening always accompanies the negative change, but not the positive. In both cases, the layer of silver iodide on the electrode will become thinner, hence the increased negative potential in the dark after illumination.

The relation between the photo-potential and the intensity of illumination has been studied, and, on theoretical grounds, a formula has been developed which is in general agreement with the experimental results.

An examination of the relation between the wave-length of the incident light and the photo-potential has shown that the electrode is most sensitive to the blue and violet rays. M. S. B.

**Apparatus for Filtering Hygroscopic Substances.** N. BAN (*Chem.-Ztg.*, 1924, **48**, 271).—The filter funnel has its rim ground flat and is covered with a thick rubber disc carrying a glass tube through which dry air from a sulphuric acid drying bottle is drawn by the pump. A. R. P.

**Special Case of Filtration.** C. DOSIOS (*Compt. rend.*, 1924, **178**, 1175—1177).—A theoretical paper dealing, from the point of view of the kinetic theory, with the removal of ultra-microscopic suspended particles from a gas. H. J. E.

**Permanent Filter Mats in Gooch Crucibles.** O. R. SWEENEY and G. N. QUAM (*J. Amer. Chem. Soc.*, 1924, **46**, 958—960).—Permanent mats for Gooch crucibles may be made by filling the holes of the crucible with coarsely powdered porcelain, on the top of which more finely powdered porcelain is sprinkled to a depth of 6—7 mm. The mat is then wetted with a cementing solution of 0.5N-potassium hydroxide solution, and the crucible dried at 110° for 10 hours, and then in a Meker burner in a small furnace for 3 hours, and finally treated several times with hydrochloric acid and *aqua regia* until constant weight is obtained. Such crucibles are suitable for the quantitative filtration of precipitates of barium sulphate and silver chloride. W. H.-R.

**Method for Determining the Approximate Index of Refraction of Liquids with a Common Microscope.** C. C. KIPLINGER (*J. Chem. Soc.*, 1924, **125**, 963—965).—A glass bead (about 1.8 mm. diameter) is held in position on a glass slide mounted on the stage of a compound microscope. The latter is focussed through the bead on a distant object; then, by moving the draw-tube, it is re-focussed after a drop of the liquid has been introduced between the bead and the slide. The refractive index is proportional to the draw-tube extension, preliminary experiments with liquids of known refractive index giving the factor of proportion-

ality. The results are accurate to two units in the second decimal place.

S. K. T.

**Apparatus for Calibrating Burette Tubes.** V. STOTT (*J. Soc. Glass Tech.*, 1924, **8**, 38—45).—The apparatus permits successive quantities of water to be transferred from a blank burette tube to a standard pipette. A piece of thermometer tubing attached to the top of the burette tube controls the rate of outflow of water from the burette, so that errors due to drainage from the walls of the burette are eliminated, and the time taken in emptying an interval of the burette during calibration is approximately equal to that required to empty the same interval on the finished burette when the stopcock is fully open. The apparatus gives an accuracy sufficient for "class A" burettes.

H. S. H.

**Calibration of the Platinum Resistance Thermometer between 0° and -193°.** F. HENNING and W. HEUSE (*Z. Physik*, 1924, **23**, 95—104).—The platinum resistance thermometer has been compared with the gas thermometer over the stated temperature range. The relation  $R/R_0 = 1 + at + bt^2 + ct^4$  has been found to hold, where  $R$  is the resistance of platinum at a temperature  $t$ , and  $R_0$  is the resistance at 0°. The freezing point of mercury was incidentally determined as  $-38.87^\circ \pm 0.01^\circ$ .

S. B.

**Lecture Experiment to Demonstrate the Chemical Action of Light.** F. VON KONEK and A. LOCZKA (*Ber.*, 1924, **57**, [B], 679—680).—The chemical action of light of different wave-lengths is readily demonstrated by placing a dilute solution of bromine in toluene at the focus of an arc light; decolorisation of the solution occurs almost instantaneously with evolution of hydrogen bromide. If the arc light is replaced by an incandescent filament, this change is not observed.

H. W.

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## Inorganic Chemistry.

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**Method of Making Hydrogen Peroxide from Persulphuric Acid.** A. BRODSKY (*Z. angew. Chem.*, 1924, **37**, 270—272).—By the electrolysis of sulphuric acid ( $d$  1.44) between a platinum anode and an aluminium cathode with a current of 3.5—4.0 amp. at 8—12 volts, a solution of persulphuric acid is obtained which decomposes on warming first to permonosulphuric acid (Caro's acid), then to sulphuric acid with the formation of hydrogen peroxide. Distillation of this solution (containing 2.0—3.5 g. of active oxygen per litre) at 65—90°/50—100 mm. yields a distillate that contains about 0.5% of hydrogen peroxide and an acid solution that may be used again. Redistillation gives a liquid containing 24% of hydrogen peroxide. The current yield using technical sulphuric acid without cooling was 65%, which fell to 40% after the first, and to 23% after the second distillation.

A. R. P.

**Concentration of Weak Solutions of Hydrogen Peroxide by Distillation in a Vacuum.** A. BRODSKY (*Z. angew. Chem.*, 1924, **37**, 272—273).—The distillation, at 50°/about 100 mm., of a very weak solution of hydrogen peroxide such as is obtained by the method described in the preceding abstract, leaves a concentrate in the distillation flask which contains 23% of hydrogen peroxide with a yield of 90%. If the liquid is concentrated further than this the yield falls off very considerably. A. R. P.

**Relation between the Stabilisation of Solutions of Hydrogen Peroxide and the Modification of Surface Tension.** (MME.) A. LISIEVICI-DRAGANESCU (*Bul. Soc. Chim. România*, 1924, **6**, 42—45).—The stability of a solution of hydrogen peroxide in water is decreased by the addition of substances which raise the surface tension of the mixture, whilst by the addition of a substance which lowers the surface tension, the initial titre of the solution remains almost unaltered for a considerable time. There appears to be no quantitative relation between the decrease in stability and the increase in surface tension due to the addition of small quantities of different substances. A. E. C.

**Possibility of Separating the Isotopes of Chlorine by Fractional Diffusion of Sodium Chloride Solutions.** B. L. VANZETTI (*Gazzetta*, 1924, **54**, 89—94).—The author describes unsuccessful attempts to separate the isotopes of chlorine by fractional diffusion of sodium chloride solutions through a series of parchment paper or animal membrane diaphragms. T. H. P.

**Properties of Colloidal Sulphur.** G. ROSSI (*Gazzetta*, 1924, **54**, 65—71; cf. A., 1914, ii, 35; 1915, ii, 152; 1922, ii, 485).—The results of experiments on the coagulation of colloidal sulphur solutions, before and after dialysis, by means of potassium chloride or bromide show that the amount of the salt required to induce coagulation increases with the proportions of sulphuric acid and sodium sulphate present in the solution. Moreover, the quantity of potassium permanganate adsorbed is greater with the dialysed than with the non-dialysed colloidal sulphur solutions. T. H. P.

**Synthesis of Ammonia at High Pressures.** W. MOLDENHAUER (*Chem.-Ztg.*, 1924, **48**, 233—234).—The yields of synthetic ammonia obtained by Claude at very high pressures are compared with the theoretical yields deduced from Haber's ammonia equilibrium formula. The yields at 740° agree well with the calculated values up to 1000 atm., the highest pressure employed. At temperatures below 700°, however, the yields at pressures above 500 atm. are higher than those calculated. The discrepancies between the actual and theoretical yields increase as the temperature falls and as the pressure rises, and are probably due to differences in the compressibilities of ammonia, nitrogen, and hydrogen. H. C. R.

**Crystal Structure of Metallic Arsenic.** A. J. BRADLEY.—(See ii, 382.)

**Preparation of Reagents Free from Arsenic.** G. D. BEAL and K. E. SPARKS (*Ind. Eng. Chem.*, 1924, **16**, 369—370).—Hydrochloric acid may be freed from arsenic by converting the arsenic into the quinquivalent form, in which condition it is least volatile, and distilling. The acid is saturated with chlorine by adding a small quantity of potassium chlorate, and distilled in a current of chlorine. When only 1 mg. of arsenic was present in 500 c.c. of the original acid, 475 c.c. of distillate could be collected free from arsenic, but with 2 g., only 180 c.c. Since arsenic trichloride is readily volatile in the presence of sufficient hydrochloric acid to prevent its hydrolysis, the arsenic can be readily removed from hot sulphuric acid by passing through it a current of hydrogen chloride after adding a small amount of sodium hydrogen sulphite. H. C. R.

**Influence on the Properties of Arsenic Sulphide Sols of some Physical Factors intervening during their Preparation.** A. BOUTARIC and M. VUILLAUME (*Compt. rend.*, 1924, **178**, 938—939).—The mean magnitude of the granules in an arsenious sulphide sol, prepared by passing hydrogen sulphide through arsenious anhydride solution and expelling the excess of the gas by means of a current of hydrogen, increases with the concentration of the anhydride solution used and, to a slight extent, with rise of temperature. If the gas is allowed merely to diffuse into the solution, the absorptive power developed is about sixty times that produced by bubbling the gas rapidly through the liquid. The opacity is also increased by prolonging the duration of the gas stream. The mean magnitude of the sol particles may be increased by protracted boiling of the solution at constant volume.

The rapidity of the flocculation caused by potassium chloride or barium chloride diminishes as the granules increase in size, but the inverse is the case when the flocculating agent is aluminium chloride. In the latter case, the speed of flocculation increases, and in the former cases diminishes, as the concentration of the sol increases. T. H. P.

**Boron Hydrides. VII. Pentaboron Hydrides.** A. STOCK and W. SIECKE (*Ber.*, 1924, **57**, [B], 562—575).—Further examination of the products of the thermal decomposition of tetraborane,  $B_4H_{10}$  (cf. Stock and Kuss, A., 1923, ii, 408), shows that the hydride,  $B_5H_9$ , is accompanied by a new *hydride*, richer in hydrogen, which is formulated  $B_5H_{10}$  for the present (the exact formula is probably  $B_5H_{10}$ ). The hydrides are so similar to one another in volatility that their separation by fractional distillation or condensation is impossible. The presence of the new hydride in the compound  $B_5H_9$  is shown by the marked depression of the freezing point of the latter. They are distinguished by the course of their spontaneous decompositions. The compound  $B_5H_9$  decomposes slowly into hydrogen and a non-volatile, colourless hydride, soluble in carbon disulphide, but insoluble in water, which appears to be identical with one of the non-volatile decomposition products of tetraborane described previously (*loc. cit.*). The substance  $B_5H_{10}$  decomposes so rapidly at the atmospheric temperature that its manipulation

is difficult; it yields hydrogen and a non-volatile, yellow hydride, insoluble in carbon disulphide, but soluble in water, which appears to be identical with the second, non-volatile decomposition product of tetraborane. The hydride,  $B_5H_9$ , can be freed from the compound,  $B_5H_9$ , by preserving it for a few weeks at the atmospheric temperature;  $B_5H_9$  is thus decomposed completely but  $B_5H_9$  to a small extent only.

The hydride,  $B_5H_9$ , combines with ammonia at the atmospheric temperature to give the solid, colourless, non-volatile compound,  $B_5H_9(NH_3)_4$ , which, when treated with hydrogen chloride at the atmospheric temperature, gives the substance  $B_5H_5Cl_4(NH_3)_4$ , together with a little diborane. Prolonged action of hydrogen chloride causes slow further substitution until 7 atoms of hydrogen have been replaced. The chlorinated ammine dissolves in water with evolution of hydrogen and production of a strongly reducing solution which gives a very characteristic precipitate with sulphuric acid or sulphate solutions.

The thermal decomposition of diborane gives also a third *pentaboron hydride*,  $B_5H_{11}$ , a colourless, mobile liquid which does not solidify at  $-110^\circ$ . The following measurements of the vapour pressure are recorded:  $-67^\circ$ , 0.2 mm.;  $-57^\circ$ , 0.8 mm.;  $-50.5^\circ$ , 1.3 mm.;  $-41.7^\circ$ , 3.9 mm.;  $-31.0^\circ$ , 9.7 mm. The new hydride decomposes more rapidly than the compound  $B_5H_9$  at the atmospheric temperature, yielding hydrogen and the solid hydride,  $B_{10}H_{14}$ , m. p.  $99.5^\circ$ .  
H. W<sub>3</sub>

**Colouring Matter of Smoky Quartz.** B. L. VANZETTI (*Gazzetta*, 1924, **54**, 95—99).—Sections cut perpendicularly to the principal axis of prisms of various specimens of smoky quartz have been examined to ascertain if such quartz contains particles capable of exhibiting Tyndall's effect. The path of an incident ray perpendicular to one face of the prism and parallel to the plane of the section is not always visible in the crystal, even when the latter is comparatively dark. In some cases, however, especially with very highly coloured and almost opaque crystals, the internal ray is visible and polarised. Both the coloration and the Tyndall effect disappear when these crystals are heated at about  $300^\circ$ . The nature of the admixture to which the coloration of the quartz is due remains undetermined.  
T. H. P.

**Weathering of Granite.** E. BLANCK and H. PETERSEN (*J. Landw.*, 1924, **71**, 181—209).—Changes in the chemical composition of weathering granite are recorded. Little alteration occurred in the initial stages of weathering, but later, iron, calcium, magnesium, and the alkalis decreased and the loss on ignition increased. The acid-soluble silica suffered little variation during the weathering process, but the proportion of aluminium dissolved decreased. Acid-soluble iron was greater in cases where considerable amounts of organic matter were present. The ratio of acid-soluble silica to alumina did not remain constant during weathering and variations were greatest in the presence of much organic

matter. The bearing of this on the theories of van Bemmelen are discussed.

A. G. P.

**Thermal Decomposition of Carbonyl Sulphide. II.** A. STOCK, W. SIECKE, and E. POHLAND (*Ber.*, 1924, **57**, [B], 719—735; cf. Stock and Seelig, A., 1919, ii, 230).—Investigation of the reactions, (i)  $\text{COS} \rightleftharpoons \text{CO} + \text{S}$  and (ii)  $2\text{COS} \rightleftharpoons \text{CO}_2 + \text{CS}_2$ , has been extended to temperatures below  $600^\circ$ . Carbonyl sulphide, prepared by the action of sulphuric acid on ammonium thiocyanate, and purified by treatment with sulphuric acid, sodium hydroxide, calcium chloride, and phosphoric acid and ultimately by distillation and fractional condensation, was decomposed either in the static or moving gas condition. At temperatures in the neighbourhood of  $400^\circ$ , the equilibrium of the change,  $\text{COS} \rightleftharpoons \text{CO} + \text{S}$ , is disturbed by the separation of sulphur, so that under these conditions this action must be completely suppressed by addition of carbon monoxide; above  $500^\circ$ , this procedure is not effective. Decomposition of carbonyl sulphide according to reaction (i) is not evident below  $400^\circ$  and reaches a maximum (64%) at  $900^\circ$ , whilst reaction (ii) reaches a maximum at about  $600^\circ$ , at which point 43% of the carbonyl sulphide is decomposed in this way, and 16% according to reaction (i). The carbon monoxide equilibrium depends on the pressure, whereas the carbon dioxide equilibrium does not.

Nearly all the reactions involved in the thermal decomposition of carbonyl sulphide depend greatly on catalytic influences and on the extent of surface exposed. The carbon dioxide decomposition which takes place uniformly in heated glass or quartz vessels does not occur in contact with an incandescent platinum wire. The carbon monoxide reaction proceeds smoothly under the latter conditions, but the catalyst is readily poisoned if even a trace of carbon disulphide is present. Quartz is a pronounced catalyst for the carbon dioxide change, but has little influence on the carbon monoxide reaction; even at the atmospheric temperature carbonyl sulphide is comparatively rapidly decomposed in quartz vessels, although it can be preserved for years in glass.

H. W.

**Absence of Helium from the Gases left after the Passage of Electrical Discharges :** (i) **between Fine Wires in a Vacuum ;** (ii) **through Hydrogen ;** (iii) **through Mercury Vapour.** S. K. ALLISON and W. D. HARKINS (*J. Amer. Chem. Soc.*, 1924, **46**, 814—824).—A powerful condenser of approximately 0.5 microfarad capacity charged to 42,000 volts was allowed to discharge through fine points of platinum or tungsten wires enclosed in a highly evacuated bulb, 168 discharges being made. The condenser was divided and reconnected in series so that it could be charged to 84,000 volts, and the discharge was allowed to pass 300 times through saturated mercury vapour at  $90^\circ$  (0.1 mm. pressure) between accurately round steel balls. The gases evolved were tested for helium by a modification of the spectroscopic method of Soddy (A., 1908, ii, 921; 1907, ii, 251), and in no case was helium observed, although the methods enable  $2 \times 10^{-10}$  g. of helium to be detected. No production of heat was observed noticeably greater than that

to be expected from the discharge alone. The failure of the electrical discharge to disintegrate the atom is due to the fact that, whilst sufficient energy is present, it is not transmitted to the nucleus in sufficiently high concentration. The condenser charged to 84,000 volts was discharged 100 times through pure hydrogen at 40 mm. pressure, but no helium was formed. W. H.-R.

**Compressibility of the Alkali Halides.** J. C. SLATER.—(See ii, 383.)

**Action of Potassium Hydroxide on Nitric Oxide.** G. BARR (*J. Chem. Soc.*, 1924, 125, 961—962).—Observations are recorded of the rate of absorption of nitric oxide at room temperatures (10—22°) by a 50% solution of potassium hydroxide. It is suggested that the reaction may be quadrimolecular. H. T.

**Photolysis of Potassium Nitrate Solutions.** W. T. ANDERSON, jun. (*J. Amer. Chem. Soc.*, 1924, 46, 797—802).—Aqueous solutions of potassium nitrate are decomposed by ultra-violet radiation of 3330 Å. and shorter wave-length. The reaction is accelerated by heat, and the products of decomposition are potassium nitrite and oxygen, but the reaction is auto-inhibited by the nitrite and “a steady state” is reached when only a small quantity of nitrate has been decomposed, whilst the addition of nitrite to a solution of potassium nitrate partly or completely inhibits the photolysis of the latter. Aqueous potassium nitrite solutions are stable in ultra-violet light. Potassium nitrate solutions obey Beer's Law; consequently nitrate-nitrite equilibria are different in stirred and unstirred solutions, the difference depending on the concentrations. In unstirred solutions, the equilibrium depends entirely on the size of the surface exposed to the light, and on the concentration and thickness of the solution. Alkali hydroxides increase the rate of photolysis and displace the “steady state” towards the nitrite, possibly owing to the formation of a peroxide. Acids decrease the rate of decomposition, but do not displace the “steady state.” Owing to the presence of a balanced action, it is not possible to derive quantum relationships, and the calculations of Warburg (*A.*, 1920, ii, 405) are shown to be unjustified. W. H.-R.

**Densities and Specific Volumes of Sodium Chloride Solutions.** R. E. HALL (*J. Washington Acad. Sci.*, 1924, 14, 167—173).—The densities of sodium chloride solutions up to concentrations of 25.5% have been determined at 25° with an accuracy of 5 parts per million. These densities can be represented by the empirical equation  $D_p = 0.997071 + 0.0070109p + 0.000013268p^2 + 0.0000003535p^3$ , where  $p$  represents % by weight of sodium chloride. H. T.

**Structure of Sodium Chlorate and Rock Salt Crystals.** C. HERMAN.—(See ii, 382.)

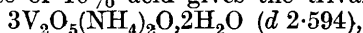
**Compressibility of the Chlorides, Bromides, and Iodides of Lithium, Rubidium, and Cæsium.** T. W. RICHARDS and E. P. R. SAERENS (*J. Amer. Chem. Soc.*, 1924, 46, 934—952).—The



compressibilities of the halides of the rarer alkali metals have been determined by the piezometer method, in which the unknown compressibility is compared with the known compressibility of mercury. The method measures cubic compressibility, and the results are in good agreement with some obtained for linear compressibility by Bridgman (*Proc. Amer. Acad. Arts Sci.*, 1908, **44**, 253; 1922, **58**, 222, etc.). The compressibilities ( $\times 10^{-6}$ , per megabar) determined at approximately  $20^\circ$  are: lithium chloride, 3.7; bromide, 5.0; iodide, 7.2; rubidium chloride, 7.3; bromide, 8.2; iodide, 9.3; caesium chloride, 5.9; bromide, 7.0; iodide, 9.3. Rubidium bromide and iodide and caesium bromide are exceptional in that the application of pressure to the freshly-fused salt produces a permanent contraction, owing to a change to a less bulky form, the same change occurring slowly in the absence of external pressure. If the compressibilities are plotted against the molecular volumes, the points for the halides of a given metal lie on a curve which, with only slight curvature, leads to the origin, but molecular volume is not the only factor influencing the compressibility (cf. Born and Landé, A., 1919, ii, 188, whose equation gives results showing a tendency in the right direction, but with an average error of 12.5%). The values may be predicted more accurately by the equation  $\beta = kV_m/U$ , where  $k=0.00006$ ,  $U$  is the heat of combination of metal and halogen, and  $V_m$  the molecular volume.

W. H.-R.

**Ammonium Vanadates.** M. LACHARTRE (*Bull. Soc. chim.*, 1924, [iv], **35**, 321—332).—Pure ammonium metavanadate ( $d$  2.326) is prepared by saturating with ammonia moist vanadium pentoxide (the purification of which is described) and crystallising from a very dilute ammonia solution. One hundred parts of water dissolve 5.18 parts of the salt at  $15^\circ$  and 10.4 parts at  $32^\circ$ ; it is only slightly soluble in hot alcohol and in ether. When heated in a vacuum to  $135$ — $210^\circ$ , the salt yields anhydrous ammonium trivanadate; above  $210^\circ$ , lower oxides of vanadium are formed. On boiling an aqueous solution, soluble ammonium divanadate and the insoluble trivanadate are formed. By the action of 4% acetic acid on boiling solutions of ammonium metavanadate, the divanadate,  $2V_2O_5 \cdot (NH_4)_2O \cdot 3H_2O$ , is obtained, which on desiccation loses  $2H_2O$ . Use of 10% acid gives the trivanadate,



desiccation of which gives an anhydrous, red salt ( $d$  2.163). The previously described yellow anhydrous trivanadate has  $d$  3.029.

When the acetic acid is replaced by nitric, hydrochloric, or sulphuric acid, indefinite acid ammonium vanadates are formed, the composition varying with the concentration of the acid added. With a large excess of hydrochloric acid, reduction of the vanadate also takes place.

S. K. T.

**Dispersity of Silver Halides in Relation to their Photographic Behaviour.** F. E. E. GERMANN and M. C. HYLAN (*Science*, 1923, **58**, 332—333).—Wightman, Trivelli, and Sheppard (*J. Physical Chem.*, 1923, **27**, 1466; *Science*, 1923, **58**, 89) report

that greater sensitivity of emulsions is associated with greater size and range of size of the silver halide grain, whereas it is now argued that, theoretically, smaller grained emulsions should be more sensitive. The discrepancy is ascribed to the retarding effect of adsorbed halide, since after its removal the observed sensitivities are reversed. A. A. E.

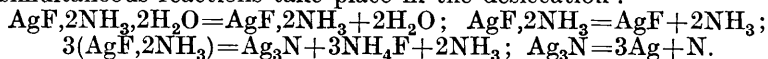
**Dispersity of Silver Halides in Relation to their Photographic Behaviour.** E. P. WIGHTMAN, A. P. H. TRIVELLI, and S. E. SHEPPARD (*Science*, 1923, **58**, 469; cf. preceding abstract).—Polemical against Germann and Hylan (*loc. cit.*). The discrepancy is explained by discoveries concerning the function of sensitive specks in the silver halide grains. A. A. E.

**Solubility of Silver Oxide in Ammonia and Methylamine Solutions.** L. J. OLMER (*Bull. Soc. chim.*, 1924, [iv], **35**, 333—339).—The ratio  $\text{NH}_3/\text{Ag}$  for solutions of silver oxide in aqueous ammonia is constant up to a concentration of about 2 g.-mol. of ammonia per litre, after which it increases slowly and regularly. The ratio decreases in course of time when a concentrated solution is kept in contact with silver oxide. An explanation is suggested based on the slow decomposition of the complex  $\text{Ag}_2\text{NH}_3\cdot\text{OH}$  into silver amide in concentrated solution.

The ratio  $\text{MeNH}_2/\text{Ag}$  is constant for solutions containing less than 2 g.-mol. of methylamine per litre; beyond this concentration it increases very rapidly, although the silver concentration passes through a maximum (0.96 g.-atom of silver to 6.25 g.-mols. of methylamine per litre). Some of the methylamine appears to be oxidised to formic acid. Anhydrous trimethylamine will not dissolve silver oxide. S. K. T.

**Silver Nitride.** L. J. OLMER and DERVIN (*Bull. Soc. chim.*, 1924, [iv], **35**, 152—160).—When silver ammonium fluoride (A., 1923, ii, 71) is heated to below  $160^\circ$  it decomposes, leaving a black residue of silver nitride,  $\text{Ag}_3\text{N}$ . The latter is more unstable towards friction than towards rise of temperature; between  $140^\circ$  and  $160^\circ$ , it sometimes explodes spontaneously after about 10 minutes, whilst at lower temperatures ( $120^\circ$ — $140^\circ$ ) it is more stable. It always explodes by contact or by a neighbouring detonation. The explosion yields a certain amount of pure nitrogen (cf. A., 1923, ii, 71), but not in the theoretical yield. The formation of the nitride by the above method is not instantaneous and depends on the temperature. The crystals of silver ammonium fluoride also decompose when kept for 8 months in the dark in a sealed tube. Decomposition is more rapid when large crystals are kept in a vacuum over sulphuric acid than when the powdered salt is kept at the ordinary pressure over this acid or over calcium oxide mixed with ammonium chloride. Powdering promotes the rate of loss of water, but not the rate of nitride formation. Silver nitride is formed before the salt loses all its water, and it may be isolated by treating the partly decomposed salt with water and filtering. It is insoluble in cold water, but dissolves in ammonia solution (7.5 mols. per litre) to the extent of 0.3 g.-atom of silver per litre. On cautious

heating in a vacuum, it decomposes quietly. Silver nitride is stable when mixed with excess of an inert substance. Four simultaneous reactions take place in the desiccation:



Ammonia catalyses the conversion of fluoride into nitride, decomposes the nitride, and hinders the volatilisation of the ammonium fluoride.

E. E. T.

### Reaction between Calcium Oxide and Nitrogen Peroxide.

J. R. PARTINGTON and F. A. WILLIAMS (*J. Chem. Soc.*, 1924, **125**, 947—958).—Nitrogen peroxide reacts with calcium oxide at all temperatures up to  $400^\circ$ , giving primarily calcium nitrite and nitrate. Secondary reactions, however, occur at higher temperatures; above  $230^\circ$ , calcium nitrite decomposes,  $\text{Ca}(\text{NO}_2)_2 = \text{CaO} + \text{NO} + \text{NO}_2$ , and in the presence of nitrogen peroxide undergoes oxidation at lower temperatures in the following ways: (i)  $\text{Ca}(\text{NO}_2)_2 + 2\text{NO}_2 = \text{Ca}(\text{NO}_3)_2 + 2\text{NO}$ , (ii)  $\text{Ca}(\text{NO}_2)_2 + \text{NO}_2 \rightarrow \text{Ca}(\text{NO}_3)_2 + 0.5\text{N}_2$ . At  $450^\circ$ , the molecular proportions of the decomposition are represented by 12.02 mols.  $\text{Ca}(\text{NO}_2)_2 \rightarrow 7.68\text{CaO} + 4.34\text{Ca}(\text{NO}_3)_2 + 14.40\text{NO} + \text{N}$ , nitrogen and nitric oxide alone being evolved. Above  $480^\circ$ , nitrogen peroxide is, in addition, given off, and at  $495^\circ$  calcium nitrate begins to decompose. Calcium nitrite is not oxidised by oxygen below its decomposition point except in the presence of nitrogen peroxide. The existence of the compound  $\text{Ca}(\text{NO}_2)_2 \cdot 4\text{H}_2\text{O}$  was confirmed.

H. T.

**Basic Calcium Arsenate.** H. V. TARTAR, L. WOOD, and E. HINER (*J. Amer. Chem. Soc.*, 1924, **46**, 809—814).—Hydrolysis of tricalcium arsenate or calcium ammonium arsenate yields a basic calcium arsenate,  $3\text{Ca}_3(\text{AsO}_4)_2 \cdot \text{Ca}(\text{OH})_2$ , 0.0048 g. of which dissolves in 100 g. of water at  $25^\circ$ . It is analogous to hydroxy-apatite,  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$ , and, like the latter, retains water tenaciously.

W. H.-R.

**Crystalline Compounds of Zinc Bromide and Iodide with Acetone.** I. COUCOULESCO (*Bul. Soc. Chim. România*, 1924, **6**, 36—38).—In the absence of moisture, zinc reacts with a mixture of ethylene dibromide, or ethylene di-iodide, and acetone to give the zinc halide with acetone of crystallisation. At the commencement of the reaction, ethylene is evolved. *Zinc bromide-acetone*,  $2\text{ZnBr}_2 \cdot 3\text{C}_3\text{H}_6\text{O}$ , colourless needles, m. p.  $32\text{--}34^\circ$ , is easily soluble in water, with slow deposition of zinc hydroxide. *Zinc iodide-acetone*,  $\text{ZnI}_2 \cdot 2\text{C}_3\text{H}_6\text{O}$ , pale yellow, elongated prisms, m. p.  $45\text{--}47^\circ$ , is deliquescent and slowly decomposed by water. A. E. C.

**Spectrum of Mercury.** H. BUISSON.—(See ii, 365.)

**Viscosities of Solutions containing Mixtures of Mercuric, Cupric, and Cobaltous Chlorides with other Chlorides. Formation of Complex Ions.** N. A. YAJNIK and R. L. UBEROY (*J. Amer. Chem. Soc.*, 1924, **46**, 802—808).—The viscosities of single solutions of the different chlorides have been observed at

different concentrations, and the results obtained utilised for calculating the viscosities of mixtures of mercuric, cupric, and cobaltous chlorides with other chlorides, by using the equation given by Kendall and Monroe (A., 1917, ii, 524), which gives satisfactory results when applied to ideal mixtures. The difference between these and the experimental values has been used to determine the composition and degree of complex ion formation. The results indicate that in mixtures of mercuric chloride with hydrochloric acid, and of cupric and cobaltous chlorides with hydrochloric acid or the chlorides of the alkali metals or magnesium, the complex anions formed have the compositions  $\text{HgCl}_4''$ ,  $\text{CuCl}_4''$ , and  $\text{CoCl}_4''$ , respectively. W. H.-R.

**The "Missing Element" between Cadmium and Mercury.** W. M. HICKS (*Nature*, 1924, **113**, 642—643).—Although it is evident that there is no unknown element between cadmium and mercury, it is suggested that, on spectral evidence, europium should be so placed (A., 1914, ii, 599; Rydberg, *ibid.*). A. A. E.

**Spectra of Aluminium, Zinc, and Carbon.** R. O. HUTCHINSON.—(See ii, 365.)

**Aluminium Amalgam, Hydroxide, and Oxide.** F. L. HAHN and E. THIELER (*Ber.*, 1924, **57**, [B], 671—679).—Aluminium amalgam, prepared by treating the metal with boiling  $N/5$ -sodium hydroxide solution until hydrogen is vigorously evolved, cooling, and then adding 10 c.c. of mercuric chloride solution followed as rapidly as possible by sufficient potassium cyanide solution to dissolve the precipitated mercuric oxide, is far more active towards water and much more constant in its properties than that obtained in the usual manner. The presence of salts of the most strongly electropositive metals, barium and potassium, accelerates the decomposition of water most markedly and continuously; with metals lower in the series, the action becomes uncertain and apparently dependent on accidental circumstances. Calcium is restrictive in  $M/1$ , inactive in  $M/10$  solution. In  $M/100$  solution, magnesium has a retarding effect, and at greater concentrations completely inhibits the action. The nobler metals accelerate the change initially, owing to the formation of local elements; as soon, however, as sufficient foreign metal has been deposited as is necessary to form a continuous layer of the metal or its amalgam, the reaction ceases. The action of copper is so pronounced that immersion of aluminium vessels in very dilute copper sulphate solution renders them subsequently immune to the action of mercury solutions.

Aluminium hydroxide, obtained by the disintegration of aluminium amalgam under ammonium nitrate solution, is coarsely granular, settles rapidly and compactly, and is easily washed. The ignited product has the unusual property of absorbing water from an atmosphere desiccated by granular calcium chloride. H. W.

**Paramagnetism of Iron in Potassium Ferricyanide.** P. COLLET.—(See ii, 378.)

**Adsorption of Iron by Manganese Dioxide : Equilibrium Displacement.** M. GELOSO (*Compt. rend.*, 1924, 178, 1001—1003).—Adsorption of iron from a solution of ferric ammonium sulphate by freshly precipitated manganese dioxide is a function of the concentration of the ferric solution. For each concentration, there is an adsorption pressure corresponding with each temperature; the system is thus univariant and no compounds are formed. As the amount of adsorption increases with rise of temperature, the phenomenon is endothermic; moreover, adsorption is correlated with the state of aggregation of the precipitate, as its extent is much decreased by prolonged digestion of the precipitate before adding the ferric solution. The relative amount of precipitant (ammonium persulphate) which conditions the size of the solid particles formed thus has some influence on the adsorption.

H. J. E.

**Equilibria involving the Oxides of Iron.** E. D. EASTMAN and R. M. EVANS (*J. Amer. Chem. Soc.*, 1924, 46, 888—903).—Equilibria in the system iron-hydrogen-oxygen have been investigated at 772° by a modification of the method of Deville (*J. Chem. Soc.*, 1871, 24, 103). The results indicate the existence of solid solutions in the composition ranges 0—5% oxygen, 20—24% oxygen, and above about 27% oxygen. Equilibrium constants in the bivariant equilibria represented by the equations (1)  $\text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O}$  ( $K_1 = [\text{H}_2\text{O}]/[\text{H}_2]$ ), (2)  $\text{Fe}_3\text{O}_4 + \text{H}_2 = 3\text{FeO} + \text{H}_2\text{O}$  ( $K_2 = [\text{H}_2\text{O}]/[\text{H}_2]$ ) have been determined between 657° and 1025°, the solid phases being solid solutions. The system iron-carbon-oxygen has also been investigated between 818° and 1039°. The bivariant equilibria are represented by the equations (3)  $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$  ( $K_3 = [\text{CO}_2]/[\text{CO}]$ ), and (4)  $\text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2$  ( $K_4 = [\text{CO}_2]/[\text{CO}]$ ). The values of  $K_4$  have been determined, the values of  $K_3$  previously found by other workers being accepted as satisfactory. The values of  $K_1$ ,  $K_2$ ,  $K_3$ , and  $K_4$  have then been used to obtain two independent series of values for the constant of the water-gas reaction,  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ . The two sets of values are in good agreement, and the values of  $I$  in the free energy equation calculated from them are satisfactorily constant. The values do not, however, agree with the direct determinations of the water-gas equilibria made by Hahn (A., 1903, ii, 711; 1904, ii, 643) and by Haber and Richardt (A., 1904, ii, 166), and the present results are considered to be more trustworthy. The most probable values of the different constants have been tabulated, and the free energy data relating to carbon monoxide and dioxide have been recalculated.

W. H.-R.

**Dissolution of Iron by Carbonic Acid.** W. LEYBOLD (*Z. angew. Chem.*, 1924, 37, 190—191).—The maximum observed solubility of iron in water containing an excess of carbon dioxide is about 1 g. of iron per litre, the process of dissolution being accompanied by liberation of hydrogen. Precipitated ferrous hydroxide is dissolved much more slowly than metallic iron. [Cf. B., 1924, 471.]

W. T. K. B.

**Magnetic Isothermals of Nickel.** P. WEISS and R. FORRER.—(See ii, 379.)

**Nickel Sulphide.** II. W. GLUUD and K. SCHÖNFELDER (*Ber.*, 1924, **57**, [B], 628—629; cf. A., 1923, ii, 423).—Oxidation by air of nickel sulphide precipitated by ammonium sulphide from solutions of nickel sulphate at 9° in the presence of varying amounts of ammonia leads to the separation of 83% of the sulphur in the elementary form; if precipitation is effected at 90° under otherwise similar conditions, only about 8.5% of the sulphur separates as such, the remainder being transformed into thiosulphate, sulphate, and polythionate. The proportion of combined sulphur increases with increasing concentration of ammonia. H. W.

**Supposed Isomorphism of Uranyl Compounds with those of the Isomorphogenic Metals of the Magnesium Group.** G. CAROBBI (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 228—231).—Experimental support cannot be obtained for Groth's suggestion ("Chemische Krystallographie," II, 483) that ammonium uranyl sulphate dihydrate, which De La Provostaye (*Ann. Chim. Phys.*, 1842, [iii], **5**, 51) showed to be monoclinic, may belong to the same group as the triclinic compounds,  $\text{MnK}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , etc., and that compounds, e.g.,  $\text{K}_2(\text{UO}_2)(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , isomorphous with those of the well-known series

$(\text{Mg}, \text{Fe}, \text{Zn}, \text{Co}, \text{Ni})(\text{K}, \text{Rb}, \text{Cs}, \text{Ti}, \text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$   
may exist. T. H. P.

**Hardness of Tin-Cadmium and Tin-Bismuth Alloys.** C. DI CAPUA (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 141—144).—The hardness of these alloys has been investigated by the method recently described (this vol., ii, 111). The hardness of tin is increased by addition of cadmium to a maximum for about 6% of the latter. With further addition of cadmium, the hardness falls rapidly until the eutectic point is reached at 28% of cadmium, remains constant over the region 28—97% Cd, and then falls to the value for pure cadmium. This behaviour is changed markedly by annealing the alloys in paraffin wax at 150° for 330 hours, the two branches of the curve in the neighbourhoods of 0% and 100% of cadmium then revealing the solid solubility of each metal in the other; about 3% of tin dissolves in cadmium and about 8% of the latter in tin (cf. Bucher, A., 1917, ii, 211).

With tin-bismuth alloys the maximum hardness corresponds with the eutectic point, but annealing causes the disappearance of this maximum and renders the curve normal, the maximum hardness being then shown by crystals of tin saturated with bismuth and the limit of solid solution being extended from 4% to 7% of bismuth. T. H. P.

**Tin Hydride.** W. VAUBEL (*Ber.*, 1924, **57**, [B], 515—517; cf. Paneth and Fürth, A., 1920, ii, 41).—Tin hydride is formed invariably when nascent hydrogen is liberated in the presence of tin; its production when tin is dissolved rapidly in concentrated hydrochloric acid accounts for the peculiar odour of the gas (Kastner,

1821). The compound obtained by the action of tin hydride on silver nitrate solution has approximately the composition  $\text{SnAg}_4$ .

During the dissolution of polished tin in hydrochloric acid, a black powder is deposited which dissolves only very slowly even in the concentrated acid; it is suggested that this is a peculiar modification of the metal which is produced by the reduction of stannous chloride by nascent hydrogen. H. W.

**Germanium. I. The Mineral Germanite and the Extraction of Germanium and Gallium therefrom.** J. S. THOMAS and W. PUGH (*J. Chem. Soc.*, 1924, **125**, 816—826).—An average sample of germanite intermixed with arsenical fahlore from Tsumeb, S.W. Africa, contained 5.1% of germanium and 0.57% of gallium. The germanium cannot be freed from arsenic by the method of Dennis and Papish (*A.*, 1922, ii, 150) unless most of the arsenic is previously removed by roasting at  $500^\circ$ . The gallium was obtained by precipitating the hydroxide from a faintly acid solution with sodium thiosulphate, after treatment of the acid extract of the mineral with hydrogen sulphide.

Metallic germanium was prepared by reducing the dioxide with potassium cyanide and carbon. H. T.

**Spectrum of Vanadium.** F. MEGGERS.—(See ii, 365.)

**Crystal Structure of Bismuth.** O. HASSEL and H. MARK.—(See ii, 382.)

**Compressibility and Pressure Coefficient of Resistance of Rhodium and Iridium.** P. W. BRIDGMAN (*Proc. Amer. Acad. Arts Sci.*, 1923, **59**, 109—115; cf. *ibid.*, 1923, **58**, 151, 166; *Proc. Nat. Acad. Sci.*, 1920, **6**, 505).—Expressions are given for the computation of  $\Delta V/V_0$  for rhodium and iridium at  $30^\circ$  and  $75^\circ$ , and of  $\Delta R/R_0$  for rhodium at  $30^\circ$  and  $65^\circ$ , and iridium at  $30^\circ$ ,  $65^\circ$ , and  $95^\circ$ . Irregularities in the related properties of the triads of the eighth periodic group are considered.

CHEMICAL ABSTRACTS.

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### Mineralogical Chemistry.

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**Anauxite and Cimolite from Bilin.** E. DITTLER and J. E. HIBSCH (*Tsch. Min. Petr. Mitt.*, 1923, **36**, 85—92).—Basalt usually weathers to a brown, clayey material; but under special conditions, as at Bilin, Bohemia, it alters to a white clay. Here the minerals (augite, plagioclase, olivine, magnetite) of the basalt are attacked



by carbonated waters, and the iron, magnesium, manganese, calcium, sodium, and potassium removed in solution as carbonates. The white product consists of an intimate mixture of minute pearly scales of anauxite (anal. I:  $3\text{Al}_2\text{O}_3, 10\text{SiO}_2, 8\text{H}_2\text{O}$ ) and earthy cimolite (anal. II:  $2\text{Al}_2\text{O}_3, 9\text{SiO}_2, 6\text{H}_2\text{O}$ ) which were separated as far as possible for analysis. The anauxite,  $d\ 2.524$ , is orthorhombic with optical characters distinct from those of kaolinite, whilst the cimolite is cloudy and structureless. When the cimolite is digested with a dilute solution of sodium hydroxide, a portion of the silica goes into solution, and an aggregate of anauxite scales remains.

	$\text{SiO}_2$ .	$\text{TiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{MgO}$ .	$\text{CaO}$ .	$\frac{\text{H}_2\text{O}}{(\text{110}^\circ)}$ .	$\frac{\text{H}_2\text{O}}{(+\text{110}^\circ)}$ .	Total.
I	56.62	0.38	26.09	2.69	0.11	0.40	4.37	9.21	99.87
II	62.49	1.09	19.53	2.88	0.46	0.49	2.41	10.07	99.42

L. J. S.

**Aragonite as a Deposit from the Bilin Spring.** E. DITTLER and J. E. HIBSCH (*Tsch. Min. Petr. Mitt.*, 1923, **36**, 80—84).—A white, laminated material is deposited in the pipes and channels of the spring of cold (temp.  $10.2^\circ$ ), carbonated water at Bilin in Bohemia. The laminae are held together by crystal aggregates,  $d\ 2.860$ . The mean of two analyses is:  $\text{CaO}$ , 54.70;  $\text{SrO}$ , 0.42;  $\text{MgO}$ , 0.45;  $\text{FeO}$ , trace;  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ , 0.34;  $\text{Na}_2\text{O}$ , 0.31;  $\text{CO}_2$ , 43.72;  $\text{H}_2\text{O}$ , 0.24%.

Analyses of the water, by W. Gintl, 1907—1908, show 6.6614 g. of total solids and 2.3171 g. of free carbon dioxide per litre, with much sodium, some calcium and magnesium, and little strontium, etc.; also, in addition to carbonates, some chlorides and sulphates. The fact that the calcium carbonate is deposited as aragonite, rather than as calcite, from a cold solution is attributed to the presence of magnesium salts in appreciable amount, and perhaps also to the presence of strontium.

L. J. S.

**Mullite.** N. L. BOWEN, J. W. GRIEG, and E. G. ZIES (*J. Wash. Acad. Sci.*, 1924, **14**, 183—191).—In the system silica-alumina,  $3\text{Al}_2\text{O}_3, 2\text{SiO}_2$  is the only compound stable at high temperatures, and should therefore be found in rocks of the appropriate composition when formed at high temperatures. An examination of buchites from the Island of Mull disclosed that the so-called sillimanite present was really the above compound and the name, mullite, is therefore proposed for this mineral. The optical properties of mullite are very similar to those of sillimanite; both are orthorhombic, but the mullite prism angle is  $89^\circ 13'$  compared with  $88^\circ 15'$  for sillimanite, and its refractive indices are lower. Mullite is found in the crowns of glass-pots that have been in use for long periods at high temperatures.

A. R. P.

**Migration of Material during Metamorphism.** FRIEDRICH BECKE (*Tsch. Min. Petr. Mitt.*, 1923, **36**, 25—41).—H. Rosenbusch postulated that the metamorphism of rocks was effected without any transference of material. More recently, V. M. Goldschmidt (1920) from a comparison of analyses of a series of phyllites grading

into schists in the Stavanger district, Norway, concluded that there has been an addition of silica, soda, and lime and a loss of water in the change from phyllite to schist. The evidence presented by analyses of a series of rocks from the Hohen Tauern, Austria, is now discussed. The schists surrounding the central mass show a similar increase, whilst the more deformed granite-gneiss of the centre shows a corresponding decrease in the same constituents. It is considered that there may be transference of alumina as well as of silica, alkalis, and lime. The final result of the metamorphism of a series of rocks is to bring about uniformity in composition.

L. J. S.

**Application of Spectrographic Analysis to the Detection of Rare Elements in Italian Materials.** C. PORLEZZA and A. DONATI (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 232—237).—Spectrographic analysis shows that Fiuggi tufa contains, in addition to the elements detectable by ordinary analysis, cobalt, nickel, lead, chromium, strontium, zirconium, yttrium, ytterbium, cerium, lanthanum, scandium, and neodymium. Soil from Capri (cf. Giesel, A., 1905, ii, 132) contains lead, copper, iron, titanium, aluminium, zirconium, silicon, yttrium, ytterbium, cerium, lanthanum, neodymium, cobalt, manganese, vanadium, chromium, barium, strontium, calcium, magnesium, potassium, sodium, and lithium. Granite from Castel d'Oria contains manganese, strontium, titanium, calcium, barium, iron, vanadium, chromium, potassium, aluminium, scandium, yttrium, and ytterbium, and Stromboli lava, manganese, strontium, titanium, calcium, iron, barium, potassium, aluminium, lead, magnesium, vanadium, chromium, cobalt, nickel, scandium, ytterbium, and yttrium.

T. H. P.

**Colouring Matter of Smoky Quartz.** B. L. VANZETTI.—(See ii, 406.)

**Weathering of Granite.**—E. BLANCK and H. PETERSEN.—(See ii, 406.)

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### Analytical Chemistry.

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**New Soxhlet Apparatus.** W. PLÜCKER (*Z. angew. Chem.*, 1924, **37**, 274).—Two pieces of glass rod in the form of a cross are sealed into the main tube some distance above the lower junction of the side tube so that the extraction thimble, which rests on the cross, is kept clear of the liquid in the tube. Thus the material to be extracted is continually drenched with fresh solvent and does not remain in a pool of liquid more or less saturated with extracted matter.

A. R. P.

**Apparatus for Extraction and Solvent Recovery.** S. A. DE LACY (*Analyst*, 1924, **49**, 220—222).—A flask, of the usual wide-mouthed type, is fitted with a cork bored with three holes, and is connected respectively with a reflux condenser, a side tube leading to a condenser which is used for removing solvent by distillation at the end of the extraction, and a frame comprising a glass rod on the upper end of which two “flats” are cut. An oval platform with a flat top and a drip point beneath it is so arranged that in one position of the frame it closes the end of the reflux condenser, whilst in another position it closes that of the distillation tube and the refluxing solvent drips into a folded filter-paper or alundum crucible containing the material to be extracted. Special types of frame for holding filter-papers and alundum crucibles are illustrated. The frame is rotated by means of a small key which fits the “flats” on the stem and rests on the top of the cork.

H. C. R.

**Extraction of a Substance Dissolved or Dispersed in a Liquid by Another, Immiscible Liquid.** A. BRUNO (*Bull. Soc. chim.*, 1924, [iv], **35**, 422—424).—The extraction is carried out in corked bottles clamped to a horizontal axle which is revolving uniformly at a rate of about 40 rotations per minute. The effect is as though each bottle revolved about its own axis so that emulsification and centrifuging cannot take place, whilst the surface of contact of the two liquids undergoes constant renewal. Control of the temperature and of the nature and pressure of the atmosphere in which the extraction takes place are the advantages claimed. [Cf. *B.*, 1924, 456.]

S. K. T.

**Ultimate Lines in the Spectra of the Electric Arc.** S. PROCOPIU.—(See ii, 364.)

**Detection of Rare Elements in Italian Minerals.** C. PORLEZZA and A. DONATI.—(See ii, 417.)

**Spectrum of Iron.** O. LAPORTE.—(See ii, 364.)

**Spectrum of Iron.** S. GOUDSMIT.—(See ii, 364.)

**Colorimetric Determination of Hydrogen-ion Concentration by the Wedge Method, and the Dissociation Constants of some Indicators.** I. M. KOLTHOFF (*Rec. trav. chim.*, 1924, **43**, 144—152).—A development of Gillespie's method (*A.*, 1920, ii, 382). The indicator is placed in two wedge-shaped vessels, one containing an acid, the other an alkaline solution. These two vessels are cemented together by means of Canada balsam and the colour adjustment is effected by moving them to a known extent, readings being taken by means of a fixed point and a scale marked on one of the wedges when the indicator solutions correspond in colour with the solution under examination. The author describes the application of the method to a number of substances, and gives dissociation constants and  $p_H$  values of the following indicators: Thymol-blue (acid range)  $2.4 \times 10^{-2}$ , 1.62; bromophenol-blue  $1.0 \times 10^{-4}$ , 4.00; methyl-orange  $2.0 \times 10^{-4}$ , 3.70; methyl-red  $9 \times 10^{-5}$ , 4.05; bromocresol-blue  $8 \times 10^{-6}$ , 5.10; bromocresol-purple

$8.5 \times 10^{-7}$ , 6.07; bromothymol-blue  $8.4 \times 10^{-8}$ , 7.08; phenol-red  $1.4 \times 10^{-8}$ , 7.85; cresol-red  $6.5 \times 10^{-9}$ , 8.17; neutral-red  $1.4 \times 10^{-7}$ , 6.85; thymol-b.  $1.1 \times 10^{-9}$ , 8.96. H. J. E.

**Micro-determination of Halogen by Baubigny and Chavanne's Method.** H. NOMURA and J. MURAI (*Bull. Soc. chim.*, 1924, [iv], 35, 217—220).—For the micro-determination of iodine, a pastille of the substance (3—7 mg.) is dropped into about 2 c.c. of cooled sulphochromic mixture (cf. A., 1903, ii, 510) containing silver nitrate, which is shaken well while heated for 20 minutes at  $140^\circ$ . After cooling, 9% aqueous alcohol is added drop by drop until the liquid is dark green. The mixture is then diluted with water and sodium hydrogen sulphite solution added until the odour just persists. The mixture is warmed and the silver iodide collected in a Pregl filter.

If chlorine and bromine are present, they are removed by passing air through the mixture during the reaction, collected in alkaline sodium sulphite solution, and precipitated by silver nitrate.

E. E. T.

**Determination of Halogen by Combustion over Platinised Asbestos in a Current of Oxygen.** K. DACHLAUER and C. THOMSEN (*Ber.*, 1924, 57, [B], 559—561).—The apparatus is modelled on that of Dennstedt. The substance is vaporised in an inner tube through which a current of air is passed and round which oxygen is driven. The volume ratio of oxygen to air should be at least 2:1, preferably 3—4:1. If oxygen is used in the inner tube explosions are liable to occur. The inner tube is loosely closed by a glass stopper wrapped with platinum wire. The combustion tube is charged with a long layer of platinised asbestos held in position by a wad of asbestos. The gaseous products of the combustion are passed through potash bulbs charged with sodium hydroxide solution (15%) containing 5% of sodium sulphite. After completion of the combustion, the contents of the bulbs are acidified with nitric acid, treated rapidly with ferric alum solution and an excess of standard silver nitrate solution, and boiled for about 15 minutes until sulphur dioxide and nitrogen peroxide are expelled; after cooling, the excess of silver nitrate is titrated with potassium thiocyanate.

H. W.

**Determination of Two Halogens in the Presence of Each Other.** H. JAHN (*Chem.-Ztg.*, 1924, 48, 150).—A neutral solution containing only two of the halogen acids is titrated with a standard solution of silver nitrate; excess of the silver nitrate is then added together with dilute nitric acid, and the total halide determined gravimetrically. From the weight of the mixed silver halides and that of the silver used in the titration the proportion of each halogen in the original solution may be calculated.

A. R. P.

**Determination of Chlorine, Bromine, and Iodine in Organic Compounds. II. Oxidation Method.** J. HESLINGA (*Rec. trav. chim.*, 1924, 43, 181—186; cf. ter Meulen and Heslinga, this vol., ii, 55).—The substance is heated in a tube in presence of, but

not in direct contact with, ferric oxide. Oxygen for the combustion is supplied in the form of air which has been bubbled through a solution of ammonia. The reaction products are trapped in alkaline sulphite solution in which the halogen is converted into potassium halide. This solution is subsequently acidified with nitric acid and the halogen determined with silver nitrate. [Cf. *B.*, 1924, 357.]

H. J. E.

**Influence of Colloids on the Titration of Chlorides by Volhard's Method.** I. M. KOLTHOFF (*Chem. Weekblad*, 1924, **21**, 188—189; cf. Burg and Koppejan, this vol., ii, 271).—The potentiometric method gives accurate results in all circumstances, provided that no material is present which removes silver ions from the solution.

S. I. L.

**Determination of Iodine in Iodides.** J. WEICHERZ and Z. KLINGER (*Chem.-Ztg.*, 1924, **48**, 269—270).—The solution of the iodide is treated in succession with carbon tetrachloride, sulphuric acid, manganese sulphate, and potassium permanganate. After shaking, oxalic acid and (if much chloride or bromide is present) formic acid are added, the mixture is again shaken, diluted, and the liberated iodine titrated with thiosulphate. In the presence of manganese sulphate, oxalic acid reduces the excess of permanganate in the cold within 30 minutes, whilst the formic acid reduces any chlorine or bromine liberated without affecting the iodine.

A. R. P.

**Simultaneous Determination of the Mineral and Organic Iodine in Algæ.** (Mlle.) J. LELIÈVRE and (Mlle.) Y. MÉNAGER (*Compt. rend.*, 1924, **178**, 1315—1316).—The methods previously described (cf. Freundler, this vol., i, 354) do not exclude the possibility of loss of iodine by either volatilisation or incomplete destruction of the tissues. The algæ are burned in presence of silver foil in a combustion tube in a current of oxygen, the silver retaining the iodine liberated; the "fixed iodine" is determined by dissolving the ash in acetic acid, treating the solution with permanganate, and titrating the resulting iodate with thiosulphate. Application of this method to iodoform and to *p*-iodotoluene yields results correct to about 1%.

Under the above conditions, *Laminaria flexicaulis* yields only about 2% of its total iodine in a volatile form, the remainder being left in the ash as soluble iodide accompanied by a trace of iodate. [Cf. *B.*, 1924, 419.]

T. H. P.

**Determination of Iodine in Iodine Metabolism.** J. F. McCLENDON (*Proc. Soc. Exp. Biol. Med.*, 1923, **20**, 351—352).—The material, mixed with calcium oxide, is ignited in oxygen, the volatile products being absorbed in sodium hydroxide solution, which, mixed with an aqueous extract of the ash, is evaporated to small bulk. At  $p_H$  1, reduction of iodate is effected with 0.1 c.c. of 0.1*N*-arsenious acid solution, 0.1 c.c. of 5% sodium nitrite solu-

tion added, the iodine extracted with carbon tetrachloride and determined colorimetrically.

CHEMICAL ABSTRACTS.

**Determination of Sulphur by means of a Thermometric Titration.** P. M. DEAN and O. O. WATTS (*J. Amer. Chem. Soc.*, 1924, **46**, 855—858).—After a preliminary conversion to a soluble sulphate, sulphur may be determined volumetrically by titration with standard barium chloride solution, which is added to the sulphate solution contained in a Dewar flask fitted with a stirring apparatus. The temperature is measured at intervals and plotted against the volume of barium chloride solution added, a break in the curve occurring at the end-point of the titration. An accuracy of about 0.2% can be obtained if the barium chloride solution is standardised thermometrically against a material similar to that to be analysed.

W. H.-R.

**Determination of Sulphates in Extremely Dilute Solutions by Hahn's Method.** I. M. KOLTHOFF and M. J. VAN CITTERT (*Z. anal. Chem.*, 1923, **63**, 392—404).—Precipitation of dilute sulphate solutions by allowing them to flow drop by drop simultaneously with a barium chloride solution into boiling *N*-hydrochloric acid, according to the method of Hahn (*A.*, 1923, ii, 339), gives results 0.4% too low if the barium sulphate is weighed after drying at 100° and 1—1.3% too low if it is ignited. If the precipitation is effected in acetic acid instead of in hydrochloric acid solution, the theoretical weight of barium sulphate is obtained after drying at 100°, but the precipitate is not as coarsely crystalline as in Hahn's method. In the presence of calcium salts, correct results are obtained only in 0.1*N*-hydrochloric acid solutions; aluminium or alkali metal salts have no influence on the results, codeine salts cause low, and phosphoric acid high results, whilst nitrates have very little effect.

A. R. P.

**Separation and Determination of Soluble Carbonates, Hydroxides, and Salts of the Sulphur Acids and of Elementary Sulphur.** K. K. JÄRVINEN (*Z. anal. Chem.*, 1923, **63**, 369—392).—Sulphuric acid is accurately determined by precipitation of the sulphuric acid as benzidine sulphate followed by titration of the precipitate with standard alkali in the presence of phenolphthalein; copper and chromium salts must be absent. Sulphites, thiosulphates, or sulphides are destroyed without being oxidised if the solution is added slowly to boiling dilute hydrochloric acid. The sulphur content of a preparation of the element may be ascertained by shaking with bromine and water until the sulphur dissolves, and adding ether; after boiling off the ether, the sulphuric acid is precipitated as the barium salt. A solution containing sulphides, polysulphides, sulphites, and thiosulphates, together with carbonates and hydroxides of the alkali metals, is analysed as follows: Sulphide is determined by adding an excess of barium chloride, filtering off an aliquot part of the solution, and titrating with an ammoniacal solution of copper chloride until the liquid

above the precipitate is faintly blue; the excess of copper is determined colorimetrically and the remainder calculated to sodium sulphide. Sulphide and polysulphide are precipitated together by ammoniacal zinc chloride, and the precipitate is oxidised with bromine to sulphate, the polysulphide being calculated by difference. The filtrate from the zinc sulphide is treated with sodium carbonate solution, rendered neutral to phenolphthalein with hydrochloric acid, and treated with iodine until a faint yellow colour persists; the sulphite is then oxidised to sulphate, which is precipitated in the cold with barium chloride, the excess of which is precipitated with sodium carbonate without filtering off the sulphate. The mixed barium salts are collected, washed, and treated with hydrochloric acid to remove the carbonate, leaving a residue of barium sulphate, which is weighed; the amount due to sulphate (determined in a separate trial by the method described above) is deducted and the remainder calculated to sodium sulphite. The filtrate from the barium carbonate-sulphate precipitate contains tetrathionate derived from the thiosulphate in the original solution; after oxidation with bromine in the presence of ether, the resulting sulphate is determined as barium sulphate and the weight calculated to sodium thiosulphate. Sodium hydroxide is determined in a portion of the original solution by titration with standard acid after treatment of the solution with barium chloride, ammonium chloride, and copper chloride in succession to remove carbonates, sulphates, sulphites, and sulphides. For the determination of sodium carbonate, the solution is boiled in a flask fitted with a Bunsen valve for 30 minutes with *N*-sodium hydroxide free from carbonate and hydrogen peroxide; the cold solution is divided into two parts, one of which is titrated directly with acid, using methyl-orange as indicator, and the other is treated with barium chloride to remove the carbonate and titrated with acid, using phenolphthalein as indicator.

A. R. P.

#### Critical Studies on Methods of Analysis. XI. Selenium.

L. A. CONGDON and W. W. BRAY (*Chem. News*, 1924, **128**, 266—268).—Dissolution of commercial selenium in nitric acid followed by evaporation to dryness, dissolution of the residue in hydrochloric acid (*d* 1.175), and precipitation of the selenium by means of sulphur dioxide or a soluble sulphite gave low and very discordant results. Gooch and Pierce's iodometric method (*A.*, 1896, ii, 334) gave somewhat high but concordant results. The most rapid and satisfactory procedure was found to be a modification of Marino's method (*A.*, 1910, ii, 155). A solution in nitric acid is evaporated to dryness and the residue dissolved in dilute sulphuric acid. An aliquot part of the solution is heated to boiling and titrated with 0.2*N*-permanganate, adding a slight excess. The precipitated manganese dioxide is filtered off on asbestos, the colour of the filtrate discharged with a measured excess of 0.2*N*-oxalic acid, and the titration finished with permanganate.

A. R. P.

#### Determination of Nitrogen in Non-homogeneous Products.

E. ROUSSEAU (*Ann. Falsif.*, 1924, **17**, 99—103).—In the case of



such substances as waste wool, horn, etc., the difficulty of obtaining an average sample for the determination of nitrogen may be overcome by heating a large quantity (40 to 50 g.) of the substance with a small quantity of sulphuric acid until it is disintegrated and then using an aliquot portion of the resulting black solution. If the substance does not dissolve in sulphuric acid, the black mixture may be mixed with calcium carbonate or calcium sulphate to form a solid which is then ground and a portion used for the analysis. An alternative method consists in sifting the material into portions consisting of particles of similar size, noting the weight of these portions, and determining the nitrogen in each, separately.

W. P. S.

**Oxidation of Hydrazine. I. Volumetric Analysis of Hydrazine by the Iodic Acid, Iodine, Bromine, and Hypochlorous Acid Methods.** W. C. BRAY and E. J. CUY (*J. Amer. Chem. Soc.*, 1924, **46**, 858—875).—Four rapid and accurate oxidation methods for the volumetric analysis of hydrazine have been developed, using (1) iodic acid in acid solution, (2) iodine in alkaline solution, (3) bromine in acid solution, and (4) hypochlorous acid in the presence of a buffer solution of mono- and di-sodium phosphates. The iodine liberated in (1) and the excess of unchanged iodine in (2) are titrated with thiosulphate solution, whilst in (3) and (4) the excess of oxidising agent is determined by treatment with potassium iodide solution and titration of the iodine liberated. The presence of ammonium salts renders method (4) very inaccurate, but does not affect methods (1) or (3), whilst in method (2) the error due to the ammonium salts may be eliminated by the use of a small excess of iodine and a large excess of alkali. Methods based on oxidation by vanadic acid, alkaline solutions of iodate or bromine, or by dichromate in acid solution are all unsatisfactory, whilst the use of Fehling's solution gives accurate results only under favourable conditions.

W. H.-R.

**Test for Nitric Acid and Nitrates.** H. WOLF and E. HEYMANN (*Z. angew. Chem.*, 1924, **37**, 195—196).—If concentrated sulphuric acid is introduced below a mixture of a solution containing the nitrate ion and an aqueous solution of 2 : 4-diamino-6-hydroxypyrimidine or one of its salts, a deep red ring is formed at the surface of separation. The coloration is visible with solutions containing down to 0.4 mg. of  $\text{NO}_3^-$  per c.c., i.e., the test is less delicate than the "brown ring" test (with ferrous sulphate), but is applicable, with suitable modification, in the presence of any other inorganic ion. In the presence of sulphites and thiosulphates, the temperature must not exceed 20—30°; chlorates must first be reduced with sulphurous acid, which must also be added in the presence of bromides or iodides. Nitrites give a red precipitate of 5-nitroso-2 : 4-diamino-6-hydroxypyrimidine with the reagent in dilute sulphuric acid solution, but this is dissolved and decolorised by concentrated sulphuric acid. In the case of nitrate solutions containing the nitrite ion, it is best to add excess of the reagent, acidify

slightly with sulphuric acid, and warm; concentrated sulphuric acid is then introduced below the mixture, without separating the nitroso compound, and the red ring is easily discernible. A dark red *solid* is obtained by treating 2:4-diamino-6-hydroxypyrimidine with a mixture of sulphuric and nitric acids; it is very sparingly soluble in organic solvents and was not obtained pure. It turns grey at 210° and does not melt below 400°. W. T. K. B.

**Detection of Phosphoric Acid with Benzidine.** F. FREY (*Chem.-Ztg.*, 1924, **48**, 281).—A small quantity of the solution to be tested is treated with nitric acid and twice its volume of the usual "molybdate mixture." After warming, the liquid, whether a precipitate is visible or not, is poured through a close-textured filter-paper and one drop of ammonia is allowed to fall into the apex of the filter. On placing a drop of an acetic acid solution of benzidine on any part of the paper, a blue colour immediately develops if phosphoric acid is present. The test will detect less than 0.01 mg. of phosphoric acid in 1 c.c. of solution. A. R. P.

**Rapid Determination of Phosphoric Acid by Copaux's Method.** J. DARIC (*Bull. Soc. chim.*, 1924, [iv], **35**, 409—414).—Copaux's method of determining phosphoric acid (A., 1921, ii, 707) is slightly less accurate, but more rapid, than the magnesium pyrophosphate method. The influence of temperature can be represented by a formula. The relative error in carefully performed analyses is always within 1%, the relative deviation from results obtained by gravimetric methods being about 0.6%. The method is applicable in presence of citrates, provided the concentrations of the hydrochloric acid and the sodium molybdate are increased, although the composition of the test solution must be strictly comparable with that being analysed. S. K. T.

**Apparatus for the Semimicro-determination of Carbon.** M. POLONOVSKI (*Bull. Soc. chim.*, 1924, [iv], **35**, 414—419).—The gases from the combustion furnace pass through absorption bulbs filled with barium hydroxide solution, thence through a control bulb-tube in which no precipitate must appear, and finally to a device for filtering with exclusion of air. A flask so fitted that the absorption vessels may be filled in the absence of air is introduced immediately after the furnace. It is followed by another control tube, which is used, when required, to demonstrate that combustion is complete. The precipitated barium carbonate is collected in the absence of air and weighed. The small quantity left on the sides of the bulbs is dissolved in hydrochloric acid and determined volumetrically. When 0.02—0.04 g. of material is used the determination is accurate to 0.5—1%. S. K. T.

**Application of Micro-analysis to the Combustion of Diamond.** M. NICLOUX and R. GUILLEMET (*Bull. Soc. chim.*, 1924, [iv], **35**, 225—228).—Pregl's method of micro-analysis was tested by the combustion of 2—6 mg. of diamond in a transparent

quartz tube. The results deviated only within the limits of experimental error. The diamond burns quietly; if the combustion is stopped the diamond is found to be white and corroded and the edges are smoothed off, which indicates that combustion takes place from the surface inwards. Heating at very high temperatures in nitrogen or carbon dioxide causes a conversion into a black substance which marks paper like graphite. E. E. T.

**Indirect Determination of Carbonic Acid and the Respiratory Quotient with the Differential Spirometer.** E. HELMREICH and R. WAGNER (*Biochem. Z.*, 1924, **145**, 77—81).—A caoutchouc bag for receiving expired air is enclosed within a large Krogh spirometer containing the respiratory air; a continuous graphic record of the relative oxygen intake and carbon dioxide output is thus obtained, and alteration in the respiratory quotient observed. J. P.

**Determination of Calcium in Blood by de Waard's Method.** A. HIRTH and A. KLOTZ (*Comp. rend. Soc. Biol.*, 1923, **89**, 49—50; from *Chem. Zentr.*, 1924, i, 367).—In the method of de Waard (*Compt. rend. Soc. Biol.*, 1923, **88**, 1153) for the determination of calcium in blood the precipitation of calcium oxalate is incomplete and the precipitate obtained is impure. G. W. R.

**Critical Studies on Methods of Analysis. VIII. Barium.** L. A. CONGDON and D. FITZGERALD (*Chem. News*, 1924, **128**, 274—276).—Precipitation of barium as sulphate or chromate gave figures 0.2—0.3% above the theoretical, whilst precipitation as oxalate in weak alcoholic solution or as carbonate in faintly ammoniacal solution gave results 0.15—0.25% below the theoretical. The oxalate precipitation was effected by adding to the neutral solution of barium chloride a hot saturated solution of ammonium oxalate containing one-third its volume of 85% alcohol; the solution was set aside over-night and the precipitate then collected on a Gooch crucible, washed with 95% alcohol, dried at 100° to constant weight, and weighed as  $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$ . Volumetric methods involving titration of barium chromate or oxalate gave very low results. A. R. P.

**Determination of Copper by the Thiocyanate Process and its Application to the Determination of Dextrose.** P. FLEURY (*Bull. Soc. chim.*, 1924, [iv], **35**, 230—235).—Comparisons are made between the Lehmann-Maquenne method of determining copper, in which the iodine liberated by the copper salt from a potassium iodide solution acidified with sulphuric acid is titrated with sodium thiosulphate, and the modification of this method due to Fleury and Boutot (*A.*, 1922, ii, 879). The iodine liberated is proportional to the amount of copper present in both methods, the proportionality being slightly more exact in the case of the potassium thiocyanate method. The results obtained by the two methods when applied to the determination of dextrose do not differ very much. A control should always be carried out on the thiocyanate. E. E. T.

**Reaction between Metallic Copper and Ferric Ion in Dilute Sulphuric Acid Solution.** D. NISHIDA (*J. Chem. Ind. Japan*, 1923, 26, 1257—1264).—The deposition of copper in the electrolytic determination of copper in dilute sulphuric or nitric acid solution is greatly retarded by the presence of ferric ion, since the copper deposited dissolves quantitatively according to the equation:  $\text{Cu} + 2\text{Fe}^{+++} = \text{Cu}^{++} + 2\text{Fe}^{++}$ . Metallic copper, especially in powder form, can be used to reduce ferric to ferrous iron in the volumetric determination of iron with potassium permanganate solution.

K. K.

**Sodium Carbonate Fusion for the Detection of Manganous and Manganic Ions.** T. SCHAUER (*Sprechsaal*, 1923, 56, 475; from *Chem. Zentr.*, 1924, i, 690).—Manganous and manganic salts may be detected by fusion with fusion mixture without addition of potassium nitrate.

G. W. R.

**Volumetric Determination of Iron by Knecht and Hibbert's Titanous Chloride Method.** L. BRANDT (*Chem.-Ztg.*, 1924, 48, 265—266, 270—271).—The most satisfactory conditions for determining iron by titration of ferric salts with titanous chloride have been worked out and the effect of other metallic salts ascertained. The solution should contain about 20 c.c. of hydrochloric acid per 100 c.c., and the indicator (potassium thiocyanate) should not be added until the end-point is nearly reached and the solution only faintly yellow. The presence of copper, antimony, vanadium, or platinum salts causes the results to be high, whilst cobalt and chromium interfere if present in sufficient amount for the colour of their solutions to mask the end-point. If the titanous chloride solution is stored in a stock-bottle connected directly with the burette and an atmosphere of carbon dioxide is maintained above the liquid in the burette and in the stock-bottle, the titre of the solution will remain unchanged for at least a week. A. R. P.

**Detection of Cobalt and Nickel Separately or in the Presence of Each Other.** C. C. PALIT (*Chem. News*, 1924, 128, 293—294).—Sodium hydrogen carbonate produces a pale pink precipitate in solutions of cobalt salts; the precipitate dissolves to a pink solution in excess of the precipitant, and addition of bromine water, chlorine water, or hydrogen peroxide changes the colour of the solution to apple-green visible at a dilution of 0.000025 g. of cobalt in 10 c.c. of liquid. Under the same conditions, nickel salts give a pale green precipitate which is insoluble in excess of the carbonate and turns bluish-black on addition of one of the above oxidising agents and warming. When both metals are present together, an excess of sodium hydrogen carbonate is added and a few drops of bromine water; on shaking, the solution turns green, showing the presence of cobalt and, on warming, the precipitate turns bluish-black indicating nickel.

A. R. P.

**Determination of Metals contained in Small Quantities in Natural Phosphates.** A. GRAMMONT (*Bull. Soc. chim.*, 1924, [iv], 35, 405—408).—The natural phosphate is attacked with

hydrochloric acid followed by sulphuric acid and the chromium then extracted with cold water and determined as follows. Excess of ammonia is added, the precipitate dissolved in hydrochloric acid, sodium carbonate added until the precipitate formed just redissolves, and, finally, sodium sulphite solution added together with sodium acetate. The precipitate is ignited and is then heated to redness with sodium carbonate and potassium chlorate, the fused mass is extracted with water, and the chromium separated by Carnot's method and finally weighed as phosphate. [Cf. *B.*, 1924, 466.]

S. K. T.

**Volumetric Determination of Tin.** J. G. F. DRUCE (*Chem. News*, 1924, 128, 273).—Knop's method (this vol., ii, 351) for determining iron by titration of ferrous chloride solutions with potassium dichromate, using diphenylamine as internal indicator, is extended to the determination of tin as stannous chloride, an excess of ferric chloride solution being added to the stannous solution and the resulting ferrous chloride titrated as above. Contrary to Knop, iron is not necessary for the production of the blue colour; solutions of stannous chloride can be titrated directly with dichromate if 15 c.c. of a solution containing 150 c.c. each of strong sulphuric and syrupy phosphoric acids per litre are added, together with two drops of a 1% solution of diphenylamine in strong sulphuric acid.

A. R. P.

**Volumetric Determination of Niobium.** W. R. SCHOELLER and E. F. WATERHOUSE (*Analyst*, 1924, 49, 215—220).—The methods of Metzger and Taylor (*A.*, 1909, ii, 702), Osborne (*A.*, 1886, 393), Levy (*A.*, 1915, ii, 491), and Giles (*A.*, 1909, ii, 352) for the volumetric determination of niobium were all examined, together with modifications of the last method, in which all operations were carried out with complete exclusion of air. In no case was a stoichiometric factor, indicating the reduction of the niobium to a definite oxide, obtained. The methods all yielded empirical factors which varied with the slightest variation in the conditions and quality of reagents employed, and it is concluded that existing methods for the volumetric determination of niobium are untrustworthy. H. C. R.

**Determination of Platinum and Palladium in Alloys.** ANONYMOUS (*Metallbörse*, 1923, 13, 2386—2387; from *Chem. Zentr.*, 1924, i, 577).—The determination of silver, gold, platinum, and palladium may be carried out by performing a preliminary assay followed by chemical separation of the metals thereby obtained.

G. W. R.

**Determination of Alcohols. I. Methyl Alcohol.** W. M. FISCHER and A. SCHMIDT (*Ber.*, 1924, 57, [B], 693—698).—The methyl alcohol in aqueous solution is treated with carbamide dissolved in sodium nitrite solution and, while a current of carbon dioxide is passed through the mixture, acetic acid is added. The evolved methyl nitrite is passed through a mixture of dry sodium nitrate and sodium hydrogen carbonate and then into an

acidified solution of potassium iodide, and the liberated iodine titrated with sodium thiosulphate. With approximately 0.1*N* solutions of methyl alcohol, the method gives results accurate to 0.2—0.3%; at greater dilutions, it is rather less accurate. Homologues of methyl alcohol interfere, but not acetone, formaldehyde, light petroleum, benzene, ether, phenol, pyridine, methyl ethyl ketone, or glycerol, etc. Allyl alcohol must be previously converted into dibromopropyl alcohol.

H. W.

#### Detection of Methyl Alcohol in Presence of Ethyl Alcohol.

A. KLING and A. LASSIEUR (*Compt. rend.*, 1924, **178**, 1006—1009).—The method based on the use of morphine or apomorphine is not trustworthy, as the coloration is not specific; the guaiacol method (Pfyl, Reif, and Hanner, A., 1922, ii, 94) is criticised for the same reason, and, moreover, the specific blue coloration given by formaldehyde is obtained only with very small quantities. A colorimetric method, based on Denigès' reaction with permanganate and Schiff's reagent, and capable of detecting 1% of methyl alcohol in ethyl alcohol, is described.

H. J. E.

**Denigès' Test for Butyric Acid.** F. BAMFORD (*Analyst*, 1924, **49**, 226—227).—Denigès' test for butyric acid (A., 1918, ii, 138) gave positive results with caproic acid and with all fractions of carefully fractionated caprylic acid, the colour intensity in the latter case indicating 20% of butyric acid. The Reichert-Meissl distillate from coconut oil also gave a positive reaction, although this is stated to be free from butyric acid. The test is therefore untrustworthy as a means of determining small quantities of butyric acid.

H. C. R.

**Titration of Oxalic Acid with Permanganate.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1924, **61**, 417—429).—Permanganate solutions may be accurately titrated with oxalic acid in presence of sulphuric acid at 75—80° under specified conditions. If manganese sulphate be added, a temperature of 40° may be employed, but at higher temperatures the results are low by reason of decomposition of oxalic acid. Hydrogen peroxide is formed in presence of air or oxygen, probably by reason of the momentary production of a higher unstable manganese oxide. If oxalic acid is added to the permanganate solution, the results are too low by reason of loss of oxygen from the latter. Accurate results are also obtained in presence of hydrochloric acid, if the temperature is above 70°.

S. I. L.

**Determination of Acetone and  $\beta$ -Hydroxybutyric Acid in Small Quantities of Urine.** N. O. ENGFELDT (*Biochem. Z.*, 1924, **144**, 556—571).—One c.c. of the urine is treated with sodium chloride, ammonia, and basic lead acetate and filtered. The filtrate is distilled with a few drops of acetic acid and a trace of talc, and the distillate is received in a freshly prepared mixture of sodium hydroxide and standard iodine solution. After acidification, the residual iodine is titrated with sodium thiosulphate and from the amount of iodine used the total acetone of the urine is calculated.

The liquid remaining in the distilling flask is then treated with potassium chromate and sulphuric acid and redistilled in order to oxidise the  $\beta$ -hydroxybutyric acid. The distillate is received in sodium hypiodide solution as before and the  $\beta$ -hydroxybutyric acid is calculated from the amount of iodine taken up. Lublin's method (A., 1923, ii, 268) is criticised. S. S. Z.

**Determination of Ketonic Compounds and of  $\beta$ -Hydroxybutyric Acid in Diabetic Urine.** H. BIERRY and (Mlle.) L. MOQUET (*Compt. rend.*, 1924, 178, 816—819; cf. Shaffer and Hubbard, A., 1916, ii, 352; Van Slyke, A., 1917, ii, 107).—The urine is treated with cupric sulphate and then rendered alkaline with calcium hydroxide suspension, and filtered. A known volume is freed from ketones by distillation in presence of dilute sulphuric acid, the residue oxidised with potassium dichromate, and a second distillate obtained. The two distillates are then redistilled in presence of a little sodium peroxide, and acetone is determined in the final distillates. If the urine contains considerable quantities of lactic or formic acid, aldehydes, or creatine, the method is much more trustworthy than that of Van Slyke. E. E. T.

**Biochemical Characterisation of Galactose in a Mixture containing Galactose and Arabinose.** M. BRIDEL and J. CHARPENTIER (*Bull. Soc. Chim. biol.*, 1924, 6, 26—34).—The results previously reported (A., 1923, ii, 882) are described in greater detail. To isolate  $\beta$ -ethylgalactoside formed by the action of emulsin on an ethyl-alcoholic solution of the products of hydrolysis of gum arabic, it is necessary to treat the mixture of galactoside and reducing sugar with hydrocyanic acid in presence of traces of ammonia, and subsequently with a solution of lead acetate which precipitates the cyanohydrin formed. The solution of  $\beta$ -ethylgalactoside, when evaporated to dryness after elimination of the lead by hydrogen sulphide, and extracted with ethyl acetate, yields crystals, m. p. 159—160°. W. O. K.

**Determination of Starch and Sugars by the Use of Picric Acid.** M. R. COE and G. L. BIDWELL (*J. Assoc. Off. Agric. Chem.*, 1924, 7, 297—304).—The material is extracted with ether and with alcohol to remove protein and fat, boiled to gelatinise the starch, which is hydrolysed with a fresh malt solution. The sugars are subsequently hydrolysed by hydrochloric acid, and the solution is neutralised and treated with picric acid. Portions are removed and heated with sodium carbonate solution and the resultant colour is matched against that of standard sugar solutions.

A. G. P.

**Determination of Lignin in Wood Cellulose.** H. WENZL (*Papierfabr.*, 1924, 22, 101—106).—An excellent reagent for dissolving the cellulose, leaving the lignin unattacked, is prepared by the gradual addition of 30 g. of phosphorus pentoxide to 100 c.c. of hydrochloric acid, *d* 1.19, while cooling by means of water. This reagent rapidly hydrolyses the cellulose at 30° when 1 g. of wood

pulp is treated with 25 c.c. of the acid. The residue of lignin is collected in a Gooch crucible on an asbestos pad after diluting the solution with hydrochloric acid. The residue is washed, dried at 110—115°, weighed, and the weight corrected for the ash after incineration. [Cf. *B.*, 1924, 464.] J. F. B.

**Determination of Carbamide by Sodium Hypobromite.** F. SCHMID (*Arch. malad. reins org. génit.*, 1923, **1**, 481—488; from *Chem. Zentr.*, 1924, i, 691).—The apparatus of Ambard and Hallion is recommended, using glass beads and without mercury. The determination can be carried out without using physical constants if a parallel determination is made with a solution containing approximately the same amount of carbamide. G. W. R.

**Nephelometric Micro-determination of Carbamide in Biological Fluids.** C. AUGUSTE (*Compt. rend. Soc. Biol.*, 1923, **89**, 991—993; from *Chem. Zentr.*, 1924, i, 692).—Carbamide may be determined nephelometrically in biological fluids after condensation with xanthidrol. The precipitate is held in suspension by the colloidal substances present. G. W. R.

**Esterification by Dilution in Inert Media.** V. BOULEZ (*Bull. Soc. chim.*, 1924, [iv], **35**, 419—420; cf. *A.*, 1907, ii, 117).—The author replies to the criticisms of Glichitch (*A.*, 1923, ii, 661) on his method for determining linalool and other terpinic alcohols in essential oils, by giving details of an improved procedure. The essential oil is acetylated in *m*-xylene solution, the mixture warmed with water, and the water separated. After a single washing with water, the xylene mixture is dried with anhydrous sodium sulphate, and filtered cold, and the filtrate is neutralised and saponified with alcoholic sodium hydroxide. Linalool, terpineol, and terpin have been acetylated quantitatively by this method.

R. B.

**Carbylamine Reaction.** M. WADEWITZ and B. RASSOW (*Z. angew. Chem.*, 1924, **37**, 191).—The usual method of testing for primary amines by means of the carbylamine reaction fails in the case of primary amines containing a further group capable of forming non-volatile salts (*e.g.*, aminophenols, aminocarboxylic acids, amino-sulphonic acids, etc.). If, after completion of the normal carbylamine reaction (as shown by separation of potassium chloride), a sample is withdrawn on a glass rod and held in the current of air breathed out from the nose, the carbon dioxide in the expired air combines with the alkali and liberates the volatile carbylamine derivative, the odour of which soon becomes noticeable.

W. T. K. B.

**Determination of Hippuric Acid in Urine.** I. SNAPPER and E. LAQUEUR (*Biochem. Z.*, 1924, **145**, 32—39).—Urine containing sodium chloride and hydrochloric acid is extracted with ethyl acetate; the extract is shaken with water to remove carbamide, and the aqueous extract re-extracted with ethyl acetate to recover dissolved hippuric acid. The combined extracts are evaporated,



and the residue is dissolved in ethyl alcohol or ethyl acetate; in one (smaller) portion (after removal of any carbamide with sodium hypobromite solution) the nitrogen of the hippuric acid is determined by Kjeldahl's method, whilst the larger portion is used for the determination of hippuric acid and carbamide, a correction being made for undecomposed carbamide. The results justify the assumptions that all the hippuric acid is extracted, and that all the nitrogen of the ethyl acetate extract corresponds with hippuric acid. In cases of albuminuria, the urine is first deproteinised by the addition of phosphoric acid.

J. P.

**Bile Secretions. IV. Colorimetric Determination of Bile Acids in Human Body Fluids.** F. ROSENTHAL and F. LAUTERBACH (*Arch. Exp. Path. Pharm.*, 1924, **101**, 1—16).—The naphthaquinonesulphonic acid reaction of Folin (A., 1922, ii, 540) is applied to glycine and taurine obtained from the bile acids by hydrolysis. Glycine reacts quantitatively, whilst in the case of taurine only two-thirds of the total amount present appears to react. To determine the bile acids, the bile (40 c.c.) is precipitated by the addition of 3 vols. of 96% alcohol, and filtered after remaining over-night. The precipitate is washed with alcohol, the filtrate and washings are concentrated, dissolved in alcohol, filtered, concentrated, and the residue is dissolved in water (10 c.c.). Five c.c. of this solution are used for determination of the free aliphatic amino-acids by the naphthaquinonesulphuric acid reaction, and the remainder for a similar determination after hydrolysis with 5% sodium hydroxide solution for 5 hours at 100°. The taurine present is determined by determining the alcohol-soluble sulphur in an alcoholic bile extract (cf. Rosenthal and v. Falkenhausen, A., 1923, ii, 667). From these results, the quantities of glycocholic and taurocholic acids present in the bile may be calculated. Full experimental details are given.

W. O. K.

**Determination of Colloidal Substances in Urine.** M. GOLDWASSER (*Z. ges. exp. Med.*, 1923, **37**, 481—496; from *Chem. Zentr.*, 1924, i, 692—693).—A complete separation can be effected by the use of a method in which the colloidal substances are separated by frothing.

G. W. R.

**Use of Electrodialysis in the Determination of Total Bases in Sera and other Substances.** R. WERNICKE (*Compt. rend. Soc. Biol.*, 1923, **89**, 748—750; from *Chem. Zentr.*, 1924, i, 506).—Electrodialysis may be conveniently used in the determination of bases in sera and similar liquids. In the electrodialysis of horse-serum, a quantitative separation of the proteins was effected.

G. W. R.

**Precipitin Reactions of a Crystalline Globulin from Human Urine.** H. S. EVERETT, S. BAYNE-JONES, and D. W. WILSON (*Bull. Johns Hopkins Hosp.*, 1923, **34**, 385—387).—The crystalline globulin isolated by Noel-Paton (*Lab. Rep. R. Coll. Phys. Edin.*, 1892, **4**, 47) from human urine can be sharply differentiated by the precipitin

test from the proteins of human serum, and should not be classed as a Bence-Jones protein.

CHEMICAL ABSTRACTS.

**Determination of Free and Combined Pepsin in Stomach Contents.** R. EGE (*Biochem. Z.*, 1924, **145**, 66—76).—Pepsin is adsorbed by the normal gastric contents to a maximum extent at  $p_H$  3 to 4, much less at  $p_H$  1, and not at all at  $p_H$  6.8. For determining total pepsin, a method is described in which the adsorbed pepsin is liberated by use of a phosphate mixture of  $p_H$  6.8. It is concluded that most pepsin figures quoted in the literature are in error in that the adsorbed pepsin is not determined. J. P.

**Evaluation of Pepsin in the Light of Recent Knowledge of Enzyme Action.** H. W. VAN URK (*Pharm. Weekblad*, 1924, **61**, 442—455).—The difficulties are too great to allow of exact quantitative determinations, but comparative results may be obtained by plotting a curve for time/formation of peptone (determined by a Kjeldahl nitrogen determination) and accepting times required for formation of equal quantities of peptone by comparison with a standard curve as inversely proportional to strengths of pepsin. [Cf. *B.*, 1924, 444.] S. I. L.

**Determination of Trypsin and Lipase in Gastric Contents.** C. W. LUEDERS and O. BERGEIM (*Amer. J. Physiol.*, 1923, **66**, 297—301).—Trypsin is determined by formaldehyde titration of the amino-acids produced on incubation with gelatin. For lipase, the substrate is an emulsion of olive oil in gum acacia solution; after addition of alcohol and ether, the liberated fatty acids are titrated with sodium hydroxide. A control determination with the olive oil emulsion and boiled gastric contents is necessary.

CHEMICAL ABSTRACTS.

**Cholesterol Content of the Bile. I. Methods for its Determination in the Contents of the Duodenum.** C. W. McCLURE and E. MORTIMER (*Boston Med. Surg. J.*, 1923, **188**, 633—635; from *Chem. Zentr.*, 1924, i, 693).—The contents of the duodenum are removed with magnesium sulphate solution and a portion is shaken with ethyl alcohol and chloroform, the mixture being clarified with anhydrous sodium carbonate. Part of the supernatant liquid is evaporated with alcoholic sodium ethoxide; the residue is extracted with chloroform, the solution concentrated, filtered, and the residue further extracted. The cholesterol in the extract is determined in a Duboseq colorimeter, after addition of acetic anhydride and strong sulphuric acid. The mixture is kept in darkness for 30 minutes before reading the colorimeter. G. W. R.

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## General and Physical Chemistry.

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**Laws of Radiation and Intensities of Complex Spectral Lines.** L. S. ORNSTEIN and H. C. BURGER (*Z. Physik*, 1924, **24**, 41—47).—The intensities of the components of complex series lines are discussed in relation to the probabilities of the various stationary states involved. S. B.

**Quantum Theory of Band Spectra.** ANON. (*Nature*, 1924, **113**, 874—875).—A short review. A. A. E.

**Quantum Theory of Radiation.** N. BOHR, H. A. KRAMERS, and J. C. SLATER (*Phil. Mag.*, 1924, [vi], **47**, 785—802).—The conception due to Slater that an atom, even before a process of transition between two stationary states, is in communication with other atoms through a virtual radiation field, is extended, and the mechanism of the emission and absorption of radiation discussed, in connexion with the conflicting results of the wave-theory of light and Einstein's theory of light-quanta. S. S.

**Relative Probabilities of Transitions involved in the Balmer Series Lines of Hydrogen.** F. C. HOYT (*Phil. Mag.*, 1924, [vi], **47**, 826—831).—The relative probabilities of the occurrence of the transitions associated with the components of the lines  $H_\alpha$  and  $H_\beta$  are computed and the figures obtained used to calculate the relative absorptions of  $H_\alpha$  and  $H_\beta$  by glowing hydrogen. The ratio of the absorptions has been deduced by Ladenburg and Reiche (*Naturwiss.*, 1923, **9**, 584) from observations on anomalous dispersion, but the experimental figures are not of sufficient accuracy to enable a choice to be made between the six hypotheses used in applying Bohr's correspondence principle. S. S.

**Approximate Calculation of the Orbits and Probabilities of Transition of the Series Electron in the Sodium Atom.** W. THOMAS (*Z. Physik*, 1924, **24**, 169—196).—A mathematical treatment of the orbital motion of the valency electron in sodium based on Bohr's theory. It is assumed that the field of force is central and that its potential is given by  $v = -e^2/r \cdot (1 + a_0\Omega/r)$ , where  $-e^2/r$  is the potential of the system if the nucleus and inner electrons can be considered as concentrated at the centre, and  $-e^2a_0\Omega/r^2$  measures the divergence of the system from that of the hydrogen atom, due to the influence of the electrons in the  $1_1$ ,  $2_1$ , and  $2_2$  orbits. In accordance with the work of Fues,  $\Omega$  is assumed to be a quadratic function of the distance from the centre, and from these data the orbits  $3_1$ ,  $3_2$ ,  $4_2$ , and  $5_2$ , which are responsible for the first three lines of the principal series, are calculated and plotted and the various constants of the orbits tabulated. The orbits thus obtained are expanded in Fourier series and the amplitudes of the component harmonics found. With the help of the

correspondence principle, the probabilities of the various transitions are evaluated and from these the intensities to be expected for the first three lines of the principal series calculated. The calculated intensities are in reasonable agreement with experiment. G. S.

**Series Spectra in the Emission of which more than one Electron are concerned.** G. WENTZEL (*Physikal. Z.*, 1924, **25**, 182—183).—The author supplements his results referring to terms of the series spectra of the alkaline-earths (A., 1923, ii, 352) by reference to the work of del Campo (*Trab. Lab. fisico*, 1923, **68**, 43) indicating the existence of a third *pp'* series in the spectrum of calcium. The values of the constants in a Ritz formula for this spectrum are calculated. It is suggested that possible electronic orbital transitions in the case of the emission of spectra involving  $N$  electrons are determined in accordance with the selection principle  $\Delta k = N$ . In the cases of calcium and neon,  $N = 2$ . In the excitation of the calcium emission spectrum, the second valency electron is possibly transferred to a  $4_2$  orbit rather than to a  $3_3$  orbit.

J. S. G. T.

**Distribution of Electrons in the Various Orbits of the Hydrogen Atom.** H. C. UREY (*Astrophys. J.*, 1924, **59**, 1—10).—An application of chemical thermodynamics to the equilibrium existing between a neutral atom, its ion, and electron gas. Equations involving partial molal free energy and fugacity are developed; it is shown that if the atoms in each of the resonated states are regarded as composing a perfect gas, the gas would be completely ionised at all temperatures and pressures. In application to the case of monatomic hydrogen, it is assumed that atoms having electrons in orbits of high quantum numbers form imperfect gases due to the volume of the atoms themselves; for  $10,000^\circ \text{K}$  and  $0.001 \text{ atm.}$ , only  $0.0007$  of the total number of atoms have their electrons in higher orbits than the first. The quantum states up to those of total quantum number 10 may be regarded as perfect gases at pressures below  $0.01 \text{ atm.}$

A. A. E.

**Influence of Ionic Deformations on Optical and Chemical Constants.** I. M. BORN and W. HEISENBERG (*Z. Physik*, 1924, **23**, 388—410).—The electric moments of atoms produced by the application of unit field have been calculated from the values of the Rydberg corrections for the series spectra of the elements. The assumption of half-number values for the azimuthal quantum numbers, instead of whole numbers, affects the results, and a comparison with figures obtained from the atomic refraction of the inert gases shows that the half-number values are the correct ones. A table of electric moments is given, calculated from the refraction of salts, and including all ions with completed outer electronic rings. Heats of sublimation calculated with the aid of this table agree satisfactorily with experiment. Calculations are made of the wave-lengths corresponding with the nuclear vibrations for the alkali halides.

S. B.

**Relation between Pressure Shift, Temperature Class, and Spectral Terms of the Iron Lines.** M. A. CATALÁN (*Nature*, 1924, **113**, 889—891).—The regular curve obtained by plotting the mean values of pressure shifts against the mean value of the sum of the terms forming each multiplet is used to interpret some groups of lines not yet classified. Two multiplets are ascribed to a septet system. The pressure effect depends little, if at all, on the azimuthal and internal quantum numbers of the orbits, but probably on the radial quantum numbers. The effect of temperature is parallel to that of pressure; increase of temperature causes ejection of the valency electrons to orbits with larger radius.

A. A. E.

**Zeeman Effect in the Spectrum of Palladium.** M. LEVITSKAYA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 193—235).—The study of the Zeeman effect in the ultra-violet portion of the spectrum of palladium has previously only been carried out by Purvis (cf. *Proc. Camb. Phil. Soc.*, 1906, **13**, 325; *Nature*, 1906, **73**, 71), who has studied 44 lines. In the present investigation, carried out with the aid of a large Rowland grating, 192 lines of palladium have been studied. The Zeeman effect in the spectrum of palladium presents three general types: quintets, quadruplets, and triplets, although that is only the primitive aspect of the phenomenon. The separation in the spectra of higher orders becomes still more complicated. Some of the quintets are made up of at least 15 constituent lines. Drawings and descriptions are given of the types of quadruplets. The triplets can be placed in three groups, (1) distinct triplets, (2) slightly diffused triplets, and (3) diffused triplets. The first group always possesses a value of  $\delta\lambda/\lambda^2$  equal to 0.9—1.15. The second has a value of  $\delta\lambda/\lambda^2$  between 1.2 and 1.3, and nearly all the diffused triplets have a value of  $\delta\lambda/\lambda^2$  about 1.4. The triplets of the first group are normal triplets. They give a value of  $e/mc$  between  $1.5 \times 10^7$  and  $1.8 \times 10^7$ . S. P. S.

**Laws Governing the Palladium Spectrum.** M. A. LEVITSKAYA (*J. Russ. Phys. Chem. Soc.*, 1918, **49**, 118—124).—The sharpest lines in the palladium spectrum appear in groups, the distance between which decreases as the wave-length shortens. The normal triplets for which  $e/mc$  lies between  $1.6 \times 10^7$  and  $1.8 \times 10^7$  were closely studied. For these, a graphical method was adopted,  $1/\lambda$  being plotted against  $m=1, 2, 3, \dots$ . A smooth curve is obtained for which an expression,  $1/\lambda=A-N/Z^2$ , is suggested, where  $A$  is the series limit,  $N=109675$ , and  $Z$  is a constant. From the curve, an approximate value for  $A$  for the corresponding series is obtained, and from this  $Z$  can be found. The curve for quadruplets is obtained with greater difficulty, as several members are missing, for although lines near them exist, these do not show the Zeeman effect. These attempts are by no means considered as final and conclusive.

P. S.

**Multiplets in the Spectrum of Vanadium.** O. LAPORTE (*Naturwiss.*, 1923, **11**, 779—782; from *Chem. Zentr.*, 1924, i, 619).—The multiplets of vanadium are given in tabular form. They

consist of even systems of series in which sextets and quartets occur. The occurrence of sextets is in agreement with the author's hypothesis that the maximum multiplicity is greater by unity than the number of the column (in the periodic system) in which the element occurs. In addition to the system of maximum multiplicity, all lower even or odd systems down to doublets or single lines can occur.

G. W. R.

**Regularities in the Spectrum of Silicon Tetrafluoride.** C. PORLEZZA (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 283—287; cf. A., 1913, ii, 814).—In addition to those given by Dufour, three new groupings are found in the band spectrum of silicon tetrafluoride: ( $X'$ ),  $N=23580-166.5m-3.5m^2$  ( $m=0, 1, 2, 3$ ); ( $Y'$ ),  $N=23624-165.5m-3.5m^2$  ( $m=0, 1, 2, 3, 4$ ); ( $Z'$ ),  $N=23416-161.5m-5.5m^2$  ( $m=0, 1, 2$ ). For  $X'$  and  $Z'$ , the co-ordination is shown by comparison with the results obtained by Dufour in the study of the longitudinal Zeeman phenomenon. Six other groupings, each of two components, are also observed.

T. H. P.

**Emission of Light by Solid Nitrogen and Origin of the Auroral Spectrum.** L. VEGARD (*Compt. rend.*, 1924, **178**, 1153—1156).—The action of cathode rays on crystalline nitrogen results in the emission of spectra which are practically identical with that of the typical aurora. The most prominent line is the green line, 5577. When the bombardment has ceased, the nitrogen remains luminous for about 5 minutes. The author claims that the observed facts confirm his conclusions regarding the constitution of the upper strata of the atmosphere.

H. J. E.

**Spectrum of Neutral Helium. II.** C. V. RAMAN and A. S. GANESAN (*Astrophys. J.*, 1924, **59**, 61—63).—The former view (*ibid.*, 1922, **56**, 119; A., 1923, ii, 805) that the coincidences observed by Silberstein (cf. A., 1923, ii, 805) are fortuitous is maintained, and supported by calculations which take into account the fact that the lines given by the combination formula are not distributed uniformly throughout the whole interval of frequency.

A. A. E.

**Balmer Series of Hydrogen.** A. E. M. GEDDES (*Proc. Roy. Soc. Edin.*, 1924, **44**, 14—20).—The separations of the main components of  $H_\alpha$  and  $H_\beta$  have been re-measured. An echelon spectrograph was used, and observations were made with the vacuum tube at room temperature, and immersed in liquid air. The separations of  $H_\alpha$  and  $H_\beta$  are given as 0.147 Å. and 0.085 Å., respectively.

S. B.

**Arc Spectrum of Phosphorus.** M. O. SALTMARSH (*Phil. Mag.*, 1924, [vi], **47**, 874—882).—The spectrum of phosphorus in the arc and in a vacuum tube containing hydrogen at low pressure has been photographed from the red to the ultra-violet at 1333 Å. The spectrum consists of 35 lines, only four of which have been previously measured; it lies entirely in the ultra-violet from 2555 to 1671 Å. A group of five close lines, widely separated from neighbouring lines, is found at 2154.77 to 2136.10 Å., which are

all within the limits corresponding with the observed radiation potential,  $5.80 \pm 0.1$  volts (Foote and Mohler, *Physical Rev.*, 1920, 15). The frequencies of all the lines are found to be connected by systems of doublets of constant frequency differences, and thus the spectrum probably obeys the Sommerfeld-Kossel displacement law. The frequencies of fifteen of the strongest lines can be expressed by means of nine terms, of which some can be arranged as multidoublets.

S. S.

**Spectra Emitted by the Stoppage of Positive Rays of Lithium.** M. MORAND (*Compt. rend.*, 1924, 178, 1528—1529).—A stream of positive rays from an anode covered with a lithium salt was directed on to an obstacle and the region of impact became luminous. The radiation consists principally of the lines of the arc spectrum of lithium together with some other lines from impurities and a line 2934.15 belonging to the spark spectrum. In one plate, this was found to be a doublet of almost equal intensity 2933.85 and 2934.5. This is in accordance with the analogy which should exist between the spark spectrum of lithium and that of helium.

L. J. H.

**Series Spectra of the Stripped Boron Atom ( $B^{III}$ ).** I. S. BOWEN and R. A. MILLIKAN (*Proc. Nat. Acad. Sci.*, 1924, 10, 199—203).—Examination of the fine structure of the strong lines in the "hot spark" spectrum of boron has revealed the following doublets, 677.01—677.16, 758.47—758.68, 1825.87—1826.41, 2066.41—2067.88, 2089.60—2090.29, and the single lines 2077.79 and 4499.0 Å. Of these only the pairs at 2066 and 2090 Å. have been described previously. The pairs at 1826 and 2090 Å. are identified with  $B^I$ , since their frequency separations of 16.2 and 15.8  $\text{cm}^{-1}$ , respectively, correspond with those of Fowler ("Report on Series in Line Spectra," 155) for  $B^I$  lines. Following the suggestion of Millikan and Bowen (this vol., ii, 214) that the strongest lines in the "hot spark" spectra are hydrogen-like, the remaining lines are attributed to  $B^{III}$ . Calculations of the possible  $B^{III}$  lines from the Bohr theory and the deviations from the simple theory for  $Al^{III}$  and  $Li^{II}$  have been made. To an average accuracy of 1 part in 3000 parts these calculated lines agree with experiment both as regards wave-length and frequency separation of the pairs. The doublets correspond with orbital jumps  $3p_2-3d$ ,  $3p_1-3d$ ;  $2p_2-3s$ ,  $2p_1-3s$ ;  $2s-2p_1$ ,  $2s-2p_2$ ; and the lines to  $3d-4f$ , and  $4f-5f'$ , respectively. These are all the  $B^{III}$  lines which could be expected to appear in any strength.

A. E. M.

**Spectrum of Helium in the Extreme Ultra-violet.** T. LYMAN (*Nature*, 1924, 113, 785).—Several new terms have been added to the  $oS-mP$  series, and a continuous spectrum extending from the limit of this series toward the extreme ultra-violet has been observed. Lines have also been observed of the enhanced series  $4N/(1/l^2 - 1/m^2)$  at 303.6 and 256.3. A new line at 591.5 fits the relation  $oS - 1\pi$ , the first evidence of inter-system combination for helium.

A. A. E.

**Preliminary Measurements of Intensity in the High-frequency Spectra of the Elements.** A. DAUVILLIER (*Compt. rend.*, 1924, **178**, 1522—1524).—A continuation of previous work (this vol., ii, 138). For the *K* series of molybdenum and of silver the ratio of intensity of the rays  $\alpha_1$  and  $\alpha_2$  is the same (2:1) as that of the rays  $\beta_1$  and  $\beta_2$ . The ratios  $(\alpha_1 + \alpha_2)/(\beta_1 + \beta_2)$ , and  $(\beta_1 + \beta_2)/\gamma$  are constant and nearly 5. This is in accordance with the system of distribution of electrons on the different levels enunciated before. The departure levels giving rise to *K* rays are all constituted of 4 and 2 electrons, respectively. Of the *L* series eight rays for gold and ten for uranium have been studied. An analogous law of variation holds for the series *L*<sub>3</sub>, but the ratios are slightly different. L. J. H.

**Soft X-Rays from Heavy Elements, Tantalum to Gold.** J. C. BOYCE (*Physical Rev.*, 1924, **23**, 575—579).—A study of soft X-radiations, excited by electron bombardment between 30 and 1500 volts, from tantalum, tungsten, osmium, iridium, platinum, and gold, yields results which are in fair agreement with the values Bohr and Coster predicted for the ionisation potentials of the *N*-level electron orbits, by means of the combination principle, from the X-ray wave-lengths measured by Siegbahn and others.

A. A. E.

**Band Spectra of the Oxide and Nitride of Boron.** W. JEVONS (*Nature*, 1924, **113**, 785).—The results of the observation of the uncondensed discharge through a mixture of oxygen and boron trichloride vapour are irreconcilable with Mulliken's statement that a band spectrum (not here observed) is due to boron monoxide, and not to boron nitride (cf. this vol., ii, 366).

A. A. E.

**Spectra of Thermionic Discharge in Carbon Monoxide. New Band Spectra.** F. BALDET (*Compt. rend.*, 1924, **178**, 1525—1527).—With a 2-electrode tube and tungsten cathode and a potential difference of 100 v., it was found that carbon monoxide at a few tenths of a millimetre pressure gave a complex band spectrum in which were observed the known second positive group, third positive group, negative ultra-violet group of carbon, the doublet spectrum observed in the tails of certain comets, and one that appears to be new. No trace of the Swan, or first positive group, nor of the hydrocarbon bands was found. The introduction of a small quantity of air brought into existence the group of bands, 3883 Å., attributed to cyanogen and the band, 3914 Å., of the negative group of nitrogen, making the spectrum resemble that of the tail of the Morehouse comet. The new band spectrum is well developed at 0.7 mm. It consists of three intense doublets, degraded towards the violet, the head of each band being itself a close doublet. The bands consist of numerous lines very close together, not resolvable near the head with the dispersion employed. The method of excitation involves a certain amount of dissociation of the gas, so it is not absolutely certain that the bands are due to carbon monoxide as such. The heads of the



first series in each case are (in air)  $4236.46 \pm 0.08$ ,  $3977.91 \pm 0.06$ , and  $3729.60 \pm 0.05 \text{ \AA}$ .  
L. J. H.

**Qualitative Studies on the Infra-red Absorption Spectra of Organic Substances.** J. LECOMTE (*Compt. rend.*, 1924, **178**, 1530—1532).—The infra-red (between 1 and  $14\mu$ ) absorptions of more than a hundred organic substances have been measured although the results with many have not yet been published. Qualitative considerations concerning the position of the bands are in harmony with the classifications of chemistry. Thus primary alcohols are characterised by a band from  $9.65$ — $9.75$ , secondary by one at  $9.05$ , and tertiary by two bands, one at  $8.50$  and the other from  $9.65$  to  $9.75$  exactly like the primary. In all the ketones examined, except for acetone, a band appears at  $6.15$ . The carboxyl group is distinguished by a band at  $5.90$ , and another lying between  $8.00$  and  $8.65$ . The influence of double and triple bonds, especially the latter, is less clear.  
L. J. H.

**Balmer Absorption Series of Hydrogen.** E. O. HULBURT (*Physical Rev.*, 1924, **23**, 593—597).—By passing condensed discharges through an under-water spark in series with a tube of hydrogen at low pressure, the absorption series has been extended to the seventh line (using dry hydrogen) and to the tenth line (using moist hydrogen). Variation of the relative intensities of the light of the spark and of the glowing hydrogen caused  $H_\alpha$ ,  $H_\beta$ , and  $H_\gamma$  to appear as emission or as absorption lines; in other cases,  $H_\gamma$  was dark with a bright centre, or  $H_\alpha$  was bright,  $H_\beta$  dark with a bright centre, and the remaining lines dark. These phenomena are well known in stellar spectra, to which a reference is made.  
A. A. E.

**Selective Absorption by Luminous Mercury Vapour.** E. P. METCALFE and B. VENKATESACHAR (*Proc. Roy. Soc.*, 1924, **A**, **105**, 520—531; cf. A., 1921, ii, 669; 1922, ii, 728).—All the satellites of the  $5461 \text{ \AA}$ . group,  $1p_1$ — $1s$ , except  $-0.237 \text{ \AA}$ ., are strongly absorbed by long columns (1 metre) of luminous mercury vapour. For all lines, except  $-0.237 \text{ \AA}$ ., the ratio (emission)/(absorption) is constant and, again excepting  $-0.237 \text{ \AA}$ ., all the satellites have been reversed. The conditions for reversal are discussed and the possible isotopic origin of some of the satellites is considered. The absorption and reversal of the lines  $5769 \text{ \AA}$ .,  $1P-2d'$ , and  $5791 \text{ \AA}$ .,  $1P-2D$ , have been observed and the satellites  $0.044 \text{ \AA}$ . and  $-0.050 \text{ \AA}$ . are reversed.  
S. K. T.

**Decomposition of Carbon Disulphide by Ultra-violet Rays.** G. BRUHAT and M. PAUTHENIER (*Compt. rend.*, 1924, **178**, 1536—1538).—If the image of a mercury arc is formed on the wall of a quartz cell containing carbon disulphide, a deposit of sulphur is obtained which takes the shape of the arc. The effect is intensified by half-silvering the quartz. When the ultra-violet light from the mercury arc is dispersed through a quartz spectroscopic and an image of the spectrum formed on the silvered wall of the cell, most of the mercury lines are obtained. The phenomenon is certainly

related to the absorption of carbon disulphide, as the lines recorded begin only with the absorption band (longest effective ray 3660 Å.), and are particularly pronounced for 3130 Å., which is close to a maximum of absorption. L. J. H.

**Absorption Spectra of Coloured Glass.**—(See ii, 472.)

**Absorption of Ultra-violet Light by Organic Compounds.**

III. L. MARCHLEWSKI and A. MOROZ (*Bull. Soc. chim.*, 1924, [iv], 35, 473—480).—Values of the coefficient of extinction,  $\alpha = 1/d \cdot \log I/I_1$ , for solutions in absolute alcohol of the readily obtainable quinones, *o*-, *m*-, and *p*-nitrophenol, and  $\alpha$  and  $\beta$  derivatives of naphthalene are tabulated;  $\alpha$  is also plotted as a function of wave-length. A. B. H.

**Ultra-violet Absorption Spectra of Eugenol.**—(See i, 637.)

**Absorption Measurements of certain Changes in the Average Wave-length of Tertiary X-Rays.** S. K. ALLISON and W. DUANE (*Proc. Nat. Acad. Sci.*, 1924, 10, 196—199).—Clark and Duane (this vol., ii, 369) have shown that X-radiation from a secondary radiator contains tertiary radiation of a constant limiting high frequency, but with maximum wave-lengths increasing as the angle of scattering increases. The shift of this maximum has been studied for silver, using tungsten  $K_\alpha$  rays as the source of primary radiation and employing the method of Ross (*Physical Rev.*, 1923, 22, 525) with screens of iodine, tellurium, and antimony for which the  $K$  critical absorption wave-lengths were respectively 0.3737, 0.3896, and 0.4065 Å. The results are in accordance with those of Clark and Duane, but the magnitude of the effect depends largely on the angle of incidence of the primary beam. Tungsten rays scattered from graphite and examined with a dysprosium screen ( $\lambda_{\text{abs.}} = 0.2308$  Å.) showed no effect at scattering angles between 20° and 120°, so that in this range no change in the energy of tertiary radiation from carbon due to the tungsten  $K_\alpha$  doublet takes place in wave-lengths up to 0.2308 Å. A. E. M.

**Absorption of Hard  $\gamma$ -Rays by Elements.** N. AHMAD (*Proc. Roy. Soc.*, 1924, A, 105, 507—519).—The absorption of hard  $\gamma$ -rays by elements is given by the expression  $1.68 \times 10^{-25}z + 1.60 \times 10^{-31}z^4$ , where  $z$  is the atomic number. Slight deviations occur after copper and mercury. Comparison with the corresponding formula for X-ray absorption shows that the first term represents an apparent absorption due to scattering, whilst the second term represents a "true" absorption. On the basis of these conclusions, two independent calculations of the effective mean wave-length of hard  $\gamma$ -rays are made. The results (0.015 and 0.019 Å.) agree closely with Ellis's determinations (A., 1922, ii, 339). S. K. T.

**Darkening of Phosphorescent Zinc Sulphide.**—(See ii, 484.)

**Secondary  $\beta$ -Rays Produced in a Gas by X-Rays.** P. AUGER (*Compt. rend.*, 1924, 178, 1535—1536).—A continuation of previous work (this vol., ii, 286). According to the author's theory, the

distribution of the secondary rays should show a maximum for the angle  $\theta_m$  with that of the primary X-ray, where  $\cos \theta_m = \sqrt{a/(a+2)}$  and  $a = h/mc^2$ . From three series of experiments, using different potentials and screens, some confirmation is obtained, but it is necessary to divide the total number of rays into two very unequal groups, the distribution of which may be represented by two symmetrical curves, analogous but with different maxima. The superposition of these curves gives the experimental distribution.

L. J. H.

**Optical Dispersion and Selective Refraction, with Application to Infra-red Natural Frequencies.** T. H. HAVELOCK (*Proc. Roy. Soc.*, 1924, **A**, 105, 488—499).—An exact equation, together with a simple approximate solution, is deduced for the maximum of selective reflection in terms of the constants of the dispersion formulæ previously studied (*A.*, 1911, ii, 165). Good agreement is found between the calculated and observed values for rock salt (Maclaurin's formula), sylvine (Marvin's formula), and fluorspar (Maclaurin's formula). For fluorspar, the calculated maximum is near the longer residual rays. Values calculated from theories of crystal structure agree only approximately with those determined experimentally. Försterling's formula (*Ann. Physik*, 1920, **61**, 577) is incorrect.

S. K. T.

**Non-metallic Elements. Connexions between their Dielectric Constants and other Physical Properties.** G. L. ADDENBROOKE (*Phil. Mag.*, 1924, [vi], **47**, 945—965).—The action of an electric field on a dielectric is assumed to consist of (a) a reversible storage of energy proportional to  $K-1$ , and (b) an attraction or stress proportional to  $(K-1)/(K+2)$ , where  $K$  is the dielectric constant. The quantity  $K_m-1$ , termed the molecular dielectric equivalent, is calculated by the relation  $K_m-1 = (K-1)(\text{Atomic weight/density})$  for ten non-metallic elements and the resulting figures for energy storage and attraction are compared with the atomic number, melting point, boiling point, latent heat, and surface tension. It is found that the electrical attractions of the elements can be correlated approximately with these physical properties.

S. S.

**Magnetic Rotation in Sputtered Cobalt Films.** L. R. INGERSOLL (*J. Opt. Soc. Amer.*, 1924, **8**, 493—500).—The Faraday and Kerr effects observed with sputtered cobalt films, deposited on a cooled surface, are increased several fold by subsequent heating to 300°. It is deduced that magnetic rotation for light of the wavelengths employed ( $0.6\mu$ — $2.3\mu$ ) is not a molecular or atomic property, but is determined by the conducting electrons.

S. B.

**Polarisation of Resonance Radiation.** G. BREIT (*Phil. Mag.*, 1924, [vi], **47**, 832—842).—A theoretical paper in which the consequences of the Zeeman effect in resonance radiation are developed quantitatively. For sodium, both in and in the absence of a magnetic field, the predicted magnitude of the polarisation is in

good agreement with the values found by Wood and Eliot (*Proc. Roy. Soc.*, 1923, **A**, **103**, 396), whilst for mercury good agreement is obtained if the time-constant for the atom is taken as  $10^{-6}$  sec. instead of  $10^{-8}$  sec. S. S.

**Influence of Concentration on Polarisation of Fluorescent Light.** E. GAVIOLA and P. PRINGSHEIM (*Z. Physik*, 1924, **24**, 24—36).—The method of measuring the degree of polarisation of light by a compensating pile of glass plates is discussed, and is applied in determining the polarisation of the fluorescence from solutions of dyes in glycerin, when excited by plane polarised light. The degree of polarisation is almost zero in highly concentrated solutions, increasing with dilution, up to a limit of about 45%. The limiting value depends on the viscosity of the solute. The dyes used were eosin and uranin. S. B.

**Line Fluorescence in certain Fluorspar Crystals and Especially Ultra-violet Fluorescence Rays.** W. DE GROOT (*Arch. Néerland.*, 1924, [iii], **A**, **7**, 207—214).—Crystals of both violet and green fluorspar, when exposed to the light from the spark discharge between electrodes of cadmium, aluminium, and zinc, show fluorescence spectra which, in addition to a large number of broad bands, contain also lines. These have been photographed by means of the quartz spectrograph. The cadmium and zinc sparks give a triplet of narrow lines between 3800 and 3860 Å. This appears to correspond with a triplet attributed by Urbain to terbium. The violet crystals give in addition, with the cadmium spark, two rays between 3400 and 3450 Å., and sometimes, after a long exposure, a faint third line. With aluminium and also with zinc, four lines appear between 3150 and 3470 Å. These correspond approximately with certain lines in the spark spectrum of gadolinium.

By projecting the spark spectrum on the fluorspar crystal an attempt has been made to determine which are the exciting rays. The triplet in the fluorescence spectrum of the green fluorspar is only excited by wave-lengths less than 2300 Å., whilst the vivid blue fluorescence is excited at the same time, and also by 3400—3800 Å. It has not been found possible to make similar observations with the violet crystals. Attempts have been made to study the absorption of ultra-violet light by fluorspar, but, in the presence of the large general absorption, no feeble selective absorption can be observed.

The theory has been put forward that the appearance of the line fluorescence may be a secondary phenomenon due to the excitation of the spectra of the rare earths, present as impurities, by the electrons given off in the photoelectric effect accompanying the true fluorescence. M. S. B.

**Photo-luminescence of Solid Solutions.** M. CURIE (*J. Phys. Radium*, 1924, **5**, 65—83).—Various effects characterising the phenomenon of photo-luminescence are briefly referred to, and

chemical and electronic theories of the phenomenon critically reviewed. The electronic theory of Lenard and Saeland (A., 1909, ii, 283) is considered to be the most satisfactory.

J. S. G. T.

[Tyndall Effect and Coloration of] Smoky Quartz.—(See ii, 406.)

**Excitation of the Hydrogen Spectrum by Electronic Impact.**

R. SEELIGER and M. WENDT (*Physikal. Z.*, 1924, 25, 160—162).—The spectrum of glowing hydrogen excited by a stream of electrons of constant velocity has been photographed and measurements have been made of the relative intensities of the lines  $H_\beta$  and  $H_\gamma$  of the Balmer series and  $\lambda 4634$  of the secondary spectrum. The ratio  $H_\gamma/\lambda 4634$  varies over a much larger range than the ratio  $H_\beta/H_\gamma$ , showing that the relative intensity of the Balmer and secondary spectra is influenced by other factors besides the velocity of the electrons, such as the catalytic influence of the walls of the vessel and of impurities on the relative proportions of atoms and molecules as postulated by Wood (A., 1922, ii, 673, 759). S. S.

**Normal Cathode Fall.** A. GÜNTHER-SCHULZE (*Z. Physik*, 1924, 24, 52—55; cf. *ibid.*, 1923, 20, 1).—Between the normal cathode fall in a vacuum tube,  $V_n$ , and the energy required to eject an electron from the electrode,  $\phi$ , the relation  $V_n = C\phi$  holds good, where  $C$  is a constant characteristic of the gas in the tube. Figures are quoted for the inert gases, hydrogen, etc., with electrodes of many different metals among which the value of  $V_n$  varies considerably. S. B.

**Emission of Positive Ions from Hot Tungsten.** W. A. JENKINS (*Phil. Mag.*, 1924, [vi], 47, 1025—1047).—Tungsten at temperatures approaching the melting point emits positively charged ions. The positive ions are not due to the presence of residual traces of gas; they only appear at temperatures above  $2500^\circ$ , and they are very heavy or very slow-moving particles, little affected by a magnetic field of 400 gauss, and probably consist of charged atoms or molecules of tungsten. The positive emission is much smaller than the electron emission at the same temperature and, like the electron emission, increases rapidly as the temperature is raised. At the highest temperatures the positive emission decreases rapidly with time. A tungsten spiral which has been made to give a large electron emission gives a larger initial positive emission when the potential in the tube is reversed. S. S.

**Photoelectric and Photochemical Activity.** O. W. RICHARDSON (*Phil. Mag.*, 1924, [vi], 47, 975—976).—A mathematical paper pointing out the connexion between the equations of Kramers (*ibid.*, 1923, [vi], 46, 836) and Milne (*ibid.*, 1924, [vi], 47, 209), and the formulæ developed by the author (*ibid.*, 1912, [vi], 23, 571). S. S.

**Variation in Photoelectric Activity with Wave-length for Metals in Air.** T. H. OSGOOD (*Proc. Roy. Soc. Edin.*, 1924, **44**, 8—13).—When employing the photoelectric effect as an indication of the physiological activity of radiation, a freshly-polished metal target should not be used, owing to fatigue phenomena, which have been compared for various metals. The activity of iron in the steady state is only 0.23% of that of the freshly-polished metal. Silver maintains 90% of its activity. S. B.

**Variation with Temperature of the Photoelectric Effect in Potassium Photoelectric Cells.** H. E. IVES (*J. Opt. Soc. Amer.*, 1924, **8**, 551—580).—The photoelectric effect from potassium in highly exhausted cells is found to diminish when the emitting surface is cooled with liquid air. The variation of the effect above 0° is negligible, but the current for yellow light at -180° is only 45% of that at room temperature. Sodium cells also show the effect.

It is suggested in explanation of these variations that the work function of the surface alters with temperature. This view is supported by the diminution of the long wave-length excitation limit as the temperature of the surface is lowered. S. B.

**Electron Emission from Magnetised and Unmagnetised Iron.** G. A. CARSE and D. JACK (*Proc. Roy. Soc. Edin.*, 1923, **43**, 226—229).—No difference could be detected between the electron emissions from magnetised and unmagnetised iron, excited by X-rays. S. B.

**Anhyseretic Properties of Iron and Nickel and the Energy Change at the Critical Temperature.** J. R. ASHWORTH (*Phil. Mag.*, 1924, [vi], **47**, 848—859).—From measurements of the magnetisation of iron and nickel wires cooling from above the critical temperatures of 1058° Abs. and 661° Abs., respectively, the anhyseretic isothermals for a range of temperatures have been determined. When hysteresis is suppressed, the relation between the applied force  $H$  and the intensity of magnetisation  $I$  is given by  $H(1/I - 1/I_0) = R_1 T$ .  $I_0$  is the maximum intensity of magnetisation,  $R_1$  is termed the ferromagnetic constant, and  $T$  is the absolute temperature. For iron  $I_0 = 1817$ ,  $R_1 = 0.6 \times 10^{-6}$ , and for nickel  $I_0 = 552$ ,  $R_1 = 3.2 \times 10^{-6}$ . Above the critical temperature, an equation of the same form holds for the paramagnetic constant  $R'$  (the reciprocal of the Curie constant). For iron,  $R' = 3.6$ , and for nickel, 20.8. When hysteresis is present,  $H$  in the above equation becomes  $(H + aI^2)$ , the intrinsic field  $aI^2$  being regarded as twofold in nature;  $a$  is the sum of two constants,  $a'$ , the intrinsic field constant which has the values, iron, 7.0, nickel, 83.7, and  $a_1$ , the ferromagnetic field constant which for iron is  $1.2 \times 10^{-6}$  and for nickel  $13.3 \times 10^{-6}$ . The theory of corresponding states holds for the magnetisation of iron and nickel at the reduced temperatures 0.42 and 0.92. When iron or nickel passes through the critical temperature, there is a change of kinetic energy per unit of temperature equivalent to that of 2 degrees of freedom, the molecular weight of iron being

55.85 and that of nickel  $2 \times 58.68$  above the critical temperature. This change of energy is found to be simply connected with the discontinuity of the true specific heat at the critical temperature.

S. S.

**The Atomic Electrical Conductivity of Metals.** F. SIMON (*Z. physikal. Chem.*, 1924, **109**, 136—142).—The author has compared the atomic electrical conductivities of the metals at corresponding temperatures. The atomic conductivity  $\lambda$  is measured by  $\kappa V^{\frac{1}{3}}$ , where  $\kappa$  is the specific conductivity and  $V$  the atomic volume. Accepting Grüneisen's formula (A., 1913, ii, 377; 1918, ii, 287) for the specific conductivity  $\kappa = C/TF(\beta\nu/T)$ , where  $F$  is Debye's atomic heat function,  $C$  and  $\beta$  are constants,  $\nu$  is the atomic frequency, and  $T$  the absolute temperature, corresponding temperatures are regarded as those for which  $\beta\nu/T$  is a constant, and the particular temperature adopted for purposes of comparison is such that  $\beta\nu = T$ . The variations in atomic conductivity, from metal to metal of the periodic table, are in accordance with Bohr's views on electronic structure.

The relationship of conductivity to the direction of vibration of the atom is discussed in reference to the conductivity in the direction of the various crystallographic axes.

M. S. B.

**Measurements of the Electrical Resistance of Indium in the Range of Temperature of Liquid Helium.** W. TUYN and H. KAMERLINGH ONNES (*Arch. Néerland.*, 1924, [iii], A, **7**, 289—294; cf. this vol., ii, 12).—The temperature at which the electrical resistance of four different samples of indium disappears has been found to be approximately  $3.40$ — $3.41^\circ$  (abs.).

M. S. B.

**Recent Results obtained with the Mass Spectrograph.** F. W. ASTON (*Nature*, 1924, **113**, 856—857).—An isotope of iron at 54 is confirmed, with intensity 0.05 of that at 56; thus the calculated atomic weight is in agreement with that determined chemically. Strontium consists almost entirely of atoms of mass-number 88, but a very faint constituent at 86 has been discovered, and  $\text{Sr}^{88}$  is shown to be more nearly  $\text{Sr}^{87.8}$ . The strongest line of barium, at 138, has been identified with a most probable mass of 137.8. Lanthanum is a simple element (139); praseodymium is also simple (141). Neodymium gives an indistinct band at 142 to 150, suggesting several isotopes not differing greatly in relative proportion. Erbium shows a similar faint effect from 164 to 176. Experiments with zirconium, niobium, and molybdenum have been completely unsuccessful.

A. A. E.

**Complexity of the Elements. I. Elements of Odd Atomic Number.** A. S. RUSSELL (*Phil. Mag.*, 1924, [vi], **47**, 1121—1140).—An extension of previous work (A., 1923, ii, 719, 748, 861), of which the present paper is a more detailed account, with reference to elements of odd atomic number. A table of atomic weights, with calculated and experimental mass numbers, is given for these elements.

A. E. M.

**Isotope Effect in Line and Band Spectra.** R. S. MULLIKEN (*Nature*, 1924, **113**, 820; cf. this vol., ii, 294, 295, and Nagaoka and others, this vol., ii, 295, 381).—Polemical. The theoretical foundations of Nagaoka's results are considered to be questionable; they are not shared by the theory of the isotope effect in band spectra. A. A. E.

**Isotopes of Mercury and Bismuth and the Satellites of their Spectral Lines.** G. RUNGE (*Nature*, 1924, **113**, 781).—A criticism of Nagaoka, Sugiura, and Mishima's statement (this vol., ii, 381) regarding the connexion between the satellites of Hg 2536 and Bi 4722 and the isotopes of mercury and bismuth; the coincidences described can be ascribed to chance. A. A. E.

**Cosmic Origin of the Radioactive Substances in the Atmosphere.** H. BONGARDS (*Astrophys. J.*, 1923, **58**, 307—313).—Previous observations of the emanation content of the atmosphere at Lindenberg are compared with those obtained by Wright and Smith at Manila; the curves change together, although the results were obtained by entirely different methods. It is concluded that the atmospheric emanation cannot originate from the earth's surface. Solar origin is suggested. A. A. E.

**Relation between Uranium and Radium. VIII. The Period of Ionium and the Ionium–Thorium Ratio in Colorado Carnotite and Joachimsthal Pitchblende.** F. SODDY and A. F. R. HITCHINS (*Phil. Mag.*, 1924, [vi], **47**, 1148—1158).—Redetermination of the average-life period of ionium from the rate of growth of radium in uranium preparations gives a mean value of  $1.08 \times 10^5$  years, which is 8% higher than the previous result of Soddy (A., 1919, ii, 443). The adoption of the value  $1.1 \times 10^5$  years is suggested for the present. Assuming this period, an exact method for the determination of ionium, applicable to very active preparations, is described. Examination by this method of the ionium–thorium mixture obtained from Colorado carnotite gave an ionium–thorium ratio of 1 : 23. Radium from this source should have as a maximum 3 parts per 2000 of the  $\gamma$ -radiation contributed by mesothorium and radiothorium. Examination of two specimens of ionium–thorium separated from different products from Joachimsthal pitchblende showed an ionium–thorium ratio of 1 : 0.9. This result is in agreement with that of Meyer and Ulrich (*Sitzungsber. Akad. Wiss. Wien*, 1923, **132**, 279) and in disagreement with an earlier result of Meyer, Ulrich, and von Welsbach, who found the ratio 3 : 7. It is suggested that this earlier preparation was contaminated through being worked up in a thorium factory. A. E. M.

**Differentiation of Radium, Mesothorium, and Radiothorium by  $\gamma$ -Rays.** W. BOTHE (*Z. Physik*, 1924, **24**, 10—19).—A  $\gamma$ -ray electrometer is described, in which a varying thickness of lead can be introduced between the source and the ionisation chamber. Radium, mesothorium, and radiothorium each give a



distinctive curve when the ionisation produced by the source is plotted against the thickness of the lead screen. S. B.

**Radioactive Constant of Radium Emanation.** (MLLES.) I. CURIE and C. CHAMIE (*Compt. rend.*, 1924, **178**, 1808—1810).—The radioactive constant for radium emanation has been found, by an entirely new method, to be 3.823 days ( $\pm 0.002$ ). This is compared with the earlier values of Mme. Curie and Rutherford, 3.85 days, and the recent determination by Bothe and Leechner, 3.810 days. G. M. B.

**Magnetic Spectrum of  $\beta$ -Rays of Mesothorium-2.** D. YOVANOVITCH and J. D'ESPINE (*Compt. rend.*, 1924, **178**, 1811—1813).—The experiments of von Baeyer, Hahn, and Mlle. Meitner (A., 1912, ii, 409) have been repeated with a narrower and more sharply-defined beam of  $\beta$ -rays. Strong lines are recorded at the following values of velocity relative to that of light: 0.368, 0.383, 0.427, 0.504, 0.571, 0.706, 0.765, 0.807, 0.931, 0.968. A well-defined continuous band extends from 0.657 to 0.968 in place of the badly-defined band described by the earlier workers. Among the feeble lines found are several corresponding with velocities of more than 0.995 times that of light, but these require further confirmation. The origin of the slower-moving  $\beta$ -rays is indicated. G. M. B.

**Number of  $\gamma$ -Rays emitted per Second from Radium-*B* and -*C* in Equilibrium with 1 g. of Radium, and the Number Emitted per Atom Disintegrating.** A. F. KOVARIK (*Physical Rev.*, 1924, **23**, 559—574).—In view of the discordance of previous results (*Proc. Nat. Acad. Sci.*, 1920, **6**, 105; Hess and Lawson, *Sitzungsber. Akad. Wiss. Wien*, 1916, **125**, 585; Moseley, A., 1912, ii, 1024), all the constants used in the calculations were re-determined with the exception of the coefficient of absorption in air. The total number of emissions which would have been produced if all the  $\gamma$ -rays from radium-*B* and radium-*C* had been absorbed in aluminium, copper, tin, platinum, or lead was found to be  $7.28 \times 10^{10}$  ( $\pm 3\%$ ) per g. of radium per second. Each radioactive transformation results in the emission of one  $\gamma$ -ray entity which produces a  $\beta$ -ray emission from a single atom. Values of the coefficient of absorption of  $\gamma$ -rays from radium-*B* and -*C*, and for secondary  $\beta$ -rays, determined from counts, are tabulated. A. A. E.

**Absence of Helium from the Gases left after the Passage of Electrical Discharges.**—(See ii, 407.)

**Electronic Theory of Valency. IV. Origin of Acidity.** T. M. LOWRY (*Phil. Mag.*, 1924, [vi], **47**, 1021—1024).—An acid is defined as a hydride from which a proton can be detached. The change in acidity on passing along a period of Mendeléev's table from methane to hydrofluoric acid etc. is explained by a progressive diminution in the size of the orbits of the shared electrons which link the protons to the central nucleus. Acylous groups such as chlorine may tend to diminish the size of the orbits, whilst basylous groups should have the converse effect. The transmission of

acidity along a chain of carbon atoms is explained by assuming that the contraction of the orbits is transmitted to electrons of the same quantum number in adjacent atoms. S. S.

**Chemical Affinity and Electron Affinity.** R. H. GERKE (*J. Amer. Chem. Soc.*, 1924, **46**, 953—958).—The energies of formation of the gaseous hydrogen halides from gaseous atoms are approximately equal to the electron affinities of the halogen atoms concerned (*i.e.*, to the energy given out when a halogen atom combines with an electron to produce a halide ion). Thus the tendency of the electro-negative atom to share the electron of the hydrogen atom is measured by the electron affinity of the former. This conclusion is confirmed by the fact that the ionisation potentials of the hydrogen halides are approximately equal to the ionisation potential of the hydrogen atom, indicating that the energy necessary to remove a hydrogen nucleus from an electron in a hydrogen atom is equal to that necessary to remove the hydrogen nucleus from its shared electron in the halide molecule. The energies of formation of the halides of the metals show a general agreement with their electron affinities, but in some cases deviations exist which are regarded as due to a distortion of the valence octets of electrons.

W. H.-R.

**Relation of Affinity and Valency and the Constitution of Intermetallic Compounds.** W. BILTZ.—(See ii, 482.)

**Calculations of the Potential Energy for some Atomic Models.** I. WOODWARD (*Phil. Mag.*, 1924, [vi], **47**, 992—1016).—The potential energy of a number of atomic models has been calculated on the basis of the theory of J. J. Thomson (*A.*, 1921, ii, 252). The results for atoms containing one to eight outer electrons (lithium to neon) differ slightly from the values quoted by Thomson, since allowance has now been made in the cases of nitrogen and fluorine for the distortion of the inner layer of electrons by the outer zone. The most stable model for an atom with twelve electrons contains an inner ring of eight electrons arranged at the corners of a cube and at a distance from the atom of  $1.258c$ , and an outer ring of four occupying the corners of a tetrahedron two edges of which are parallel to two edges of the cube and at a distance from the centre of the atom of  $3.973c$ . The distortion of the inner layer by the outer electrons is neglected. For an atom with 22 electrons the arrangements (8.8.6) and (8.12.2) are almost equally stable and are more probable than a possible structure in which the two inner layers of the latter arrangement degenerate into one layer. Preliminary calculations are given for an atom with 27 electrons. An empirical relation is found to hold approximately between the potential energy of the most stable form and the number of electrons, namely, that  $V/n(n+2)=\text{constant}$ , where  $V$  is the potential energy and  $n$  the number of electrons. S. S.

**X-Ray Diffraction Patterns from Crystalline and Liquid Benzene.** E. D. EASTMAN (*J. Amer. Chem. Soc.*, 1924, **46**, 917—923).—Measurements of the planar spacings in crystalline benzene

at  $-20^{\circ}$  have been made by a modification of the method of Hull (*Physical Rev.*, 1917, **10**, 661; 1921, **17**, 571), using filtered radiation from molybdenum. The results are in good agreement with those obtained by another experimental method by Broomé (*Physikal. Z.*, 1923, **24**, 124). Subject to certain assumptions regarding the interpretation of the X-ray spectra, the axial ratios of the unit rhombic cell have been provisionally determined as 0.775 : 1 : 0.725, with a minimum of 4 molecules to the unit cell, but further studies are necessary before the character of the unit cell can be conclusively established. Experiments have also been made with liquid benzene, and an interference maximum has been found at  $4.83$ , and this with others obtained by Debye and Scherrer (*Nachr. Kgl. Ges. Wiss. Göttingen*, 1916) correspond in position with lines given by the crystals. This correspondence may be due either to the presence of crystal nuclei in the liquid, or to scattering centres having a regular spacing within the molecules.

W. H.-R.

**Space Lattice of Triphenylmethane.** K. BECKER (*Z. Physik*, 1924, **24**, 65—68).—The results of a previous investigation (*ibid.*, 1923, **14**, 369) are upheld against criticism from Mark and Weissenberg (*ibid.*, 1923, **17**, 347). It is concluded, however, that the dimensions of the lattice previously given are all too small, and that the crystal unit contains 4 and not 3 molecules.

S. B.

**Space Lattice of Triphenylmethane.** H. MARK and K. WEISSENBERG (*Z. Physik*, 1924, **24**, 68).—The modification of Becker's views announced in the previous abstract removes the essential discrepancy between his conclusions and those of the authors.

S. B.

**X-Ray Spectra of Amalgams.** C. v. SIMSON (*Z. Physikal. Chem.*, 1924, **109**, 183—198).—The X-ray spectra of amalgams have been examined by the powder method. In tin, zinc, and cadmium amalgams, hexagonal lattices were found differing from those of the pure metals. Crystals of lead amalgam containing 20% of mercury have the same face-centred lattice as pure lead, contracted in dimensions by 1.6%.

S. B.

**Metastability of Elements and Compounds as a Consequence of Enantiotropy and Monotropy.** IV. E. COHEN and J. KOOP (*Z. physikal. Chem.*, 1924, **109**, 81—96; cf. A., 1920, ii, 611, 622, 625).—The physical constants of substances existing in several different modifications are sometimes erroneous in consequence of the fact that such substances consist of mixtures of two or more forms. For this reason the transition point of ammonium nitrate (III—IV) and the accompanying change in specific volume have been redetermined. The transition point, observed dilatometrically, is  $32.3^{\circ}$ ; this is in close agreement with the value,  $32.1^{\circ}$ , found by Early and Lowry (*T.*, 1919, **115**, 1387).

For the change in specific volume, two different methods gave 0.0220 c.c./g. and 0.0221 c.c./g., respectively, the latter being regarded as more trustworthy. This is in agreement with the

value found by Behn (*Proc. Roy. Soc.*, 1908, **A**, **80**, 444), 0.022 at 32°, but differs by as much as 9% from Bridgman's determinations (*Proc. Amer. Acad. Arts and Sci.*, 1916, **51**, 581). This divergency is attributed to incomplete transformation in the latter case. M. S. B.

**Metastability of Elements and Compounds as a Consequence of Enantiotropy and Monotropy. V.** E. COHEN and A. L. T. MOESVELD (*Z. physikal. Chem.*, 1924, **109**, 97—99; cf. preceding abstract and also Wyckoff, A., 1923, ii, 300).—The authors illustrate the danger of mistaking a metastable mixture of polymorphs for a pure modification by reference to the X-ray examination of the crystal structure of silver iodide, which has been described both as cubic (cf. Wilsey, A., 1921, ii, 548; Davey, *Physical Rev.*, 1922, **19**, 248) and hexagonal (Aminoff, *Geol. För. Förh.*, 1922, **44**, 444). M. S. B.

**Metastability of Elements and Compounds as a Consequence of Enantiotropy and Monotropy. VI.** E. COHEN, W. D. HELDERMAN, and A. L. T. MOESVELD (*Z. physikal. Chem.*, 1924, **109**, 100—108; cf. preceding abstracts).—The variations in the values obtained for the heats of solution of certain salts are due to the fact that the substances used are mixtures of two or more polymorphic forms which have different heats of solution. As an illustration, the authors have determined the heats of solution of  $\alpha$ - and  $\beta$ -cadmium iodide, as well as mixtures of the two. The molecular heat of solution of the stable  $\alpha$ -modification at 18.2° is -976 g.-cals., and of the meta-stable  $\beta$ -form, -927 g.-cals., the difference representing the heat evolved when the  $\beta$ -iodide is transformed into the  $\alpha$ -form. A mixture gives a heat of solution lying between these two values. M. S. B.

**Metastability of Elements and Compounds as a Consequence of Enantiotropy and Monotropy. VII.** E. COHEN (*Z. physikal. Chem.*, 1924, **109**, 109—110).—A historical note on some early observations of Deville indicating the slowness with which unstable monoclinic sulphur changes into the stable rhombic form at low temperatures. M. S. B.

**Conditions of Stability of Thermodynamical Equilibrium and an Accurate Formulation of the Le Chatelier-Braune Principle. V.** R. BURSIAK (*J. Russ. Phys. Chem. Soc.*, 1918, **49**, 87—100).—A mathematical paper in which a proof is given of an unproved statement of P. S. Erenfest, namely, inequality (19)  $[p_{hh} \cdot p_{kk} - (p_{hk})^2] \leq [p_{hh} \cdot p_{kk}]$  (*J. Russ. Phys. Chem. Soc.* 1909, **41**, 347), from which follows an accurate formulation of the above-mentioned principle. P. S.

**Specific Heats of certain Organic Liquids at Elevated Temperatures.** J. W. WILLIAMS and F. DANIELS (*J. Amer. Chem. Soc.*, 1924, **46**, 903—917).—The specific heats of benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, isopropyl alcohol, ethyl alcohol, isoamyl alcohol, *n*-butyl alcohol, nitrobenzene,

chloroform, carbon tetrachloride, and heptane have been determined over small temperature intervals from 30° to nearly 80°, by a modification of the adiabatic calorimeter method of Richards (A., 1910, ii, 19). The results are expressed graphically and in the form of empirical equations, and physical constants related to the specific heats have been calculated. The majority of the liquids have specific heats which increase as straight line functions of the temperature, but, in the case of the alcohols and benzene, the gradient of the curves ( $dC_p/dT$ ) becomes greater as the temperature rises. In unassociated liquids, the product of specific heat and density is approximately constant, and equals about 0.35 cal. per c.c.; conversely if the product is greater than about 0.4 cal. per c.c., the presence of associated molecules may be inferred. Slight irregularities in the curves in the cases of ethylbenzene and carbon tetrachloride are regarded as due to a change in equilibrium between different kinds of molecules. W. H.-R.

**Equation of State and Compressibility of Mercury.** K. K. JÄRVINEN (*Z. physikal. Chem.*, 1924, **109**, 275—286).—The value of the compressibility of mercury obtained from the author's equation of state (*ibid.*, 1921, **97**, 445) is in much closer agreement with the determinations of Oersted and of Jamin than with those of Regnault. The experimental methods are examined, and it is concluded that the large correction, required in the Regnault method, for the expansion of the piezometer tube is very uncertain. In the Oersted method, the pressure is applied both internally and externally to the tube, and the corresponding correction is smaller and more simple. By the reduction of previous observations of de Metz, the compressibilities of mercury and glass are given as  $1.19 \times 10^{-6}$  and  $0.62 \times 10^{-6}$  at 0°. S. B.

**Thermochemical Researches on Stereoisomeric Aldoximes** (see i, 645) and **Ketoximes** (see i, 646).

**Contraction of Evacuated Bulbs in the Determination of the Density of Gases.** E. MOLES and R. MIRAVALLS (*J. Chim. Physique*, 1924, **21**, 1—9).—The contraction of evacuated bulbs has been measured accurately: (1) by the simple hydrostatic method of Crafts (*Compt. rend.*, 1888, **106**, 662); (2) by the method of Rayleigh (*Proc. Roy. Soc.*, 1888, **43**, 362; 1892, **50**, 462); and (3) by the method of Travers ("Study of Gases," p. 119). The results obtained by all three methods are in good agreement, method (3) giving very slightly larger values for the contraction, in agreement with the fact that method (3) measures the external, and methods (1) and (2) measure the internal contraction. If  $V$  is the volume of the bulb,  $w$  its weight (excluding the weight of taps, valves, etc.), and  $x$  the compressibility of the bulb per litre under a pressure of one atmosphere, it is found that a general relation exists which may be written  $x = 15.5V/w \times 0.0012$ , where 0.0012 is the weight of 1 c.c. of air under the conditions of experiment, and 15.5 is a constant practically independent of the size of the bulb, the thickness of its walls, and the particular glass of which it is constructed. W. H.-R.

**Standard Density of Nitrogen.** E. MOLES and J. M. CLAVERA (*J. Chim. physique*, 1924, **21**, 10—14; cf. Moles, *ibid.*, 1921, **19**, 283).—The author's previous work on the density of nitrogen, prepared by the ignition of sodium azide, has been continued with greater accuracy. The weight of 1 litre of nitrogen at 0° and 760 mm. is determined as 1.25042 g. The mean value deduced from the observations of Rayleigh, de Leduc, Gray, and of Moles and Clavera, is 1.25051 at 0°, 760 mm., and at latitude 45°. Under standard conditions of 0°, 760 mm., and  $g=980.665$ , the mean value becomes 1.25056. The corresponding atomic weight of nitrogen is 14.008.

W. H.-R.

**Density of Liquids and Temperature.** J. J. SASLAWSKY (*Z. physikal. Chem.*, 1924, **109**, 111—135).—The equation  $\delta_t = \delta_k(1 + 2.73\sqrt{T/T_0})$  represents the relationship between density and temperature for liquids, through the whole temperature-range of their existence, where  $\delta_t$  is the density at the temperature of observation  $t$ ,  $\delta_k$  the critical density,  $T_0=1.05T_k(\text{abs.})$ , and  $T$  is the difference between  $T_0$  and  $t(\text{abs.})$ . This formula may be used to calculate the critical density, and, when applied to a very large number of different liquids of all types, gives values which do not, in general, differ by more than about 2%, and often less, from the experimental value.

M. S. B.

**Density of Liquid and Solid Bodies.** A. DAMIENS (*Bull. Soc. chim.*, 1924, [iv], **35**, 455—463).—The volume occupied by a known weight of the substance is determined by making use of a flask with a graduated neck.

A. B. H.

**Densities and Specific Volumes of Sodium Chloride Solutions.**—(See ii, 408.)

**Compressibility of Chlorides, Bromides, and Iodides of Lithium, Rubidium, and Cæsium.**—(See ii, 408.)

**Compressibility and Pressure Coefficient of Rhodium and Iridium.**—(See ii, 415.)

**Theory of Solutions.** A. F. CORE (*Phil. Mag.*, 1924, [vi], **47**, 977—991).—A reply to Cavenagh (*ibid.*, 1922, [vi], **45**, 606). The "gas method" of discussing the problem of solutions is shown to be valid within certain limiting conditions. The theoretical treatment of solutions in terms of fugacities or activities of the components is preferred to the method advocated by Cavenagh since fugacities can be deduced readily from experimental data. Cavenagh's proposed method of determining the degree of association of a solvent from a study of the colligative properties of solutions is considered to be invalid.

S. S.

**Variation with Temperature of the Atomic Condensation [Molecular Complexity] of Antimony, Gold, and Silver.** A. JOUNIAUX (*Bull. Soc. chim.*, 1924, [iv], **35**, 463—473).—By combining the Dupré vapour-pressure formula with the Clausius-Clapeyron equation, a relation is obtained which permits of the

calculation of the heat of vaporisation. Comparison with the value derived from Trouton's rule at the same temperature shows antimony to be monatomic between the melting and boiling points. Ebullioscopic measurements with amalgams of antimony show that it is still monatomic at 357°, although cryoscopic and ebullioscopic measurements with solutions of antimony in iodine afford evidence of polymerisation at lower temperatures.

Similar calculations for gold and silver show that the former is monatomic below its melting point. In the liquid state, the molecular weight increases rapidly with temperature. Silver appears to be monatomic between 350° and 2000°. A. B. H.

**Liquefaction of Binary Gaseous Systems. Sulphur Dioxide-Ethane.** W. MUND and P. HERRENT (*J. Chim. physique*, 1924, **21**, 51—70).—Mixtures of sulphur dioxide and ethane containing 88.7, 73.6, and 40.4% of sulphur dioxide have been investigated at temperatures from 27—40°, 35—54°, and 35—99°, respectively. The total volume and the volume of liquid (if any) were measured in each case, and the  $p$ - $v$  curves determined at different temperatures, but the compositions of the gaseous and liquid phases were not determined when two phases were present. The results indicate that the value of  $dv/dp$  for the homogeneous liquid system is always numerically greater (smaller in absolute value owing to the negative sign) than that for the two-phase system. The results are in general agreement with the theory of Kuenen (*Z. Physikal Chem.*, 1902, **41**, 43). W. H.-R.

**Molecular Solution Volumes in Ethyl Alcohol.** G. J. BURROWS and F. EASTWOOD (*Proc. Roy. Soc. New South Wales*, 1923, **57**, 118—125).—For sixteen aromatic compounds the difference between the molecular solution volume in ethyl alcohol and the molecular volume of the molten substance is found to increase with increase in degree of association of the pure liquid substance. The co-volume of non-associated solutes in ethyl alcohol is 20 c.c.; a smaller co-volume than this indicates that the solute is associated in the liquid state. S. K. T.

**Volumes in the Neighbourhood of the Critical State of Miscibility.** N. PERRAKIS (*Compt. rend.*, 1924, **178**, 1482—1483).—The volume changes which occur in the mixing of benzene with methyl, ethyl, propyl, and *n*-butyl alcohols at 20° have been determined. The dependence of the volume change on the molecular composition of the mixtures is shown by a series of curves. A. B. H.

**Complexity of the Solid State.** A. SMITS (*Nature*, 1924, **113**, 855).—Partial distillation of carefully purified crystalline violet phosphorus gives a residue having a much lower, and a distillate having a much higher, vapour pressure than the original substance. The result is explained by the author's theory of allotropy; every crystalline state consists of mixed crystals, built up from molecules of different kinds which can undergo transformations leading to a chemical equilibrium. When this inner equilibrium is established,

a pure substance behaves as a single one, but if the equilibrium is established slowly (as in the case of violet phosphorus), or the transformations are stopped (*e.g.* by intensive drying), it behaves as a mixture. Dry sulphur trioxide behaves distinctly as a mixture; the vapour pressure of the solid can be changed continuously by evaporation (208 to 22 mm./0°), and liquids having different vapour pressures (200 and 172 mm./20°) are obtained. X-Ray analysis does not distinguish mixed crystals from their components, so that the inner equilibrium cannot yet be studied by this method.

A. A. E.

**Further Proof of the Theorem of Corresponding States.**

W. HERZ (*Z. anorg. Chem.*, 1924, **133**, 176—178).—The ratios  $v_{1/10}/v_{10}$  and  $v_{20}/v_{100}$ , where  $v_{1/10}$ ,  $v_{10}$ ,  $v_{20}$ , and  $v_{100}$  are the specific volumes at 0° corresponding with 0.1*p*, 10*p*, 20*p*, and 100*p*, *p* being the critical pressure, have been calculated for a large number of substances, each ratio being found approximately constant; the theorem thus holds for pressures from 0.1 to 100 times the critical pressure.

S. I. L.

**Internal Friction and Fusibility of Binary Systems.**

N. S. KURNAKOV [with D. KROTKOV, M. OKSMANN, N. BEKETOV, S. PERELMUTTER, F. KANOV, and J. FINKEL] (*Z. anorg. Chem.*, 1924, **135**, 81—117).—An account of work already abstracted from Russian sources (*A.*, 1915, ii, 524; 1917, ii, 360, 361).

S. I. L.

**Drying Agents, and Addition of Known Percentages of Water Vapour to Air.**

J. OBERMILLER (*Z. physikal. Chem.*, 1924, **109**, 145—164).—The simplest method of adding water vapour in any desired quantity to a current of air is to pass the air over a solid salt moistened to give a surface layer of saturated solution. The vapour pressure of such a system sometimes varies but slightly with temperature. The amount of water vapour so added to air has been determined for a series of salts and other substances. A hair hygrometer and also chemical methods were employed in the measurements. The substances employed are also discussed with reference to their use as drying agents. The highly hygroscopic character and chemical inertness of dried wool and other textiles suggest their use in the drying of gases.

S. B.

**Discontinuity of the Drying Process.**

E. A. FISHER (*Proc. Roy. Soc.*, 1924, **A**, **105**, 571—582).—Previous experiments on the rate of drying of fabrics (*ibid.*, 1923, **A**, **103**, 664) were repeated and the results confirmed. The entirely different results obtained by Davis and Eyre (*A.*, 1923, ii, 838) may be due to internal movements in the fabric, since unmilled fabrics do not give a smooth dehydration curve. (*Cf. B.*, 1924, 542.)

S. K. T.

**Diffusion in Solutions of Strong Electrolytes.**

I. D. GÖTZ and G. P. PAMFIL (*Z. physikal. Chem.*, 1924, **109**, 165—182).—The diffusion velocities of potassium permanganate, ferric chloride, and eosin-blue have been determined in solutions of various strong electrolytes. The change in the velocity of diffusion produced by



a strong electrolyte in solutions of varying concentrations is proportional to the equivalent conductivity. The authors conclude that the degree of hydration of the diffusing substances is not affected by the presence of strong electrolytes, and that the dissociation of the latter must be complete even at considerable concentrations. S. B.

**Diffusion Coefficients of Salts by Weber's Method.** F. HOELTZENBEIN (*Z. Physik*, 1924, **24**, 1—9).—Weber's method of determining diffusion coefficients from the gradual change of *E.M.F.* in a concentration cell gives untrustworthy results, owing to polarisation disturbances for which it has not been possible to devise a satisfactory correction. S. B.

**Dialysis.** Y. TERADA (*Z. physikal. Chem.*, 1924, **109**, 199—222).—The velocities of dialysis through parchment of thirty substances have been compared. In general, the velocity runs parallel with the diffusion coefficient. Exceptions are found particularly among substances with slow moving anions or cations. Increase in the hydrogen-ion concentration of the liquid increases the dialysing velocity of anions and diminishes that of cations. Both the dialysis and the diffusion velocities of strong acids and bases are increased by the addition of neutral salts. S. B.

**Viscosity of Aqueous Mixtures of Chromic Anhydride and Alkalis. Viscosity of Chromates and Sulphates in Relation to Isomorphism.** L. J. SIMON (*Compt. rend.*, 1924, **178**, 1606—1609).—The viscosities of the solutions obtained by mixing equimolecular solutions of chromic anhydride and of sodium or potassium hydroxide in varying proportions have been determined. Discontinuities occur in the viscosity curves when the composition of the solution corresponds with either the normal chromates or the bichromates, the precise form of the curves depending on whether the relative proportion of the two solutions is taken as the abscissa or the viscosities for solutions of equimolecular concentrations are compared. Except in high concentrations, the viscosities of equivalent solutions of sodium chromate and sodium sulphate, and of potassium chromate and potassium sulphate are identical, and the author concludes that within certain concentration limits isomorphous solutes produce the same change in the viscosity of the aqueous solvent. C. I.

**Theory of the Solubility Relations of Strong Electrolytes.** O. SCHÄRER (*Physikal. Z.*, 1924, **25**, 145—159).—Strong electrolytes are assumed to be completely dissociated and the increase or decrease of the solubility product in the presence of added salts is accounted for by the electrical forces between the charged ions. The mean cross-section of the ions has been calculated from available data on the variation of the solubility product and in general is of the correct order of magnitude ( $1-4 \times 10^{-8}$  cm.). The only marked discrepancy is afforded by the data for the solubility of thallous chloride in solutions containing alkali metal chlorides, thallous sulphate, or thallous nitrate, for which small negative values of the

mean ionic radius are indicated. The view that the ions have independent activity coefficients is shown to be a necessary consequence of the theory if the mean cross-section of the ions does not vary greatly. S. S.

**Action of Bicarbonate and Secondary Phosphate on the Dissociation of Calcium.** H. BEHRENDT (*Biochem. Z.*, 1924, **146**, 318—322).—The value of the solubility product  $[Ca^{++}][C_2O_4^{--}]$ —determined by the method of Brinkman and van Dam—is given as 0.056—0.057. In agreement with the findings of Rona and Takahashi (*A.*, 1913, i, 544),  $[Ca^{++}][HCO_3^-]/[H^+]$  is found to be 367.8. J. P.

**Determinations of Conductivity of Electrolytes by Methods other than that of Kohlrausch.** W. C. DE LIEFDE (*Chem. Weekblad*, 1924, **21**, 242—248).—Whilst Kohlrausch's method is most suitable for ordinary determinations, other methods are desirable where rapidity or special accuracy is required. For rapid work where accuracy is not vital, the alternating current galvanometer is recommended; for very accurate work, the method of Taylor and Acree (*A.*, 1917, ii, 7) has been found best, using the Vreeland oscillator or the Hall and Adams audion. The methods of obtaining the most accurate results with an alternating current circuit are discussed. The most suitable cell has usually to be selected for each electrolyte, and under good conditions an accuracy of 0.001% may be obtained. S. I. L.

**Electric Conductivity and Transition Points of Glasses.** H. SCHÖNBORN.—(See *B.*, 1924, 513.)

**Conductance of Electrolytes for Very High Frequencies.** J. GRANIER (*Compt. rend.*, 1924, **178**, 1520—1522).—The resistance of electrolytes has been measured for frequencies corresponding with wave-lengths of from 43,500 to 3.8 m. Difficulties were encountered with the surface effect at the electrodes, but these were overcome by means of a specially constructed cell with moulded carbon cylinders as electrodes, the electrolyte being contained in the annular space between them. Under these conditions, no appreciable variation in conductance was found, showing that the electrolytic resistance comes into play even for extremely small displacements of the ions. L. J. H.

**Theory of Anomalous Ionic Mobilities.** H. SCHMICK (*Z. Physik*, 1924, **24**, 56—64; cf. Born, *ibid.*, 1920, **1**, 221).—The maximum Born dipole effect has been calculated for different effective radii of electrolytic ions. Anomalies among ionic mobilities, such as the high mobility of caesium ions in comparison with that of lithium, are explained by the increase of the effective radius of the ionic charge which accompanies a diminution in the true ionic radius. S. B.

**Rôle of the Surface Layer in the Electrical Conductivity of Solid Salts.** P. VAILLANT (*J. Phys. Radium*, 1924, **5**, 84—91).—In continuation of previous work (*A.*, 1922, ii, 418), the author finds that hysteresis effects are exhibited by the electrical con-

ductivities of various pure salts, when the solid salt is taken at various rates through a temperature cycle having a range of about  $25^{\circ}$  at atmospheric temperature. The effect is attributed to the existence of an ionised surface layer of the salt, the ions in this layer being derived by a process of thermionic emission from the interior of the salt. Variations in the conductivity of the salts with the applied voltage are shown to be in agreement with this hypothesis.

J. S. G. T.

**Effect of an Electric Current on the Motion of Mercury Globules in Dilute Sulphuric Acid.** J. E. P. WAGSTAFF (*Phil. Mag.*, 1924, [vi], **47**, 802—815).—The velocity of small globules of mercury upwards against gravity in an inclined glass tube containing  $N/10$ -sulphuric acid is proportional to the potential gradient in the tube for a given size of drop and fixed inclination of the tube, and varies in a regular manner with the size of the drop and the inclination of the tube. It is shown that the electrical and gravitational effects balance when  $a^2 V_0 V / 27 \times 10^4 d = \frac{4}{3} \pi a^3 (\rho - \lambda) g \sin \theta$ , where  $a$  is the radius of the drop,  $V_0$  the potential between mercury and acid (taken to be 1.0 volt),  $V/l$  the potential gradient along the tube,  $d$  the thickness of the double layer,  $\rho$  and  $\lambda$  the densities of mercury and acid respectively,  $g$  the gravitational constant, and  $\theta$  the angle at which the tube is inclined to the horizontal. For a drop of radius 0.1072 cm.,  $d = 1.01 \times 10^{-8}$  cm. For a given inclination of the tube the equilibrium potential gradient is independent of the size of the drop, whence it follows that  $ad/V_0$  is constant  $= 1.089 \times 10^{-9}$ . This indicates that the charge on a drop is proportional to the cube of its radius, and it is calculated that a drop of 1 mm. radius has one mercury ion to every twenty-two mercury atoms in the surface layer. The thickness of the double layer should vary inversely as the radius of the drop, but below a critical radius of 40  $\mu\mu$  the double layer is absent. The theory of the Lippmann capillary electrometer is discussed.

S. S.

**Significance of the Electrode Potential.** J. HEYROVSKY (*Chem. News*, 1924, **128**, 357).—A reply to a criticism of a previous paper (A., 1923, i, 114) by Butler (*Proc. Roy. Soc.*, 1923, **A**, **104**, 667). It is claimed that all the stages in the author's cyclic process are reversible and that the sum of the electrode potentials is not equal to zero.

G. S.

**Hydrogen Overvoltage of Metals and their Characteristic Properties. I. Overvoltage and Valency.** E. J. WEEKS (*Chem. News*, 1924, **128**, 359).—Newbery's suggestion (T., 1916, **109**, 1107) that the overvoltage is a function of the valency is discussed, and it is claimed that available data do not support any such hypothesis. A table is given of the overvoltages of the various metals. There is a general decrease of overvoltage with valency but no simple connexion between the two.

G. S.

**Contact Difference of Potentials between Metals in a Vacuum.** R. VIEWEG (*Ann. Physik*, 1924, [iv], **74**, 146—170).—The contact differences of potential between brass and the metals

aluminium, nickel, copper, gold, and platinum have been measured. The metals, contained in a vessel in which the pressure could be reduced from atmospheric to less than  $10^{-4}$  mm., could be heated electrically to a high temperature. Reduction of pressure in the chamber produced little effect on the value of the contact difference of potential. When heated for a short while to a red heat, all the metals investigated became considerably more electropositive relative to brass. Further continued heating at the same or higher temperatures produced very little further alteration in the value of the contact difference of potential. The values obtained before and after heating were: Nickel, +0.16, +0.47; copper, -0.04, +0.44; platinum, -0.32, -0.23; gold, -0.23, +0.02; aluminium, +0.29, +0.87 volt. The results indicate that whilst the contact difference of potential between metals is largely determined by the nature of the superficial layers of the respective metals, the whole of the effect is not attributable to this origin. The observations afford no evidence of any effect due to occluded gases. J. S. G. T.

**Measurement of Decomposition Potentials.** A. L. FERGUSON and G. VAN ZYL (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 337—352).—In view of the controversy as to the relative merits of the commutator and direct methods of measuring decomposition potentials and overvoltages, an arrangement is described which allows of measurements being made by both methods at the same time and under identical conditions. The direct method gives higher values than the commutator method, the differences becoming greater the smaller the electrodes and the higher the applied potential. The potentials obtained by the commutator method are always higher on charge than on discharge, this difference becoming greater the smaller the electrode and the higher the current. All measurements made by the commutator method are averages, and depend largely on the operation and mechanical construction of the apparatus. It is concluded that the commutator method can probably never give values for charge potentials which are the same as those obtained by the direct method, and that the values for charge potentials in the latter case cannot be used, as has been done by previous workers, in connexion with discharge values obtained by the commutator method. W. T. K. B.

**Palladium Electrodes.** J. C. ANDREWS (*J. Biol. Chem.*, 1924, **59**, 479—494).—Palladium electrodes for hydrogen-ion determinations are much less trustworthy than platinum electrodes, because the amorphous palladium undergoes a more or less rapid change to crystalline palladium. The change is positively catalysed by high hydrogen-ion concentrations, the mechanism being probably an electronic exchange facilitated by the higher solution tension of amorphous palladium, and therefore palladium electrodes give erratic results with solutions of high  $p_H$ . D. R. N.

**Silver Chloride Battery for Potential Purposes.** H. A. ERIKSON (*J. Opt. Soc. Amer.*, 1924, **8**, 549—550).—A description is given of a low-current battery, generating about 100 volts, for use

with electrometers. One electrode of each cell is a zinc rod, the other a silver wire coated with silver chloride. The liquid is a 5% solution of zinc chloride, acidified with hydrochloric acid. S. B.

**Electromotive Characteristics of Glasses.** H. SCHILLER (*Ann. Physik*, 1924, [iv], **74**, 105—135).—Observations on the electromotive behaviour of various samples of glass show that when the glass is subjected to a high potential gradient, a counter-electromotive force is set up which is of the same order of magnitude as that of the applied field. It would seem that the glass may behave either as a solid electrolyte or towards conducting solutions as a simple or mixed electrode as suggested by Horovitz (*Z. Physik*, 1923, **15**, 369). When the glasses are used as electrodes in concentration cells the observed *E.M.F.* agree with those calculated by the usual logarithmic formula. It follows that it is possible to assign to the glasses a solution pressure which is determined by the particular ion concerned in the electromotive action. J. S. G. T.

**Colloidal State.** G. ROSSI (*Gazzetta*, 1924, **54**, 227—247).—Results obtained with colloidal sulphur (cf. A., 1914, ii, 35; 1915, ii, 97, 152; 1922, ii, 485; this vol., ii, 330) lead to the conclusion that colloidal solutions are those in which dispersion of the substance is maintained by means of forces other than simple affinity of the solvent for the solute. When the solvent has little or no influence, the maintenance of the disperse condition being due to the action of electrical charges, the disperse systems are suspensoid colloidal solutions. In the case of emulsoid colloidal solutions, the solvent has an influence, although this alone may not be sufficient to maintain the dispersion. T. H. P.

**So-called Colloids of the First Order.** P. P. DE WEIMARN (*Bull. Soc. chim.*, 1924, [iv], **35**, 530—531).—A claim for recognition of previous work. S. K. T.

**Distribution of Colloidal Particles.** E. F. BURTON and J. E. CURRIE (*Phil. Mag.*, 1924, [vi], **47**, 721—724).—A continuation of the previous work of Burton and Bishop (*Proc. Roy. Soc.*, 1922, **A**, **100**, 414). Colloidal solutions of gamboge, arsenious sulphide, copper, and silver, after standing in vertical tubes for a period of 4 months, with no abrupt temperature changes and in absence of light, have been shown to possess a uniform distribution of the particles throughout. It is suggested that this is due to the electrical charges carried by the particles. A. E. M.

**Forces Regulating the Size of Colloidal Particles.** E. F. BURTON (*Univ. Wisconsin Colloid Symposium Monograph*, 1923, 174—186).—A consideration of the slow rate of fall, of the forces coming into play in the formation of the nucleus, of the rôle of surface tension in causing the agglomeration, of small particles, and of the mutual action of colloidal particles due to their electrical charges. Results are given for the rate of fall of silver particles in water. There may be a lower limit to the size of surfaces to which surface-tension laws apply. It is assumed that the conglomeration

of sub-microscopic crystals is regulated chiefly by the fundamental surface-tension law, *i.e.*,  $T \times A$  tends to a minimum. Cessation of growth is apparently due to electrical charges which limit the concentration of suspensoid solutions and increase Brownian movement.

CHEMICAL ABSTRACTS.

**Preparation of Colloidal Gold for the Lange Test.** F. T. GREY (*Biochem. J.*, 1924, **18**, 448—450).—The colloidal gold is prepared by heating a solution of gold chloride with formaldehyde solution, care being taken that neutrality is maintained during the process.

S. S. Z.

**Absorption Spectrum of Gelatin as a Function of Hydrogen-ion Concentration.** H. P. HIGLEY and J. H. MATHEWS (*J. Amer. Chem. Soc.*, 1924, **46**, 852—855).—The effect of hydrogen-ion concentration on the absorption of light by gelatin sols has been investigated by a spectrophotometric method. The results are expressed in the form of curves, in which the  $p_H$  values are plotted against wave-lengths for definite fractions of light absorbed, the fractions being 0.75, 0.6, 0.4, and 0.0 (transparent). The curves are all of the same form and exhibit maxima of wave-lengths at  $p_H$  3.5 and 6.6, coinciding with the maxima found by Loeb ("Proteins and the Theory of Colloidal Behaviour") and by Wilson and Kern. Two very pronounced minima occur at  $p_H$  4.69 (the isoelectric point) and at 7.65 (a point of minimum swelling found by Wilson and Kern). A sharp shift of the absorption band towards the ultra-violet occurs as  $p_H$  4.69 and 7.65 are approached.

W. H.-R.

**Isoelectric Point of Gelatin at 40°.** D. I. HITCHCOCK (*J. Gen. Physiol.*, 1924, **6**, 457—462).—Experiments at 40° on the osmotic pressure, viscosity, and  $p_H$  of solutions of gelatin containing varying amounts of acid or of alkali give no support to the view that gelatin at 40° has any isoelectric point other than that at  $p_H$  4.7.

W. O. K.

**Ultimate Units in Protein Solutions and the Changes which Accompany the Process of Solution of Proteins.** J. LOEB and M. KUNITZ (*J. Gen. Physiol.*, 1924, **6**, 479—500).—Particles of casein suspended in trichloroacetic acid, sulphuric acid, or sulphosalicylic acid do not swell, and there is practically no increase in the viscosity of the suspensions. Solutions of albumin in dilute acid have a viscosity very little higher than that of water. On the other hand, particles of casein suspended in acids such as hydrochloric acid or orthophosphoric acid, in which they swell and ultimately dissolve, effect marked changes in the viscosity. Experiments on the viscosity of suspensions of two varieties of casein, a "more soluble" and a "less soluble" variety, support the view that the viscosity of the suspension is determined by the volume of the aggregates of protein particles which swell in accordance with the Donnan equilibrium. The changes in volume of the particles are parallel to the changes in viscosity. It is calculated on the basis of the measurements made that when 1 g. of isoelectric

casein is dissolved in hydrochloric acid so that the solution has a  $p_H$  of 2.45, more than one-half of the casein must be present in the form of particles too small to give rise to a Donnan equilibrium, whilst the rest is capable of undergoing swelling in acid solution.

W. O. K.

**Valency Rule and Hofmeister Series in Colloidal Behaviour of Proteins. III. Influence of Salts on Osmotic Pressure, Membrane Potentials, and Swelling of Sodium Gelatin.** M. KUNITZ (*J. Gen. Physiol.*, 1924, 6, 547—564).—The work of Loeb (A., 1921, i, 136, 367) has been extended by observations on solutions of sodium gelatin. The valency rules enunciated by Loeb are found to hold good. In the swelling of gelatin, the salt concentration must be below  $N/4$ , or anomalous results are obtained owing to the change in the solubility of the protein. C. R. H.

**Behaviour of Oil and of Oleic Acid towards Water.** J. F. CARRIÈRE (*Rec. trav. chim.*, 1924, 43, 283—296).—A surface layer of neutral oil (triolein) on water is completely displaced by oleic acid when the latter is dropped on to the surface, since the surface pressure of oleic acid is greater than that of the oil (cf. Marcelin, A., 1921, ii, 488; 1922, ii, 686). When a drop of oleic acid floats on water, an equilibrium is established in the sense that the surface tension of water saturated with oleic acid = surface tension of oleic acid + interfacial tension oleic acid/water. The first two factors being accurately known, the last is calculated to be 10.5 dynes per cm., instead of 15.0 as recorded in the literature. In the same way, the interfacial tension oil/water is calculated to be 26 dynes per cm. instead of 19.25. To explain the difference between the surface tensions of water surfaces saturated respectively with neutral oil and oleic acid, it is assumed, with Lewis and Harkins, that the saturated surface contains a single molecular layer of oil or acid, and that the surface tension is inversely proportional to the density of the molecular layer, or directly proportional to the square of the mean distance between the molecules in the layer. Owing to the greater freedom of the molecules of the free fatty acid, these may be supposed to attain a denser distribution in the surface than the less mobile molecules of the triglyceride. From the known surface tensions of the saturated water surfaces, the relative inter-molecular distances are calculated. It is also possible, making use of data given by Pockels (*Naturwiss.*, 1917, 5, 137, 149) to calculate the absolute "molecular field" for both oil and oleic acid. The theory holds only for saturated surfaces.

E. H. R.

**Behaviour of Aqueous and Ethyl-alcoholic Solutions of Mercuric Chloride towards Different Adsorbents.** M. A. RAKUZIN and A. N. NESMEJANOV (*Münch. med. Woch.*, 1923, 70, 1409—1410; from *Chem. Zentr.*, 1924, i, 687).—Kaolin and aluminium hydroxide do not adsorb mercuric chloride from aqueous solution. Activated wood charcoal adsorbs mercuric chloride almost completely from aqueous solution but less completely from ethyl-

alcoholic solution. From a solution of potassium mercuric iodide, the activated charcoal adsorbs only mercuric iodide. G. W. R.

**Adsorption by Hydrophilic Colloids.** A. LASNITZKI and L. F. LOEB (*Biochem. Z.*, 1924, **146**, 96—107).—The adsorption of butyric and isovaleric acids by starch and gelatin sols has been determined by measuring the decrement in the lowering of surface tension, using the drop method of Rona and Michaelis. At room temperature and at 36°, the Freundlich equation applies, whilst at 0° adsorption is markedly lowered or is completely arrested.

J. P.

**Surface Tension of Saponin Solutions.** H. WASTL (*Biochem. Z.*, 1924, **146**, 376—379).—An investigation of the effect of dilute acid and alkali in altering the surface tension of solutions of various saponins. In acid solution, the surface tension of Merck saponin is diminished; in alkaline solution, it is slightly increased; whilst primula saponin shows a marked increase in acid solution and a slight diminution in the presence of alkali. Digitonin and sapindus saponins behave similarly to Merck saponin, whilst others resemble primula saponin; chestnut saponin is relatively little influenced by acid.

J. P.

**Forces at Phase Boundaries and the Adsorption at the Surface of Separation between Air and a Solution of an Inorganic Electrolyte.** A. FRUMKIN (*Z. physikal. Chem.*, 1924, **109**, 34—48).—A cell made up as follows: Calomel electrode|Saturated KCl soln.|Soln. of electe. A|Air|0.01N H<sub>2</sub>SO<sub>4</sub> soln.|Saturated KCl soln.|Calomel electrode, has been found, after correction for diffusion potentials, to possess an *E.M.F.* which, in some cases, is only a few millivolts, but in others may reach nearly 100 millivolts. One of the two solutions in contact with air is allowed to run down the inside wall of a wide tube, whilst the other passes from a fine capillary down the centre of the tube. The magnitude of the potential difference is unaffected by the velocity of flow of the two streams, by a reversal of their positions, or by the nature of the gas separating them. It depends, however, on the concentration of the solution and on the nature of the anion, but very little on the cation. The surface of the solution becomes negatively charged. Acids produce a much stronger charge than the corresponding salts.

It has been shown that, since the surface tension of water is raised by salts, the concentration at the surface must be less than in the interior of the solution. The change in surface tension may therefore be used as a measure of the surface concentration. Thus the larger the relative concentration of electrolyte at the surface, the larger is the negative potential. The ions appear to be more strongly adsorbed at the surface the less their tendency to hydrate. For that reason bivalent ions produce, in general, a much smaller charge than univalent anions. This also probably explains why the anion is adsorbed, or orientated towards the surface, thus producing a negative charge, rather than the cation.



The salts which most strongly increase the surface tension of the water produce a slight positive charge in concentrated solutions. This cannot be ascribed to cation adsorption. Ammonia, in common with the aliphatic amines, produces a strong positive charge which is attributable to the adsorption of the ammonia at the surface of the solution, and to the lowering of the surface tension of the water. The formation of complexes appears to favour the adsorption of the anion, since the charge at the surface of a cadmium iodide or a zinc chloride solution is above the average for iodides and chlorides.

M. S. B.

**Plasticity.** I. O. RUFF.—(See ii, 492.)

**Ionisation of Gases during Chemical Reactions.** A. PINKUS (*J. Chim. physique*, 1924, **21**, 71—77).—A discussion of the work of Brewer and Daniels (A., 1923, ii, 721) and of the author's earlier work (cf. A., 1918, ii, 286; 1921, ii, 368, 369). The author's failure to detect ionisation in the reaction between nitric oxide and oxygen is attributed to the small quantities of gases used in the static method, and to the fact that the arrangement of the electrode enabled the greater number of the ions produced to escape detection.

W. H.-R.

**Irreversible Reduction of Organic Compounds. I. The Relation between apparent Reduction Potential and Hydrogen-ion Concentration.** J. B. CONANT and R. E. LUTZ (*J. Amer. Chem. Soc.*, 1924, **46**, 1254—1267).—The "apparent reduction potential" of a compound, which is reduced irreversibly by a soluble reducing agent, may be defined as the potential at which the substance begins to show reduction. The oxidation-reduction potentials of a series of reducing agents in 0.002*M* solution, one-half being in the oxidised, the other in the reduced, state, were compared with the normal hydrogen electrode in buffer solutions of  $p_H$  from 0.76 to 12.7 at 24°, and the substances to be investigated were added, the occurrence of reduction being evidenced by an immediate rise in potential. The reducing agents employed and the oxidation-reduction potentials in solution of  $p_H$  0.76 were as follows: 1:4-naphthaquinone, 0.426; chloroanilic acid, 0.375; (methylene-blue); sulphonated thioindigo scarlet, 0.320; sulphonated alizarin-indigo, 0.315; sulphonated Ciba scarlet, 0.275; "indigo-disulphonate," 0.250; "anthraquinone-1:5-disulphonate," 0.194; "anthraquinone-2:7-disulphonate," 0.184; "anthraquinone-2:6-disulphonate," 0.183; "anthraquinone-2-sulphonate," 0.142; sulphonated naphthanthraquinone, 0.180; and titanium chloride, 0.020. The apparent reduction potentials of substances, investigated in the same buffer solution, were as follows: sodium *m*-nitrobenzene-sulphonate, *m*-nitrobenzoic acid, *m*-nitrophenol, and *p*-nitrophenyl-acetic acid, +0.06; benzoylacrylic acid, +0.08; 2:4-dinitrobenzoic acid, +0.23; "dinitro- $\alpha$ -naphtholsulphonate" and picric acid, +0.26; and orange II, +0.35 volt. The values obtained decrease with decrease in hydrogen-ion concentration. The effect of rise in

temperature is slight but definitely positive, and may be the cause of the temperature coefficients of the irreversible reduction processes. Catalysts had no effect on the rates of reduction. The results obtained accord with the assumption that the controlling factor in the reduction process is the reversible addition of both hydrogen ions and electrons, followed by some irreversible change.

F. G. W.

#### **Change of Volume accompanying Formation of Compounds.**

F. EPHRAIM (*Helv. Chim. Acta*, 1924, 7, 474—485; cf. this vol., ii, 315).—The percentage contraction accompanying the formation of salts of benzenesulphonic and 1- and 2-naphthalenesulphonic acids from their elements is, within small limits, independent of the metal, but varies with the acid radical. A striking regularity is shown by the percentage contractions in the formation of the alkyl (methyl to amyl) esters of the fatty acids (formic to valeric), whereas the molecular volume differences obtained by Kopp's method vary in an irregular manner. In these calculations, the atomic volumes used are C 3.4, H 14.4, O 13.33. The percentage contraction in the formation of the halogen-substituted paraffin compounds is constant when the atomic volumes of the halogens are taken as Cl 40, Br 50, I 53 instead of the usual Cl 22.8, Br 27.1, I 34.25. Kopp's atomic volumes are criticised on the ground that they take no account of the contraction which occurs when combination takes place. Regularities in the percentage contraction are found in some groups of minerals; in others there are irregularities which are not yet accounted for.

E. H. R.

#### **Dyeing Processes. I. Fixation of Acid Wool Dyes of the Type of Orange II.**

P. RUGGLI and A. FISCHLI (*Helv. Chim. Acta*, 1924, 7, 496—507).—The relative importance of solubility of the dye and affinity of the fibre for the dye is illustrated by experiments on the rate of absorption of mono-, di-, tri-, and tetra-sulphonic acids of benzeneazo- $\beta$ -naphthol by wool from the dye-bath. In presence of excess of sulphuric acid, as in the normal dyeing process, the monosulphonic acid is absorbed most, and the tetrasulphonic acid least rapidly; this is due to the greater influence of the sulphuric acid in lowering the solubility of the monosulphonic acid. When equilibrium is reached, however, the tetra- and tri-sulphonic acids are absorbed more completely than the di- and mono-sulphonic acids on account of their greater affinity for the fibre. When no excess of sulphuric acid is used, affinity only comes into play, and the rate of absorption at all stages increases with the number of sulphonic acid groups. [Cf. *B.*, 1924, 554.]

E. H. R.

#### **Dyeing Processes. III. Fixation of some Substantive Cotton Dyes.**

P. RUGGLI and A. FISCHLI (*Helv. Chim. Acta*, 1924, 7, 514—517).—Measurements of the rate of absorption of certain substantive dyes by cotton show that the rate of dyeing varies inversely as the solubility of the dye in water. Addition

of alcohol to a solution of chrysophenine increases the solubility and retards the rate of dyeing, whilst it lowers the solubility of some other dyes and increases the rate of dyeing. The addition of sodium sulphate or carbonate diminishes the rate of dyeing but leads to a better exhaustion of the dye-bath. [Cf. *B.*, 1924, 554.]

E. H. R.

**Equilibrium between Fused Metals and Salts. II.** R. LORENZ.—(See ii, 485.)

**Electronic Theory and Heats of Formation of Salts.** R. AUDUBERT (*Compt. rend.*, 1924, **178**, 1814—1816).—The heats of formation of salts are given within 5% by the formula  $Q = A(b/m^2 - a/n^2)$ , where  $A$  is a general constant,  $a$  and  $b$  depend on the atomic number and valency of the cation and anion, respectively, and  $m$  and  $n$  are whole numbers characteristic of the elements composing them.

The formation of a cation must be endothermic, but this does not appear in tables of observed values, since these are calculated from an arbitrary zero. The true energy of ionisation of silver is calculated from the dimensions of the known face-centred cubic lattice to be  $-88.3$  kg.-cal. per equivalent in place of the value  $-25.3$  given in the tables. The addition of  $-63$  kg.-cal. to all cations is therefore necessary. All these values are then negative, increasing with the electronegativity of the metal and agreeing within 4 or 5% with the calculated value  $q = Aa/n^2$ . A quantity  $+63$  kg.-cal. is to be added to the values for anions, which are then all positive and given by  $q = Ab/m^2$ .

G. M. B.

**Calorimetry of Saturated Fluids.** N. S. OSBORNE (*J. Opt. Soc. Amer.*, 1924, **8**, 519—540).—Calorimetric measurements, combined with temperature and pressure observations, on saturated fluids (liquid and vapour phases always present), permit most of the important thermal properties of the body to be evaluated. Refinements of experimental methods are discussed.

S. B.

**Surface Actions and the Law of Distribution of Molecular Velocities.** C. E. GUYE (*J. Chim. physique*, 1924, **21**, 15—24).—In gaseous systems molecular dissociation may be produced by the collision of molecules either with one another or with the boundary surface of any solid in contact with the gas. For dissociation, the normal components of the velocities must exceed a certain minimum value  $v_0$ . If perfect elasticity is assumed during the collision of a molecule with the surface, an application of the Maxwell law of distribution of molecular velocities indicates: (1) that in the collision of a molecule with the boundary surface, the chance of dissociation occurring is much greater than in a collision between two molecules, and (2) that, in unit time, the absolute number of collisions with unit area of the surface which result in dissociation, may be greater than the absolute number of collisions between molecules which result in dissociation, in unit volume. This effect is greatest when  $v_0$  is large, i.e., when the molecule is stable. This provides a general explanation of the catalytic action of surfaces,

the specific action of different surfaces being affected by physical conditions such as porosity, and by the fact that with some surfaces the collisions are not perfectly elastic. The smaller the elasticity, the less will be the dissociating effect of collisions with the surface, so that, if the elasticity is sufficiently small, the surface may have no catalytic action at all. If arbitrary values are given to  $v_0$  so as to give a reasonable time for the dissociation of 1 c.c. of gas, it is possible by application of the distribution law to calculate approximately the temperature coefficient of the velocity of the reaction.

W. H.-R.

**Catalysis. XVII. Temperature Coefficients of some Reactions in the Light and in the Dark.** R. C. BANERJI and N. R. DHAR (*Z. anorg. Chem.*, 1924, **134**, 172—190).—Temperature coefficients ( $c = K_{t+10}/K_t$ ) have been determined for a number of reactions in the light ( $c_L$ ) and in the dark ( $c_D$ ) as follows: decomposition of trichloroacetic acid in aqueous solution into chloroform and carbon dioxide (80° to 90°)  $c_D$  4.28,  $c_L$  3.6; oxidation of sodium nitrite with iodine (50° to 60°)  $c_D$  2.5,  $c_L$  1.4; inversion of sucrose (30° to 40°)  $c_D$  3.82,  $c_L$  2.78; oxidation of neutral ferrous sulphate with iodine (17.5° to 27.5°)  $c_D$  3.45,  $c_L$  2.0; oxidation of oxalic acid with iodic acid (59° to 69°)  $c_D$  2.98,  $c_L$  2.2—2.5; oxidation of oxalic acid with chromic acid in the presence of manganous sulphate and sulphuric acid (0° to 25°)  $c_D$  2.98; oxidation of oxalic acid with permanganate (0° to 20°)  $c$  3.23. The last three reactions appear, at any rate in the dark, to be unimolecular, the first in respect to iodic acid, the second to oxalic acid, and the third to permanganate, each being of zero order with respect to the other reacting substance. The values of the velocity coefficient for the above reactions are all many times those calculated from Dushman's equation (A., 1921, ii, 315), and it is suggested that this is due to catalytic effects.

A. R. P.

**Activation by Iron of Charcoals containing Nitrogen.** O. WARBURG and W. BREFELD (*Biochem. Z.*, 1924, **145**, 461—480).—Hydrogen cyanide inhibits the oxidation of leucine by oxygen in the presence of blood charcoal but does not influence its adsorption. Sugar charcoal is not specifically affected by hydrogen cyanide, whilst a sugar charcoal containing silica (prepared by fusion in the presence of potassium silicate) adsorbs leucine as well as sugar charcoal, but does not catalyse its oxidation, nor is it activated by the addition of iron, a result which is ascribed to the formation of iron silicate. Charcoal prepared from dried blood containing added silicate is active, as also is that from sugar containing silica to which hæmin has been added. The oxidative activity of such charcoals increases with increase in the amount of hæmin, the most active preparations being obtained from pure hæmin alone. These preparations are seven to ten times as active as technical blood charcoal, but are much less active adsorbents. The oxidative activity calculated on the basis of adsorption is 100—300 times that of blood charcoal. Active charcoals are also obtained from dyestuffs containing nitrogen, such as induline, safranine, neutral-red, and

Bismarck-brown, containing 0.1—0.2% of iron as an impurity. When the pure dyestuffs are used, the charcoal obtained is much less active, but its activity may be increased by the addition of iron. Charcoals prepared from nitrogen-free compounds cannot be activated by the addition of iron. It is concluded that the capacity of blood charcoal to oxidise amino-acids in the presence of oxygen is due to the catalytic activity of iron attached to nitrogen, and is not dependent on the adsorbent power of the charcoal. J. P.

**Poisoning of Nickel Catalysts.** F. WOLFF (*J. pr. Chem.*, 1924, [ii], 107, 159—164).—The catalytic activity of reduced nickel in the reduction of cinnamic acid is depressed by the presence of ferric or nickel hydroxide; it falls at first rapidly, then more slowly, the rate being determined by the amount of "clogging" substance present. It is supposed that the catalyst is not homogeneous but that parts, being more porous, are more active and at the same time more sensitive to foreign substances. With a soluble substance such as potassium ferrocyanide, it is supposed that the ferrocyanide ion is adsorbed; a sharp kink is again shown on the curve activity/concentration. This indicates the point at which the whole surface of the catalyst is covered by an adsorbed film. W. A. S.

**Active Agents in Luminescent Fluorspars and in Corundum and Spinel.** T. TANAKA (*J. Opt. Soc. Amer.*, 1924, 8, 501—510).—Samarium is the active agent in the cathodo-luminescence of most samples of fluorspar. Other rare earths and also thallium are occasionally active. Chromium is the principal agent in corundum, and manganese in artificial ruby and spinel. S. B.

**Photochemical Hydrolysis of [Aqueous Solutions of] Monochloro- and Monobromo-acetic Acids and the Einstein Law.** E. RUDBERG (*Z. Physik*, 1924, 24, 247—263).—An experimental investigation of the hydrolysis of monochloroacetic and monobromoacetic acids under the influence of ultra-violet light. The number of chlorine or bromine atoms freed by the action of monochromatic light was determined electrometrically. A concentration of chlorine or bromine ions corresponding with a silver deposit of 0.001 mg. could be estimated. The light energy absorbed was determined by a sensitive thermopile. In the case of both acids, the action of the light became noticeable between 3130 and 2660 Å., and the measurements were carried out for  $\lambda=2536$  Å. In the case of chloroacetic acid the action follows the Einstein law,  $N=Q/h\nu$ . For monobromoacetic acid, the number of molecules transformed is only 0.34 of the number of quanta absorbed. This fraction increases as the solution changes from acid to alkaline, but the increase is shown to be inconsistent with the assumption of a simple collision reaction between the active molecules and hydroxyl ions. G. S.

**Supposed Phosphorescence in Phototropic Transformations.** B. ZANELLA (*Gazzetta*, 1924, 54, 247—250).—The conclusions drawn by Gallagher from the effects produced on a

photographic plate by compounds undergoing phototropic transformation (A., 1922, ii, 11) are fallacious. The two phototropic modifications of benzaldehyde phenylhydrazone produce exactly similar effects, which are due solely to the chemical action of the decomposition products of the substance and not to emission of either light or electrons. The bright phosphorescence observed by Gallagher when certain phototropic substances are heated in an oven could not be detected. T. H. P.

**Physical Laws of the Formation of Ozone by the Silent Discharge.** A. CHASSY (*Compt. rend.*, 1924, **178**, 1484—1485).—In the formation of ozone from pure oxygen by the silent discharge the ratio of the quantity of heat evolved to the quantity of ozone formed is constant and independent of the frequency and voltage of the discharge, provided the final concentration of ozone is constant. The rapidity of formation is proportional to the frequency. For low concentrations of ozone, the ratio of the heat evolved in calories to the volume of oxygen transformed in c.c. at S.T.P. is 7.04; the ratio is constant between 0° and 25°. A. B. H.

**Vacuum Evaporation of Aqueous Fluids at Low Temperature.** A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1924, **146**, 305—306).—A vacuum apparatus for the rapid evaporation of aqueous solutions is described. The solutions are placed in shallow vessels on a tray warmed by a system of hot-water pipes, whilst the inner surface of the jacket of the apparatus, which is packed with a mixture of salt and ice, serves to condense the evaporated water. J. P.

**All-metal High Vacuum Pump System.** I. BACKHURST and G. W. C. KAYE (*Phil. Mag.*, 1924, [vi], **47**, 918—929).—An all-steel mercury vapour jet pump working against a fore-vacuum of 4 mm. from an oil piston pump provides a fore-vacuum of 0.001 mm. for a mercury vapour condensation pump of the Langmuir type designed to give rapid working and to attain a vacuum of less than  $10^{-6}$  mm. The volume of vapour removed is 300 c.c./sec. at pressures above 0.03 mm. but increases rapidly as the pressure falls and below 0.0015 mm. is constant at 6000 c.c./sec. Temperature control is not critical and the system requires little or no attention when running. A short *résumé* of existing vacuum pumps is given and a bibliography is appended. S. S.

**A Metal Annular-jet Vacuum Pump.** I. BACKHURST and G. W. C. KAYE (*Phil. Mag.*, 1924, [vi], **47**, 1016—1020).—The mercury vapour jet pump previously described (see preceding abstract) is difficult to construct owing to the welded joints. A new type of pump has therefore been devised the outer wall of which consists of one piece of seamless steel tube closed by screwed caps which are made gas-tight by copper or nickel plating. When the upper cap is removed the inner parts can readily be removed for cleaning and adjustment. The mercury vapour ascends from the boiler through a central tube, strikes a deflector and passes through an annular jet formed by the rim of the deflector and an adjustable sleeve. The

position of the deflector can also be varied to enable the pump to work as efficiently as possible over the desired pressure range. The pump will readily produce a vacuum of  $10^{-5}$  mm. working against a back pressure of 1 mm. or less. The speed of working is high, varying from 1000 to 7000 c.c./sec., depending on the back pressure and upon the pressure in the vessel to be exhausted. S. S.

**Simple Electric Thermo-regulator.** S. C. BRADFORD (*Biochem. J.*, 1924, **18**, 381—383).

**Dilatometer for Use with Very Unstable Compounds.** J. HUME (*Chem. News*, 1924, **128**, 360).—The dilatometer was designed for use with substances which had to be kept at  $0^{\circ}$  until the experiment was begun. It consists of a U-tube, which forms the bulb of the dilatometer, one end being sealed to a capillary tube, the other connected through a stop-cock with a funnel. Liquid and crystals were placed in the funnel, the crystals allowed to settle, and the stop-cock was opened to fill the dilatometer. Such an instrument was found to overcome all the difficulties met with in the use of the ordinary dilatometer. G. S.

**Modification of the Washburn-Cottrell [Ebullioscopic] Apparatus.** W. SWIENTOSLAWSKI, J. WASZKOSIENRENSKI, and W. ROMEI (*Bull. Soc. chim.*, 1924, [iv], **35**, 542—545).—The bulb of the Beckmann thermometer is placed between the forks of a Y-tube, the funnel-shaped bottom of which is immersed in the liquid. The thermometer and forks are surrounded by a glass tube. On boiling the liquid, a portion is drawn up the Y-tube and is thrown on to the bulb of the thermometer from the ends of the forks. [Cf. A., 1919, ii, 447.] S. K. T.

**Fractionation Device for Distillation under Reduced Pressure.** E. ANDRÉ (*Bull. Soc. chim.*, 1924, [iv], **35**, 647—648).

**Mercury Seals on Ground Joints in Horizontal or Inverted Positions.** J. A. CARROLL (*Nature*, 1924, **113**, 858).—An adherent film is obtained by running the mercury over a thick solution of celluloid or collodion in amyl acetate. A. A. E.

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### Inorganic Chemistry.

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**Chemico-physical Calculations relating to the Degree of Dissociation of the Dissolved Substances in Mineral Waters.** C. PORLEZZA (*Annali Chim. Appl.*, 1924, **14**, 128—154).—Methods are given for calculating the mean degree of dissociation of the dissolved matter of mineral waters from the electrical conductivity, the rise in boiling point, or the depression of the freezing point (cf. Hintz and Grünhut, A., 1908, ii, 1075). T. H. P.



**Activity of Hydrogen Ion in Aqueous Solutions of Hydrogen Fluoride.** W. F. K. WYNNE-JONES and L. J. HUDLESTON (*J. Chem. Soc.*, 1924, **125**, 1031—1035).—Measurements of the *E.M.F.* of the cell  $\text{H}_2|\text{HF}|\text{KCl}(\text{sat.}), \text{HgCl}|\text{Hg}$  were made using varying strengths of hydrofluoric acid. The results indicate that the values of the activity of the hydrogen ion and its concentration agree, within the limits of experimental error, in hydrofluoric acid solutions weaker than 0.4*N*, but that in more strongly acid solutions the value of the activity of the hydrogen ion is greater than its concentration. A. R. P.

**Thermal Formation of Ozone.** E. H. RIESENFELD and M. BEJA (*Z. anorg. Chem.*, 1924, **133**, 245—262).—The equilibrium between oxygen and ozone at high temperatures has been examined by analysis of the gases left after explosion of various ozone-oxygen mixtures. Mixtures containing less than 37% by volume of ozone give a theoretical explosion temperature of 2130° Abs.; after explosion, the amount of ozone is below the limit of analytical detection, which was found to be  $2 \times 10^{-6}\%$  by volume, using starch-iodide paper. Mixtures containing 45—94% of ozone, giving maximum explosion temperatures of 2385—3175° Abs., give after explosion a gas containing from  $2 \times 10^{-6}$  to  $1 \times 10^{-5}\%$  of ozone, independent of the original concentration of ozone. The Nernst theorem indicates a final ozone concentration of  $4.2 \times 10^{-5}\%$ , if pure ozone be exploded at constant volume. The results indicate that thermal formation of ozone cannot have been observed by previous workers. S. I. L.

**Constitution of the Thionic Acids.** I. VOGEL (*Chem. News*, 1924, **128**, 325—327, 342—345).—The following formulæ are proposed as representing the known reactions of the acids: trithionic acid,  $\text{H}\cdot\text{SO}_2\cdot\text{O}\cdot\text{S}\cdot\text{SO}_2\cdot\text{OH}$ ; tetrathionic acid,  $\text{H}\cdot\text{S}\cdot\text{SO}_2\cdot\text{O}\cdot\text{S}\cdot\text{SO}_2\cdot\text{OH}$ ; pentathionic acid,  $\text{H}\cdot\text{S}_2\cdot\text{SO}_2\cdot\text{O}\cdot\text{S}\cdot\text{SO}_2\cdot\text{OH}$ . The evidence in support of these formulæ is as follows: two atoms of sulphur in the pentathionates are essentially different from the other three as they may be removed successively or together and the residue of the molecule (trithionic acid) can exist alone or unite with sulphur to form first tetra- then penta-thionic acid; 1 mol. of pentathionic acid liberates 2 atoms of sulphur when treated with bromine; tetrathionic acid is fairly stable and behaves in an analogous manner to persulphuric acid, its oxygen analogue, *i.e.*, it readily sulphurises substances such as sulphites and cyanides. These formulæ also account for the presence of bivalent sulphur, the strong acidity of the acids, and for the fact that they do not form complex ions. A. R. P.

**Formation and Decomposition of Polythionates.** E. JOSEPHY (*Z. anorg. Chem.*, 1924, **135**, 21—41).—A new method of formation of pentathionic acid is the action of sulphur dioxide on sulphur in water, (a)  $5\text{S} + 5\text{SO}_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{S}_5\text{O}_6$ . Sulphur also produces pentathionate and tetrathionate by action on trithionate. In Wackenroder's solution, tetrathionic acid is formed

directly, (b)  $3\text{SO}_2 + \text{H}_2\text{S} = \text{H}_2\text{S}_4\text{O}_6$ , whilst the sulphur formed,  $\text{SO}_2 + 2\text{H}_2\text{S} = 3\text{S} + 2\text{H}_2\text{O}$ , reacts also with the sulphur dioxide according to equation (a). Pentathionic acid is similarly formed in the decomposition of thiosulphates by acids, by reaction (a) between the sulphur and sulphur dioxide formed. These reactions explain all the hitherto observed cases of formation of polythionic acids without assuming hypothetical intermediate products; no indications of new sulphur compounds were observed.

Trithionic acid is the least stable of these acids, tetrathionic the most stable. Decomposition occurs according to the equations  $\text{S}_5\text{O}_6'' \rightarrow \text{S}_4\text{O}_6'' + \text{S}$ ;  $\text{S}_4\text{O}_6'' \rightarrow \text{S}_3\text{O}_6'' + \text{S}$ ;  $\text{S}_3\text{O}_6'' \rightarrow \text{SO}_4'' + \text{SO}_2 + \text{S}$ ; at  $100^\circ$ , the formation of tetrathionic acid by Wackenroder's reaction is reversed,  $\text{H}_2\text{S}_4\text{O}_6 \rightarrow \text{H}_2\text{S} + 3\text{SO}_2$ . The methods of analysis of mixtures of the polythionic acids adopted for the work are given in detail. S. I. L.

**Peroxidation of Nitric Oxide. III. Increase in Velocity of Peroxidation of Nitric Oxide at Low Temperatures.** E. BRINER, W. PFEIFFER, and G. MALET (*J. Chim. physique*, 1924, **21**, 25—44; cf. A., 1923, ii, 485).—The action between nitric oxide and oxygen has been studied at temperatures from  $+75^\circ$  to  $-193^\circ$ , the gases being diluted with nitrogen to prevent the reaction being too rapid for accurate measurement. The reaction is expressed by the equation  $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$ , and is of the third order, but in the presence of a large excess of oxygen may be considered as of the second order. Some nitrogen trioxide is also formed:  $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$ . The velocity of reaction increases greatly as the temperature is lowered, particularly at very low temperatures. The temperature coefficient of the velocity constant (defined as the ratio of the velocity constants at two temperatures differing by  $10^\circ$ ) decreases from 0.96 at  $70^\circ$  to 0.85 at  $-180^\circ$ , in contrast to the values of 2—3 for ordinary reactions. The results obtained have been used to calculate the absolute and relative velocity constants, the temperature coefficients, and the times of half reaction. W. H.-R.

**Peroxidation of Nitric Oxide. IV. Action of Low Temperatures and of Certain Catalysts on the Gases of the Nitrifying Arc.** E. BRINER, W. PFEIFFER, and G. MALET (*J. Chim. physique*, 1924, **21**, 45—50; cf. preceding abstract).—A current of air was passed through an electric arc maintained between copper electrodes. The gases leaving the arc, containing about 2% of nitric oxide, were cooled rapidly to temperatures from  $+100^\circ$  to  $-120^\circ$ , and then passed through oxidation vessels in which the extent of oxidation of the nitric oxide was studied. The oxidation of nitric oxide is greatly facilitated by the cooling of the gases, particularly if the cooling takes place immediately the gases leave the arc. Charcoal, glass wool, and platinised asbestos have no appreciable catalytic effect on the reaction, in contradiction to the results of Burdick (A., 1922, ii, 272), which are considered to have been affected by the presence of moisture. W. H.-R.

**Arc Spectrum of Phosphorus.** M. O. SALTMARSH.—(See ii, 436.)

**Reaction between Phosphorous Acid and Mercuric Chloride.** A. D. MITCHELL (*J. Chem. Soc.*, 1924, **125**, 1013—1030).—The interaction of phosphorous acid and mercuric chloride is controlled to a large extent by the reversible change which phosphorous acid itself undergoes (cf. Mitchell, T., 1920, **117**, 1324). In the absence of chlorine ions other than those supplied by the mercuric chloride itself, the normal form of phosphorous acid plays the greatest part in the reduction of the mercuric chloride until such a point that the accumulation of chloride ions reduces the reaction:  $\text{HgCl}_2 + \text{H}_3\text{PO}_3$  (normal)  $+ \text{H}_2\text{O} = \text{H}_3\text{PO}_4 + \text{Hg} + 2\text{H}^+ + \text{Cl}^-$ , to a lower order of magnitude. When sufficient chlorine ions are present either initially or during the course of the reaction, the second form of phosphorous acid is responsible for the greater part of the reaction. If the hydrogen-ion concentration of the solution is very low, *e.g.*, in the presence of sodium acetate, the reaction takes place very rapidly, more than 96% of the theoretical mercurous chloride being formed in 9 minutes instead of the 24 hours required in 0.1*N*-acid solutions. There is also some evidence of the formation of complexes.

A. R. P.

**Spectra of Stripped Boron Atom ( $\text{B}^{\text{III}}$ ).** I. S. BOWEN and R. A. MILLIKAN.—(See ii, 437.)

**Band Spectra of Boron Nitride and Oxide.** W. JEVONS.—(See ii, 438.)

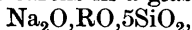
**Reaction between Boron Nitride and Various Metallic Oxides.** U. SBORGI and E. GAGLIARDO (*Annali Chim. Appl.*, 1924, **14**, 113—123).—Particulars are given of the yields of nitric oxide obtained by passing air over mixtures of boron nitride with varying proportions of a number of different oxides and mixtures of oxides (cf. A., 1922, ii, 564). With ferric oxide containing a small proportion of bismuth oxide or antimony oxide, as much as 79% of nitric oxide is obtained.

T. H. P.

**Spectrum of Silicon Tetrafluoride.** C. PORLEZZA.—(See ii, 436.)

**Absorption Spectra of Coloured Glass.** P. P. FEDOTIEFF [with A. VON LEBEDEV] (*Z. anorg. Chem.*, 1924, **134**, 87—101).—The influence of the replacement of one alkali metal by another on the variation in colour of glasses of the composition  $\text{R}_2\text{O} \cdot \text{PbO} \cdot 5\text{SiO}_2$  is investigated. Absorption curves in the visible and ultra-violet region and also a number of absorption spectra photographs in the ultra-violet region, are given. With increase of the atomic weight of the alkali metal, the colour of the glass moves from the red to violet. This is clearly shown by the addition of the oxides,  $\text{FeO}(\text{Fe}_2\text{O}_3)$ ,  $\text{CoO}$ ,  $\text{NiO}$ , and  $\text{MnO}_2$ , less clearly by  $\text{CuO}$  on account of the much less colour intensity of the glass, whilst with  $\text{Cr}_2\text{O}_3$  and  $\text{UO}_3$  the colour of the glass is so feeble that the substitution

of one alkali metal for another scarcely influences the colour. The substitution of alkaline-earths in a glass of composition



as indicated by a few experiments, shows a similar but much less marked influence on the colour with the colouring oxides  $\text{CoO}$ ,  $\text{NiO}$ , and  $\text{CuO}$ . In a sodium or potassium glass, in passing from iron to nickel the colour moves from red to violet, whilst in the case of a lithium glass no such change was observed. J. B. F.

**Preparation of Persilicates.** A. H. ERDENBRECHER (*Chem.-Ztg.*, 1924, **48**, 310—311).—Anhydrous or crystalline sodium metasilicate when triturated with 82% hydrogen peroxide in the presence of alcohol or ether, yields a porous mass containing up to 15.5% of active oxygen. On treating this mass with water, a certain amount of silicic acid is precipitated, but redissolves on warming the mixture. The substance absorbs moisture and carbon dioxide from the air with the liberation of oxygen, and evolves water and oxygen when heated. A. R. P.

**Action of Nitrogen on Silicon obtained from Cooled Molten Aluminium.** H. FUNK (*Z. anorg. Chem.*, 1924, **133**, 67—72).—The finely-divided silicon obtained by cooling a 10% solution of that element in molten aluminium forms the nitride,  $\text{Si}_3\text{N}_4$ , after heating for 10 minutes at  $1450^\circ$  in a current of nitrogen; crystalline silicon requires several hours' heating (Weiss and Engelhardt, A., 1910, ii, 122). S. K. T.

**Silicon Analogue of Calcium Cyanamide.** L. WÖHLER and O. BOCK (*Z. anorg. Chem.*, 1924, **134**, 221—250).—When nitrogen is passed over calcium disilicide heated at  $1150^\circ$  a grey mass containing about 22.5% of nitrogen is formed. This consists principally of calcium silicocyanamide, calcium silicocyanide, and elementary silicon, formed thus:  $2\text{CaSi}_2 + 2\text{N}_2 = \text{CaSiN}_2 + \text{Si} + \text{Ca}(\text{SiN})_2$ , together with small quantities of calcium nitride,  $\text{Ca}_3\text{N}_2$ , and silicon nitride,  $\text{Si}_3\text{N}_4$ . Under similar conditions, calcium monosilicide yields first an intermediate product,  $\text{Ca}_2\text{Si}_2 + \text{N}_2 = \text{Ca}_2\text{Si}_2\text{N}_2$ , then calcium silicocyanamide,  $\text{Ca}_2\text{Si}_2\text{N}_2 + \text{N}_2 = 2\text{CaSiN}_2$ , but a considerable portion of the monosilicide is transformed into disilicide and calcium during the heating. Neither calcium silicocyanamide nor the substance  $\text{Ca}_2\text{Si}_2\text{N}_2$  could be isolated from the reaction product, but both substances dissolved in hydrochloric acid without separation of silica. Calcium silicocyanide is insoluble in hydrochloric acid, but soluble in a mixture of hydrofluoric and sulphuric acids, to which it yields its nitrogen as ammonium salt. The rate of absorption of nitrogen by calcium disilicide is greatly accelerated by addition of calcium chloride or of less than 5% of calcium fluoride to the reaction mixture and takes place at temperatures as low as  $850^\circ$  in the presence of these catalysts. In the presence of 50% of calcium chloride, a mixture of lime and ferro-silicon containing 90% Si absorbs 20.7% of nitrogen at  $1050^\circ$  to  $1100^\circ$  forming calcium silicocyanamide and calcium metasilicate. Barium oxide and magnesia under similar conditions give analogous products. A. R. P.

**Transformation of the Diamond.** G. FRIEDEL and G. RIBAUD (*Compt. rend.*, 1924, **178**, 1126—1129).—When the diamond is heated at 1500°, superficial blackening occurs; this surface layer may be removed by heating in the oxidising flame; it appears to contain only a small proportion of graphite. Above 1800°, transformation into graphite occurs more rapidly; this was observed at various temperatures up to 1885°, above which the substance disintegrates into small fragments. At higher temperatures, diamond is unstable and rapidly changes into graphite; the change apparently begins at the surface and may thus be influenced by the surrounding medium. The theoretical aspect of the birefringence of diamond and its formation in nature is discussed in the light of the foregoing observations. H. J. E.

**Adsorption. II. Determination of the Adsorption of Gases from Gas Mixtures [by Wood Charcoal].** R. LORENZ and E. WIEDBRAUCK (*Z. anorg. Chem.*, 1924, **134**, 251—264).—The apparatus used consists essentially of two gasometers of a capacity of 60 litres connected in parallel with a drying apparatus, pressure regulator, adsorption tubes, smaller gasometers for measuring the volume and pressure of the issuing gases, and a vacuum pump. Before and after the absorption tubes, by-passes allow a sample of the gas to be withdrawn for analysis. During adsorption the tubes are immersed in a freezing mixture, and when the adsorbed gas is to be removed from the charcoal the cooling apparatus is replaced by an electrically heated tube furnace. An account is given of some experiments carried out to show the reproducibility of the results on gas mixtures containing two or more of the following gases: oxygen, nitrogen, hydrogen, and carbon dioxide. For fuller details, the original must be consulted. A. R. P.

**Adsorption. III. Reversal during the Adsorption of Carbon Dioxide and Hydrogen by Wood Charcoal.** R. LORENZ and E. WIEDBRAUCK (*Z. anorg. Chem.*, 1924, **135**, 42—48).—When a mixture containing 5% of carbon dioxide and 95% of hydrogen is passed over wood charcoal, the volume of hydrogen adsorbed per unit of time is fairly constant, whilst the volume of carbon dioxide is at first smaller, but rises continuously to a value nearly double that of the hydrogen. Whereas of the total adsorbed the proportion of hydrogen is at first more than 80% and then falls rapidly, that of carbon dioxide is at first under 10% and then rises rapidly. Alteration of temperature does not much alter the relative adsorption. S. I. L.

**Pyrogenic Formation of Carbonyl Chloride.** E. BIESALSKI (*Z. angew. Chem.*, 1924, **37**, 314—317).—In the presence of copper oxide or many anhydrous metallic chlorides, carbon tetrachloride and air yield varying quantities of carbonyl chloride at temperatures between 120° and 750°. With ferric chloride, a maximum yield of 25% is obtained at 250°, whilst with thorium chloride the yield is 8% and with ferrous chloride 11% at 450°. In the absence

of a catalyst, the yield is 3% at 600° and 6% at 750°; both these yields are increased in the presence of coke or porous earthenware. Chloroform and air yield 9% of the theoretical weight of carbonyl chloride when passed over chlorinated copper oxide at 450°, and smaller yields are obtained under the same conditions from mixtures of air and chlorinated hydrocarbons of the ethylene or methane series.

A. R. P.

**Decomposition of Carbon Disulphide by Ultra-violet Rays.** G. BRUHAT and M. PAUTHENIER.—(See ii, 439.)

**Preparation of Thiocarbonyl Chloride. II.** R. DE FAZI (*Gazzetta*, 1924, **54**, 251—254; cf. A., 1923, ii, 411).—When carbon tetrachloride and sulphur are heated together in a sealed tube at 200°, traces of thiocarbonyl chloride and sulphur chloride are formed, the yield of the former being somewhat greater, although still small, if a little iodine or powdered iron is present. Ferrous sulphide and carbon tetrachloride do not react at temperatures below 100°, but give thiocarbonyl chloride either in presence of iodine or if the reaction is effected at 150° in a sealed tube. None of these methods gives yields of thiocarbonyl chloride of any practical value.

T. H. P.

**Explanation of Cold-working on the Basis of Electrical Measurements.** W. GEISS and J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1924, **133**, 107—112).—Experiments on the effect of stretching and compression on the conductivity of metals (cf. Heyn and Bauer, *Int. Z. Metallographie*, 1911, **1**, 16; Bridgman, *Physical Rev.*, 1921, **17**, 161) show that small changes in atomic distances are insufficient to account for the variations in the electrical conductivity of pure metals caused by cold-drawing (cf. A., 1923, ii, 866). It is suggested that cold-drawing may induce anisotropy in the crystallite, although experiment shows that any such change must be confined to the surface of the individual crystallites.

S. K. T.

**Chemical Kinetics of the Solution of Alkali and Alkaline-earth Metal Amalgams in Acids.** W. FRAENKEL and H. HEINZ (*Z. anorg. Chem.*, 1924, **133**, 153—175).—The velocity of solution is the same under suitable conditions; stirring must be efficient, but the rate of stirring has very little effect on the reaction velocity, and the reaction proceeds directly with no induction period. The velocity of solution of the completely fluid amalgams of the alkaline-earth metals corresponds with a reaction of the first order; amalgams containing a second phase, such as the fluid amalgams of the alkali metals, show a linear relation between time and amount dissolved. The temperature coefficient is 1.51—1.24 for 10° rise in temperature. The influence of hydrogen-ion concentration is very complicated. The velocity constants are not independent of the volumes of the amalgams, but increase as these become smaller. The potentials measured fall between the values for the dissolved metals and the hydrogen potential, parallelism between velocity of solution and potential being observed in the series of

alkaline-earth metal amalgams, but not with the alkali metals. No relation was observed between velocity of solution and the coefficient of diffusion of the metal in mercury. S. I. L.

**Insoluble Alkali Metaphosphates.** P. PASCAL (*Compt. rend.*, 1924, **178**, 1541—1543).—The preparation and properties of five forms of insoluble alkali metaphosphates (falling into two distinct groups) are described. Dehydration of monosodium phosphate at 250° gives an insoluble metaphosphate (Maddrell's salt) which does not form soluble complexes with salts of iron and uranium. At 505°, it passes irreversibly into a trimetaphosphate. Monopotassium phosphate changes directly into the trimetaphosphate at 170°, and this, heated above 320°, is transformed into an insoluble salt mixed with a little hexametaphosphate. The viscosity of solutions of metaphosphates prepared by ignition of monoalkali phosphates and chilling the product (Kurrol's salts) in saline solutions reveals their colloidal nature, and this property is employed to study the transformations caused by varying the temperature of ignition. Thus four interconvertible varieties are recognised. The colloidal character which always accompanies the crystalline structure disappears in the amorphous salts produced at extreme temperatures. J. W. B.

**Ebullioscopic Study of the Formation of Double Salts between Mercuric Cyanide and the Halides of the Alkali and Alkaline-earth Metals.** F. BOURION and E. ROUYER (*Compt. rend.*, 1924, **178**, 1171—1174).—Ebullioscopic methods indicate the existence of the following double salts:  $\text{Hg}(\text{CN})_2 \cdot \text{KCl}$ ;  $\text{Hg}(\text{CN})_2 \cdot \text{NH}_4\text{Cl}$ ;  $\text{Hg}(\text{CN})_2 \cdot \text{NaCl}$ ;  $\text{Hg}(\text{CN})_2 \cdot \text{KBr}$ ;  $\text{Hg}(\text{CN})_2 \cdot \text{KI}$ ;  $\text{Hg}(\text{CN})_2 \cdot \text{MgCl}_2$ ; and  $2\text{Hg}(\text{CN})_2 \cdot \text{BaCl}_2$ . With the exception of the magnesium chloride compound, all were isolated. Iodides appear to show a greater tendency than bromides to form such compounds and bromides than chlorides. H. J. E.

**Potassium Carbonate Solution and Carbon Dioxide. I. and II.** A. SIEVERTS and A. FRITZSCHE (*Z. anorg. Chem.*, 1924, **133**, 1—16; 17—35).—I. The value of  $k$  ( $=[\text{KHCO}_3]^2/[\text{K}_2\text{CO}_3]p$ , where  $p$  is the partial pressure of carbon dioxide) for the equilibrium between potassium carbonate, potassium hydrogen carbonate, and carbon dioxide in an aqueous solution 2*N* with respect to potassium, is approximately constant for a given temperature between 30° and 97°, but is smaller the higher the temperature. Similar results hold between 30° and 50° for *N*-solutions. When the potassium present as hydrogen carbonate exceeds 90% of the whole, 10% higher values are found. The ratio  $\beta/\alpha^2$ , where  $\alpha$  and  $\beta$  are the dissociation constants of the hydrogen carbonate and carbonate respectively, is practically independent of the potassium concentration, but this is not so for the carbonic acid concentration when  $p=1$ . The degree of hydrolysis of carbon dioxide probably varies with the nature and the concentration of the alkali metal. These latter influences are probably the cause of the differences previously observed between the behaviour of sodium and potassium carbonate solutions (cf. A., 1903, ii, 413).

II. The rate of absorption of carbon dioxide by potassium carbonate solution is approximately proportional to the partial pressure of the gas and is decreased by increase in temperature or by absence of stirring. The rate is greater the lower the potassium concentration; this is not a viscosity effect. The amount of carbon dioxide absorbed at a given temperature, potassium concentration, and carbon dioxide pressure is proportional to the time. The amount of hydrogen carbonate formed is the smaller the higher the concentration of the carbonate solution (cf. A., 1922, ii, 487).  
S. K. T.

**Action of Ammonia on Potassium Chlorate and the Replacement of Chlorine by Nascent Nitrogen.** K. A. HOFMANN and W. LINNMANN (*Ber.*, 1924, 57, [B], 818—824).—Gaseous ammonia, mixed with air, reacts so readily with solid potassium chlorate that the reaction may become dangerous if the concentration of the ammonia is considerable. To secure a controlled reaction, therefore, the potassium chlorate is distributed over an excess of porous clay and the mixture is heated, generally to about 250°, in a current of air and ammonia until reaction commences, after which the heating is discontinued until the initial vigour of the change has subsided. The course of the action is shown by the schemes  $\text{KClO}_3 + 2\text{NH}_3 \rightarrow \text{KCl} + 2\text{N} + 3\text{H}_2\text{O}$  and  $\text{KClO}_3 + \text{N} \rightarrow \text{KNO}_3 + \text{Cl}$ . It is shown that the ammonia reacts directly with the chlorate and not with previously liberated oxygen, that the change occurs at the surface of the chlorate and not in the gaseous layer, and that nitric acid is not formed intermediately. Incidence of the reaction is ascribed to the relatively unsaturated nature of the potassium chlorate and ammonia molecules and the consequent possibility of the production of intermediate additive products (cf. A., 1913, ii, 62, 609). In confirmation of this view, it is shown that the saturated potassium perchlorate molecule does not react with ammonia at moderate temperatures and that, at higher temperatures, the production of nitrate is due entirely to the intermediate formation of potassium chlorate.  
H. W.

**Decomposition of Potassium Dichromate in Aqueous Solution.** T. SABALITSCHKA and G. KUBISCH (*Pharm. Zentralh.*, 1924, 65, 272—274).—In an attempt to discover whether dilute solutions of potassium dichromate contain any potassium hydrogen chromate, dichromate solutions were subjected to dialysis and the ratio of potassium to chromium in the solution below the dialyser was determined. In all cases, this ratio, although not constant, was greater than 1. Under the same conditions, chromic acid dialysed more quickly than potassium chromate. It is inferred that potassium dichromate is partly decomposed into the normal chromate and the trichromate in dilute aqueous solution:  
 $2\text{K}_2\text{Cr}_2\text{O}_7 \rightleftharpoons \text{K}_2\text{CrO}_4 + \text{K}_2\text{Cr}_3\text{O}_{10}$ .  
A. R. P.

**Double Decomposition,  $(\text{NH}_4)_2\text{B}_4\text{O}_7 + \text{Na}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{B}_4\text{O}_7 + (\text{NH}_4)_2\text{SO}_4$ , in Aqueous Solution.** I. U. SBORGI and E. GALLICHI (*Gazzetta*, 1924, 54, 255—282).—The ternary system,



$(\text{NH}_4)_2\text{B}_4\text{O}_7\text{--Na}_2\text{B}_4\text{O}_7\text{--H}_2\text{O}$ , is here considered. Determinations have been made of the binary and ternary cryohydrates, the transformation point of borax in presence of ammonium borate, the solubility curves of the separate components, the isotherms for the temperatures  $25^\circ$ ,  $35^\circ$ ,  $45^\circ$ ,  $50.5^\circ$ ,  $55^\circ$ ,  $57^\circ$ , and  $65^\circ$ . The principal numerical results are: the binary cryohydric points, ice- $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$ ,  $-0.45^\circ$ , and ice- $(\text{NH}_4)_2\text{B}_4\text{O}_7\cdot 4\text{H}_2\text{O}$ ,  $-1.07^\circ$ ; the ternary cryohydric point,  $-1.23^\circ$ ; the transformation point,  $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O--Na}_2\text{B}_4\text{O}_7\cdot 5\text{H}_2\text{O}$ ,  $60^\circ$ , or, in presence of  $(\text{NH}_4)_2\text{B}_4\text{O}_7\cdot 4\text{H}_2\text{O}$ ,  $50.55^\circ$ . T. H. P.

**Double Decomposition,  $(\text{NH}_4)_2\text{B}_4\text{O}_7 + \text{Na}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{B}_4\text{O}_7 + (\text{NH}_4)_2\text{SO}_4$ , in Aqueous Solution.** II. U. SBORGI and E. GALLICHI (*Gazzetta*, 1924, **54**, 283—297).—Results are given of an investigation of the ternary system,  $(\text{NH}_4)_2\text{B}_4\text{O}_7\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ , at various temperatures. The binary cryohydric point, ice- $(\text{NH}_4)_2\text{SO}_4$ , is  $-19.05^\circ$ , and the ternary cryohydric point is  $-19.90^\circ$ . The system  $(\text{NH}_4)_2\text{SO}_4\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$  was studied completely by Dawson (T., 1918, **113**, 675). T. H. P.

**Double Decomposition.  $(\text{NH}_4)_2\text{B}_4\text{O}_7 + \text{Na}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{B}_4\text{O}_7 + (\text{NH}_4)_2\text{SO}_4$ , in Aqueous Solution.** III. U. SBORGI, E. BOVALINI, and L. CAPPELLINI (*Gazzetta*, 1924, **54**, 298—321).—Data are given for the ternary system,  $\text{Na}_2\text{B}_4\text{O}_7\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ . The principal results are as follows: binary cryohydric points, ice- $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$ ,  $-0.45^\circ$ , and ice- $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ ,  $-1.2^\circ$ ; ternary cryohydric point,  $-1.38^\circ$ ; transformation point,  $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O--Na}_2\text{SO}_4$ ,  $32.4^\circ$ , or, in presence of  $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$ ,  $31.9^\circ$ ; transformation point,  $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O--Na}_2\text{B}_4\text{O}_7\cdot 5\text{H}_2\text{O}$ ,  $60^\circ$ , or, in presence of  $\text{Na}_2\text{SO}_4$ ,  $49.3^\circ$ ; boiling point of solution saturated with  $\text{Na}_2\text{SO}_4$ ,  $102.2^\circ$ , with  $\text{Na}_2\text{B}_4\text{O}_7\cdot 5\text{H}_2\text{O}$ ,  $102.9^\circ$ , and with  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{B}_4\text{O}_7\cdot 5\text{H}_2\text{O}$ ,  $104^\circ$ . T. H. P.

**Double Decomposition,  $(\text{NH}_4)_2\text{B}_4\text{O}_7 + \text{Na}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{B}_4\text{O}_7 + (\text{NH}_4)_2\text{SO}_4$ , in Aqueous Solution.** IV. U. SBORGI and L. STEFANINI (*Gazzetta*, 1924, **54**, 322—338).—By thermometric investigations on the quaternary system, the fundamental points of the system have been established. T. H. P.

**Examination of the Binary System Sodium Sulphite-Water by Extrapolation from the Ternary System Sulphite-Sulphate-Water.** N. B. LEWIS and A. C. D. RIVETT (*J. Chem. Soc.*, 1924, **125**, 1156—1162).—Hartley and Barrett's results for the solubility of pure sodium sulphite below  $22^\circ$  are confirmed by extrapolation to zero sulphate of curves showing the solubility of sodium sulphate in solutions containing up to 10% of sulphate, but above this temperature quite different results are obtained, probably owing to the formation of mixed crystals of sulphite and sulphate, which, in the limiting case of zero sulphate, correspond with a form of sodium sulphite which is metastable to that obtained by these authors. This form has a transition point of  $31.5^\circ$ , at which temperature it is converted into the anhydrous salt; the

corresponding concentration of sulphite is 27.2%. At higher temperatures, the solubility diminishes in a manner similar to that of sodium sulphate. By evaporating dilute solutions of commercial sodium sulphite containing sulphate, two other curves, one metastable to the other, and both metastable to the solid contained in the solution, are obtained having transition points of 36° and 30% and 39° and 31.5% of sodium sulphite, respectively. These results indicate that sodium sulphite and sodium sulphate form mixed crystals of varying stabilities, and that the sodium sulphite in these crystals, if it could be obtained in a pure state, would be metastable with respect to the pure form of sodium sulphite having the transition point of 22°. A. R. P.

#### Miscibility of Anhydrous Sodium Sulphite and Sulphate.

N. B. LEWIS and A. C. D. RIVETT (*J. Chem. Soc.*, 1924, 125, 1162—1167).—An investigation of the system sodium sulphite-sodium sulphate-water at 40°, 45°, and 60° by analysing solutions and moist solids in equilibrium with each other shows that there are five solution curves and five corresponding series of mixed crystals of the anhydrous salts. Solutions very rich in sulphate yield crystals very poor in sulphite; solutions containing more than 10% of sulphite give crystals richer in sulphite than the solution. The third curve is metastable with respect to the fourth, the solids of which series are richer in sulphate than the solutions from which they are derived. A. R. P.

**Action of Heat in a Vacuum on Sodium Thiosulphate and Sulphite.** PICON (*Compt. rend.*, 1924, 178, 1548—1550).—On prolonged heating at 300° in a vacuum, hydrated sodium thiosulphate loses water only. With the anhydrous salt, the main decomposition (which proceeds very slowly at 120° and is complete in 6 hours at 380—385°) is into sodium sulphite and free sulphur, small quantities of sulphate and polysulphide also being formed. Above 400°, the proportion of sulphate and polysulphide increases until rapid heating at 600° causes almost complete decomposition in accordance with the equation  $4\text{Na}_2\text{S}_2\text{O}_3 = 3\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_3$ . At 700° in a vacuum, sodium sulphite is rapidly converted into sulphate and sulphide;  $4\text{Na}_2\text{SO}_3 = 3\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}$ . In air the anhydrous thiosulphate is stable at 100° for 15 days, but at 120° slow decomposition (complete in one month) into sulphate and sulphur dioxide occurs. Since the salt always contains traces of sulphur, the primary decomposition is probably into sulphur and the sulphite, atmospheric oxidation converting the latter into sulphate and sulphur dioxide;  $\text{Na}_2\text{S}_2\text{O}_3 + 3\text{O} = \text{SO}_2 + \text{Na}_2\text{SO}_4$ . The formula  $\text{S}:\text{SO}(\text{ONa})_2$  is proposed for sodium thiosulphate. J. W. B.

#### Dissociation of some Acid Phosphates and Oxides by Heat.

D. BALAREW (*Z. anorg. Chem.*, 1924, 134, 75—78).—When the velocity of decomposition is great, the transition point can only be detected in the heating curve when the dissociation temperature is dependent on the external pressure. If the velocity of decom-

position is small, the heating curve shows no clear halt-point, and the dissociation temperature can only be determined accurately when independent of the external pressure. In an equilibrium process, no clear point of inflexion can be observed, and it is only possible to estimate the temperature at which the thermal effects of dehydration begin to exert a measurable influence on the course of the heating curve. Disodium hydrogen phosphate and uranium trioxide show transition points at  $250^{\circ}$  and  $360^{\circ}$ , respectively; these are independent of the external pressure, the temperatures obtaining at the transition point under 710 mm. and 30 mm. pressure being very similar. Strontium hydrogen phosphate shows no inflexion point in the heating curve, nor does the calcium salt at low pressures. The dehydrated phosphate does not, under microscopical examination, have the appearance of an effloresced salt, but shows that the individual granules at the moment of dehydration are melted. This phenomenon probably explains the absence of a very definite inflexion in the heating curve. The heating curves of lead dioxide are of a form which indicates that the formation from the dioxide of lead sesquioxide and red lead takes place in two stages, namely, decomposition into the monoxide and oxygen, followed by reunion with oxygen. J. B. F.

**How are Metals Attacked by Acids ?** R. GANS (*Z. physikal. Chem.*, 1924, **109**, 49—64).—The effect of 32.4% nitric acid on plates of gold-silver alloys of different compositions has been studied. The velocity of reaction is very much influenced by the content of silver; for example, an alloy of 76.43 at.-% of silver loses nearly all its silver in 470 mins., whilst one of 54.91 at.-% has lost only 18.8% after 26,340 mins. Velocity of diffusion and saturation of the acid in the neighbourhood of the plate do not appear to influence the result materially. The rate of attack increases to some extent with the thickness of the plate, possibly owing to the greater inhomogeneity in the distribution of the silver, with consequent channelling by the acid into the interior.

After removal of the silver a reddish-brown skeleton of gold remains, retaining the same form as the original except for a slight contraction, even after treatment of an alloy of 92 at.-% of silver with nitric acid. If the porous gold be heated at a low red heat, a very large contraction takes place, and ordinary compact yellow gold is left. The change is regarded as consisting simply in the filling up of the holes with neighbouring pieces of gold—a conclusion which is supported by the fact that, when the silver has only been partly extracted, heating or polishing the remaining alloy greatly reduces the rate of dissolution of the silver that is left. The difficult dissolution of silver in the dilute alloys is thus apparently due simply to the protective coating of gold which surrounds the particles.

Experiments have been made to determine whether the silver sulphide layer, formed when hydrogen sulphide attacks metallic silver, protects the silver from further action. Measurements made over a period of about 5000 hours show that the action is

very rapid at first, slows down after about 200 hours, as if it were approaching a limit, but after 500 hours increases again and then continues at an approximately constant velocity, giving no indication of completion. The reaction is evidently a complicated one, but there are some processes (Tammann, A., 1920, ii, 248) which involve pure diffusion phenomena only, for instance, the action of iodine vapour on silver, and a mathematical formula has been developed expressing the thickness of the layer formed in terms of the time, the area of the plate of metal, and the diffusion coefficient of the gas.

M. S. B.

**Influence of Crystal Habit on Photochemical Decomposition in Silver Bromide Crystals.** S. E. SHEPPARD and A. P. H. TRIVELLI (*Phot. J.*, 1923, **63**, 334).—Whilst visible photochemical decomposition commences at isolated points, its further increase is vectorial, and is orientated according to definite directions in the crystal. The accretion of the photo-product, which proceeds mainly by discontinuous increments along the lines of more rapid growth, is not uniform.

CHEMICAL ABSTRACTS.

**Electrometric Investigation of the Reaction between Thiosulphate and Silver Nitrate.** E. MÜLLER (*Z. anorg. Chem.*, 1924, **134**, 202—207).—When silver nitrate is added to a solution of sodium thiosulphate and the potential between a silver indicator electrode and a normal calomel electrode immersed in the liquid is measured and plotted against the volume of silver solution added, a marked deflection in the curve occurs at a point corresponding with the formation of  $\text{NaAgS}_2\text{O}_3$ . Further addition of the silver solution causes the formation of a white precipitate of  $\text{Ag}_2\text{S}_2\text{O}_3$ , which simultaneously becomes brown, due to decomposition into silver sulphide, and eventually a second deflection in the potential curve occurs at a point a little beyond that corresponding with the formation of  $\text{Ag}_2\text{S}_2\text{O}_3$ , due to adsorption of silver nitrate by the precipitate. If the titration is carried out at  $0^\circ$ , no decomposition of silver thiosulphate occurs until there is an excess of silver nitrate present, and the second deflection in the potential curve denotes a stoicheiometric relation between the reacting substances. In the presence of sodium acetate, the titration may be carried out at  $75^\circ$ , at which temperature the potential change at the end-point is much more marked. No indication of the formation of the complex salt,  $\text{Na}_4\text{Ag}_2(\text{S}_2\text{O}_3)_3$ , is afforded by the potentiometric titration.

A. R. P.

**High-temperature Researches. XVII. Vapour Pressures of Alkaline-earth Metals.** O. RUFF and H. HARTMANN (*Z. anorg. Chem.*, 1924, **133**, 29—45).—Measurements of the vapour pressures of the alkaline-earth metals at a series of temperatures by the method previously described (A., 1919, ii, 265) gave the following (extrapolated) values for the boiling points ( $T$ ): magnesium,  $1086^\circ$ ; calcium,  $1175^\circ$ ; strontium,  $1151^\circ$ ; and barium,  $1146^\circ$ . From these values, the latent heats of evaporation at the boiling point,  $\lambda$ , are calculated from de Forcrand's formula (the

vapour-pressure curves gave improbable high values): Mg, 30,900 cal.; Ca, 33,100 cal.; Sr, 32,500 cal., and Ba, 32,400 cal. The conventional chemical constants ( $= 0.14 \lambda/T$ ) and the critical temperatures ( $= 1.55 T$ ) are calculated also. S. K. T.

**Systematic Doctrine of Affinity. XXVI. Heats of Formation of Intermetallic Compounds. III. Calcium Alloys.** W. BILTZ and W. WAGNER (*Z. anorg. Chem.*, 1924, **134**, 1—12).—Calcium-zinc and calcium-aluminium alloys were prepared by melting together the metals in stoichiometric proportions in an atmosphere of argon. The existence of a metallic compound of the composition  $\text{CaZn}$  is doubtful. The heats of formation of these intermetallic compounds were determined from the heats of solution of the component metals and of the intermetallic compounds in hydrochloric acid of strength  $\text{HCl} : 20\text{H}_2\text{O}$ , in the case of zinc, and  $\text{HCl} : 8.8\text{H}_2\text{O}$  for aluminium and cadmium compounds, with the addition of a little platinic chloride as catalyst in each case. The values obtained were  $\text{Ca} + 10\text{Zn} = \text{CaZn}_{10} + 48$  Cal.;  $\text{Ca} + 4\text{Zn} = \text{CaZn}_4 + 29.5$  Cal.;  $2\text{Ca} + 3\text{Zn} = \text{Ca}_2\text{Zn}_3 + 40$  Cal.;  $4\text{Ca} + \text{Zn} = \text{Ca}_4\text{Zn} + 32$  Cal.;  $\text{Ca} + 3\text{Cd} = \text{CaCd}_3 + 30$  Cal.;  $\text{Ca} + 3\text{Al} = \text{CaAl}_3 + 51$  Cal.;  $3\text{Ca} + 4\text{Mg} = \text{Ca}_3\text{Mg}_4 + 43$  Cal. The densities ( $d_4^{25}$ ) were  $\text{CaZn}_{10}$ , 6.397;  $\text{CaZn}_4$ , 5.425;  $\text{Ca}_2\text{Zn}_3$ , 3.997;  $\text{Ca}_4\text{Zn}$ , 2.099;  $\text{CaCd}_3$ , 6.309;  $\text{CaAl}_3$ , 2.382. The alloy is formed in all cases from the components with a contraction in volume. J. B. F.

**Systematic Doctrine of Affinity. XXIX. Relation of Affinity and Valency and the Constitution of Intermetallic Compounds.** W. BILTZ (*Z. anorg. Chem.*, 1924, **134**, 37—48).—The experimental data obtained in previous researches on the heat of formation of intermetallic compounds are reviewed. The heat of formation, per g.-atom of each metal in turn, is calculated for each compound; thus, for example, in the case of the four zinc compounds,  $\text{CaZn}_{10}$ ,  $\text{CaZn}_4$ ,  $\text{CaZn}_{1.5}$ , and  $\text{CaZn}_{0.25}$ , respectively, the heats of formation per g.-atom of zinc are 4.8, 7.4, 13, and 32 Cal., respectively. If these heats of formation are plotted against the valency numbers (number of atoms of variable element with one atom of fixed element in each case), then for those metals which exhibit more than two valencies the valency bar is broken, whilst for compounds of similar type the slope of the valency bar is constant. Further, the heat of formation becomes less per g.-atom as the number of atoms in the molecule increases, hence the affinity likewise diminishes. If the affinity in the lowest type is small, then the tendency to form more complex compounds is essentially small. Thus the affinity in the compounds  $\text{CaZn}_{0.25}$  to  $\text{CaZn}_{1.5}$  is relatively great, becoming very small in  $\text{CaZn}_{10}$ . The results are very similar to those obtained for the heat of formation of the higher oxides of potassium and the compounds of ammonia with silver iodide, the heat of formation diminishing as the saturation proceeds. The composition of intermetallic compounds does not in general follow the stoichiometric values of salt chemistry, but is more complex. The affinity is influenced by the relative electrochemical character of the metals. Inter-

metallic compounds are bad conductors relatively to their components. The uncombined metal contains free negative electrons which are the source of combining energy. In the formation of an intermetallic compound, the free electrons of one constituent may combine with the atom of the other to form a polar compound; implying high energy of formation in simple primary compounds. A further possibility is that the electrons return in the bond with the re-formation of the atom from the ion; accordingly, the intermetallic compound is rich in metal atoms, whilst in the uncombined metal the metallic ion and the free electron prevail. [Cf. A., 1922, ii, 566.] J. B. F.

**Rôle of Water in Reactions in the Solid State. I. D. BALAREW** (*Z. anorg. Chem.*, 1924, **134**, 117—124).—Tension of water vapour in the system calcium oxide-silica determines, not only the velocity of the reaction between the oxides, but also the initial temperature at which the reaction proceeds with measurable velocity. A mixture containing equivalent proportions of the two oxides, when heated at  $920^{\circ}$  in a stream of hydrogen saturated with water vapour at  $95^{\circ}$ , showed 46% of combined calcium oxide after a period of 150 minutes, but, in an atmosphere of slightly moist hydrogen, only 14% after 120 minutes. Even at this temperature, adsorption of water takes place, and although no definite compound is formed, some of the chemical properties of the hydrate exist. In the system barium oxide-calcium carbonate no reaction takes place between the solid phases. At about  $360^{\circ}$ , the barium hydroxide always present in the oxide melts, and only as such reacts with the calcium carbonate. The reaction between barium oxide and other carbonates and sulphates is very similar. The dissociation pressure of the carbon dioxide and sulphur trioxide may also be a factor. In the system sodium sulphate-barium carbonate no detectable reaction takes place at  $430^{\circ}$  when these substances are carefully dried, whilst in presence of water vapour double decomposition becomes rapidly possible. The natural formation of wollastonite is considered. In the interior of the earth, the tension of water vapour will be high (above 1 atm.) and the reaction between calcium carbonate and silicates is thereby facilitated. On the other hand, the high water vapour tension may result in the formation of calcium hydroxide by hydrolysis, which will melt and as such react with silicates. J. B. F.

**Calcium Sulphate Solutions.** P. JOLIBOIS and L. CHASSEVENT (*Compt. rend.*, 1924, **178**, 1543—1546; cf. A., 1923, ii, 417, 565).—The solubility curve of  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  is traced in its metastable region. The rate of crystallisation of the dihydrate, measured by successive determinations of the concentration of the solution in contact with the crystals, is small at low temperatures, reaches a maximum at some temperature below the transition temperature ( $107^{\circ}$ ), and vanishes at this temperature. Seeding the solution with the dihydrate starts immediate crystallisation proportional to the weight of the dihydrate added, but the addition of anhydrous calcium sulphate (calcined at  $200\text{--}1000^{\circ}$ ) does not affect the

crystallisation curve. The explanation of the setting of plaster of Paris, calcined at high temperatures, must therefore not be sought in the starting of crystallisation, but rather in that transformation into the hemihydrate in contact with the solution is slower the higher the temperature of calcination in consequence of a diminution in the active surface. J. W. B.

**Interchange of Acids between Solid Phases.** J. A. HEDVALL and J. HEUBERGER (*Z. anorg. Chem.*, 1924, **135**, 49—80; cf. A., 1922, ii, 766; 1923, ii, 860).—The alkaline-earth oxides were heated separately and successively with various orthophosphates and pyrophosphates, the temperatures at which reaction commenced, rise in temperature due to reaction, as determined from temperature-time curves, and nature of the product, being recorded in each case. Each oxide reacts with all the orthophosphates at about the same temperature, 300—350° for barium, 450—470° for strontium, and about 520° for calcium oxide, the reaction in most cases being in the sense  $R_3(PO_4)_2 + 3XO \rightarrow X_3(PO_4)_2 + 3RO$ . With pyrophosphates, the reaction conforms to the general equation  $3R_2P_2O_7 + 3XO = 2R_3(PO_4)_2 + X_3(PO_4)_2$ , excess of oxide then reacting as with the orthophosphates; the reaction temperatures are for each case nearly independent of the proportions, and certain regularities are observed throughout.

The general reaction for the exchange of acid,  $MO + M'A = MA + M'O + Q$ , occurs very rapidly, requiring only a few seconds, and is the more vigorous as MO is more basic than M'O. The temperature at which reaction commences is lowest for barium oxide and highest for calcium oxide. The reactions cannot be explained by assuming an active gas phase, but are to be regarded as real lattice reactions. With silver nitrate, which has a transition temperature of about 160°, the oxides react at 164—172°; with silver sulphate (transition temperature 411°) barium oxide reacts at 342°, strontium and calcium oxides at 422°. The reaction temperature must depend on the particle mobility, not only in the oxide lattice, but in the salt lattice. S. I. L.

**Darkening of Phosphorescent Zinc Sulphide.** L. B. LOEB (*Z. physikal. Chem.*, 1924, **109**, 77—78).—Loeb and Schmiedeskamp (A., 1922, ii, 8) have been misunderstood (cf. Schleede, A., 1923, ii, 813; Lenard, A., 1923, ii, 109). Their experimental results made the correctness of Perrin's theory possible, but were not sufficient to prove it. The two processes may be quite different. According to Lenard's experiments (*loc. cit.*), the phosphorescence of zinc sulphide is excited by longer wave-lengths than are necessary to bring about the blackening. M. S. B.

**Equilibrium between Fused Metals and Salts. II.** R. LORENZ (*Z. anorg. Chem.*, 1924, **134**, 105—116).—Theoretical. The equilibrium  $Cd + PbCl_2 \rightleftharpoons Pb + CdCl_2$  is worked out from the point of view of the law of mass action, and formulæ are deduced which are tested by the experimental observations of Tammann and others; the value of the reaction constant thus calculated is

surprisingly constant. For this special case, the law of mass action is valid for all concentrations of the liquid phase.

J. B. F.

**Voltages of the Daniel Cell with Fluid Chlorides, and the Potential Series of the Metals in Fluid Chlorides.** G. TAMMANN (*Z. anorg. Chem.*, 1924, **133**, 267—276).—The separation of the fused chlorides in the cell  $\text{Pb}|\text{PbCl}_2|\text{AgCl}|\text{Ag}$  by a glass partition causes a fall in the voltage of 0.228 volt at 530° and 0.266 volt at 696°. The glass partition was strongly attacked. The potential difference for the cell  $\text{Zn}|\text{ZnCl}_2|\text{PbCl}_2|\text{Pb}$  is 0.269 at 600° and 0.261 at 700°, both values being considerably greater than the differences of the values for the cells  $\text{Zn}|\text{ZnCl}_2|\text{AgCl}|\text{Ag}$  and  $\text{Pb}|\text{PbCl}_2|\text{AgCl}|\text{Ag}$  at the corresponding temperatures. The potential differences for the metals may, however, be determined from the voltages of cells consisting of the fused chloride in contact with the metal and chlorine. The differences between the values for the cells  $\text{Cd}|\text{CdCl}_2|\text{Cl}_2$  and  $\text{Pb}|\text{PbCl}_2|\text{Cl}_2$  agree fairly well with the calculated differences between cadmium and lead at 600° and 700°; if the difference is known for any pair of metals, the equilibrium for a mixture of the metals in contact with a mixture of their chlorides can be calculated. Several possible cases are considered theoretically. The reactions between various metals and the fused chlorides of others have been examined qualitatively, and are classified into four groups according to the vigour of reaction. Comparison of the potential series of the metals in solutions of their salts with the order given by heats of formation of the chlorides shows that only iron, cobalt, and nickel change their places, becoming nobler at the higher temperatures.

S. I. L.

**Reduction of Thin Films of Oxide on Copper and Nickel.** G. TAMMANN and C. F. MARAIS (*Z. anorg. Chem.*, 1924, **135**, 127—142).—The alteration in thickness of a film of oxide may be measured by the time taken for the boundary between two interference colours to move over a measured surface interval, the film being wedge-shaped; this rate in millimetres per minute is plotted against the velocity of the hydrogen used for reduction. The rate of diminution of thickness of a nickel oxide film increases with the velocity of the gas, but finally reaches a constant value. At suitable rates, the rate of diminution of copper oxide films is also independent of the velocity of the gas; the films diminish regularly for thicknesses above 360  $\mu\mu$  and below 280  $\mu\mu$ ; between these limits the rate of reduction is much greater, and varies with the time. For thicknesses above 410  $\mu\mu$ , the colours do not change regularly; such films apparently become reduced, forming a film of metal without alteration of thickness. The rate of diminution is given by:  $\log dl/dt = 0.523 (t-114)$  up to 248°, and  $\log dl/dt = 1.54 (t-204)$  above 248°; using carbon monoxide, the corresponding expressions are 0.276 ( $t-250$ ) up to 610°, and 1.25 ( $t-527$ ) above 610°; with carbon monoxide, the reduction requires a much higher temperature than with hydrogen. The results are in conflict with those of Wright and Luff (*J. Chem. Soc.*, 1878, i, 1);



the precipitated oxide is reduced by all agents at lower temperatures than the oxide film on the metal, the respective temperatures using carbon monoxide being  $410^{\circ}$  for the film and  $135^{\circ}$  for the precipitated form.

In the reduction of copper oxide films by carbon monoxide, the rate is proportional to the thickness of the films, the thin films permeable by oxygen being more quickly reduced than thicker, more stable films; the boundary is between 275 and  $350\ \mu\mu$ . The course of the reduction of nickel oxide films by hydrogen suggests that an intermediate lower oxide not easily permeable by hydrogen at lower temperatures is formed.

S. I. L.

**X-Ray Spectra of Amalgams.** C. VON SIMSON.—(See ii, 449.)

**Heats of Solution of Metals in Mercury and in Gold Amalgam, and some Heats of Mixing for Amalgams.** G.

TAMMANN and E. OHLER (*Z. anorg. Chem.*, 1924, **135**, 118—126).

—The atomic heats of solution in mercury of cadmium, tin, and lead at the ordinary temperatures have been determined as +505, -2541, and -1658 g.-cal. The atomic heats calculated from the temperature coefficients of the potentials by Richards and Lewis (A., 1899, ii, 267) and van Heteren (A., 1905, ii, 39) for cadmium and tin respectively were +505 and -3000 g.-cal. At  $97^{\circ}$  the following atomic heats of solution were determined: cadmium, +473.4; tin, -3148; lead, -2172; zinc, -1835; bismuth, -3730; gold, -2047 g.-cal.; from these values the specific heats of the amalgams ( $c_1$ ) and the heat capacity of the mercury contained in 1 g. of each ( $c_{Hg}$ ) have been calculated at  $14^{\circ}$  as follows:  $c_1$ : cadmium, 0.03376; tin, 0.03311; lead, 0.03300;  $c_{Hg}$ : cadmium, 0.03251; tin, 0.03320, and lead, 0.03307. The atomic heats of fusion at  $14^{\circ}$  and  $97^{\circ}$  calculated from these figures are: cadmium, -744 and -961.3; tin, -957 and -1271; and lead, -550 and -706.5, respectively.

The heat of solution for 1 g.-atom of magnesium in mercury has been calculated from the heats of solution of magnesium and its amalgam in hydrochloric acid as +17,300 g.-cal. The atomic heats of solution in gold amalgam (about 0.2% Au) have been determined as zinc, +13,930; tin, +8938; cadmium, +9270; lead, -2195; and bismuth, -3675, respectively; the values indicate that the compound of zinc with gold is not dissociated in mercury solution at the concentration of experiment. The heats of admixture of magnesium or cerium amalgams with the amalgams of tin and zinc, which are considerable in a damp atmosphere, are very small in a dry inert atmosphere, indicating that the heats required to decompose the amalgams are completely compensated by the heats of formation of the alloys.

S. I. L.

**Catalysis. XXIV. Action of Nitric Acid on Mercury at Different Temperatures and in the Presence of Different Catalysts.** C. C. PALIT and N. R. DHAR (*Z. anorg. Chem.*, 1924, **134**, 191—201).—The first product of the action of nitric acid on mercury is mercurous nitrite, which is formed in greatest quantity

by the use of 26% nitric acid at 30°. The yield is greatly increased in the presence of mercurous or ferric nitrate, but no mercurous nitrite is formed if sodium nitrite or carbamide is added to the nitric acid or if the temperature is allowed to rise above 52°. Sodium nitrite and nitric acid interact readily with mercury in the cold to give a complex sodium mercurinitrite, whilst carbamide and nitric acid have very little action on the metal. Ferrous sulphate accelerates dissolution of mercury and other metals in nitric acid at the ordinary temperature owing to the formation of nitrous acid either by direct reduction of the nitric acid by the ferrous sulphate or by the intermediate formation of the nitric oxide-ferrous sulphate complex, which then yields nitrous acid, thus:  $\text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O} \rightleftharpoons 3\text{HNO}_2$ . Ferric nitrate has a slight retarding action on the rate of dissolution of mercury in nitric acid although it accelerates dissolution of copper and silver in the acid.

A. R. P.

**Constitution of Mercurous Compounds.** E. SCHILOW (*Z. anorg. Chem.*, 1924, **133**, 55—66).—The transport number of mercurous ions in dilute nitric acid solutions of mercurous nitrate is 0.48; this proves that dissociation takes place according to the equation  $\text{Hg}_2(\text{NO}_3)_2 \rightleftharpoons \text{Hg}_2^{++} + 2\text{NO}_3'$ . The result is confirmed by conductivity measurements. The  $\text{Hg}_2^{++}$  ion may be regarded as consisting of two mercury atoms, each with six outer electrons and one valency electron, which have shared their valency electrons and so formed two complete octets.

S. K. T.

**Systematic Doctrine of Affinity. XXVII. Heats of Formation of Intermetallic Compounds. IV. Cerium Alloys.** W. BILTZ and H. PIEPER (*Z. anorg. Chem.*, 1924, **134**, 13—24).—The purified cerium contained about 94% Ce associated with about 4.5% of rare earths. Alloys of cerium with magnesium and aluminium, respectively, were prepared and the heats of formation of the intermetallic compounds determined in a manner similar to that previously described (see this vol., ii, 482). The heat of solution varies slightly with the strength of the hydrochloric acid used. For  $\text{CeAl}_4$ ,  $\text{HCl} : 8.8\text{H}_2\text{O}$  was used, and for other alloys,  $\text{HCl} : 20\text{H}_2\text{O}$ . The cerium-magnesium alloys were protected with a coating of paraffin or collodion. The values obtained were:  $\text{Ce} + 3\text{Mg} = \text{CeMg}_3 + 17 \text{ Cal.}$ ;  $\text{Ce} + \text{Mg} = \text{CeMg} + 13 \text{ Cal.}$ ;  $3\text{Ce} + \text{Al} = \text{Ce}_3\text{Al} + 22 \text{ Cal.}$ ;  $\text{Ce} + 4\text{Al} = \text{CeAl}_4 + 39 \text{ Cal.}$  The densities ( $d_4^{25}$ ) were: Mg, 1.75; Ce, 6.61;  $\text{CeMg}_3$ , 3.32;  $\text{CeMg}$ , 4.60;  $\text{Ce}_3\text{Al}$ , 6.21;  $\text{CeAl}_4$ , 4.02. The volume changes, with one exception, show an increase and were:  $\text{CeMg}_3$ , +2.7;  $\text{CeMg}$ , +2.8;  $\text{Ce}_3\text{Al}$ , -1.8;  $\text{CeAl}_4$ , +1.2(% change in each case). The cerium-magnesium alloys are less stable in the air than cerium-aluminium alloys. The densities of the cerium alloys are lower than those of previous observers, the difference being attributed to the variation of the purity of the cerium metal used.

J. B. F.

**Aluminium Oxide Gel and Sol.** A. LOTTERMOSER and F. FRIEDRICH (*Ber.*, 1924, **57**, [B], 808—813).—A method is described

for the preparation of an aluminium oxide gel, almost completely free from electrolytes, which does not alter on keeping. 0.1*N*-Ammonia solution cooled in ice was kept very gently stirred by a circulating current of air, and 0.1*N*-aluminium chloride solution was added intermittently; the milky product was then dialysed in a collodion membrane until the washings were free from chlorine, the conductivity after 40—50 hours being about 0.00001 ohm<sup>-1</sup>. The gel so obtained was stable and could be peptised by aluminium chloride even after 6 months. It was not possible to obtain the gel absolutely free from the last traces of electrolyte. It could also be peptised by ammonia, forming a new although unstable sol in which the disperse phase is negatively charged. Measurements of the viscosity of the stable gel were made from 17° to 100° to determine the reason for the rule that aluminium oxide should be precipitated at 70—80°; the results show that the viscosity increases noticeably above 80°. F. A. M.

### Plasticity. III. Plastic Masses with Aluminium Oxide.

O. RUFF and W. GOEBEL (*Z. anorg. Chem.*, 1924, **133**, 220—229).—The conditions for obtaining plastic masses are similar to those required with zirconia (see ii, 492); the best results were obtained with normal hydrochloric and nitric acid solutions, the products being finally heated at 1800°; the burnt forms were almost equal to those ordinarily obtained in ceramics. S. I. L.

**The System Aluminium Oxide-Silica.** N. L. BOWEN and J. W. GREIG (*J. Amer. Ceram. Soc.*, 1924, **7**, 238—254).—A preparation composed of 3Al<sub>2</sub>O<sub>3</sub>:2SiO<sub>2</sub> is a homogeneous aggregate of crystals of one kind at all temperatures up to the m. p., 1810°. A slight excess of alumina causes inhomogeneity, corundum also appearing; a slight excess of silica brings in a little cristobalite below 1545° and a little glass (liquid) above that temperature. Only one eutectic occurs, that between 3Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub> and cristobalite. There is no eutectic between 3Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub> and corundum as the 3:2 compound melts incongruently, breaking up into corundum and liquid at 1810°; corundum finally disappears at about 1920° and the mixture is then completely molten. The breaking up of 3Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub> into corundum and liquid at 1810° is exhibited in all preparations containing down to 55% Al<sub>2</sub>O<sub>3</sub>. This range includes the 1:1 ratio (63% Al<sub>2</sub>O<sub>3</sub>), so that a mixture of that composition, whilst it consists as it approaches 1810° of liquid and crystals of Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>, experiences at this point an abrupt increase in the quantity of liquid accompanied by the formation of a little corundum and a heat effect that was previously regarded as fixing the m. p. of the 1:1 compound; the same heat effect obtained in slightly more aluminous mixtures was regarded as the result of the melting of the eutectic between a 1:1 compound and corundum. The optical properties of large crystals of 3Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub> and those of natural sillimanite were compared and found to be very closely related although the two do not form solid solutions together.

When natural sillimanite is heated above  $1545^{\circ}$  it behaves exactly like a mixture of  $1\text{Al}_2\text{O}_3 : 1\text{SiO}_2$  except that the changes take place less rapidly owing to differences in structure. The presence of much iron or titanium in solid solution may alter the refractive index and make the crystals optically indistinguishable from sillimanite. The compound  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  and sillimanite give identical X-ray spectra. [Cf. *B.*, 1924, 512.] H. S. H.

**Precipitation of Manganese from Meteoric Solutions.** G. A. THIEL (*Amer. J. Sci.*, 1924, [v], 7, 457—472).—Very dilute solutions of manganese sulphate or hydrogen carbonate (32 to 200 parts Mn per million), with or without peat solution or ferrous sulphate, were kept in contact for several months at the ordinary temperature with various minerals and rocks in a powdered form, and the amount of manganese deposited was determined. Magnesium carbonate, either as a mineral or as a rock constituent, is the most active agent for precipitating manganese from such solutions. Iron carbonate and calcium carbonate produce partial precipitation from carbonate solutions, but have no effect on sulphate solution in association with humic acid. Silicates are very inactive. Experiments were also made on the relative solubilities of manganese and iron minerals in various dilute solutions. The results are discussed in connexion with the deposition of manganese ores by cold meteoric waters. L. J. S.

**Kopp's Law Applied to Crystalline Substances and Isomolar Complex Compounds.** W. BILTZ and E. BIRK (*Z. angew. Chem.*, 1924, 134, 125—136).—The density of the anhydrous halides and hexammine halides of manganese, zinc, and bi- and ter-valent iron and chromium have been determined at  $25^{\circ}$  compared with that of petroleum,  $d_4^{25}$  0.7975. The results are as follows:  $\text{Mn}(\text{NH}_3)_6\text{Cl}_2$ , 1.372;  $\text{Mn}(\text{NH}_3)_6\text{Br}_2$ , 1.784;  $\text{Mn}(\text{NH}_3)_6\text{I}_2$ , 2.087;  $\text{Zn}(\text{NH}_3)_6\text{Cl}_2$ , 1.492;  $\text{Zn}(\text{NH}_3)_6\text{Br}_2$ , 1.906;  $\text{Zn}(\text{NH}_3)_6\text{I}_2$ , 2.114;  $\text{FeCl}_2$  (fused), 3.162;  $\text{FeBr}_2$  (sublimed), 4.624;  $\text{FeI}_2$  (sublimed), 5.315;  $\text{Fe}(\text{NH}_3)_6\text{Cl}_2$ , 1.428;  $\text{Fe}(\text{NH}_3)_6\text{Br}_2$ , 1.811;  $\text{Fe}(\text{NH}_3)_6\text{I}_2$ , 2.052;  $\text{FeCl}_3$  (sublimed), 2.898;  $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$ , 1.540;  $\text{CrCl}_2$ , 2.878;  $\text{CrBr}_2$ , 4.356;  $\text{CrI}_2$ , 5.196;  $\text{Cr}(\text{NH}_3)_6\text{Cl}_2$ , 1.392;  $\text{Cr}(\text{NH}_3)_6\text{Br}_2$ , 1.717;  $\text{Cr}(\text{NH}_3)_6\text{I}_2$ , 1.852;  $\text{CrCl}_3$ , 2.784;  $\text{CrBr}_3$ , 4.250;  $\text{CrI}_3$ , 4.915;  $\text{Cr}(\text{NH}_3)_6\text{Br}_3$ , 2.151;  $\text{Cr}(\text{NH}_3)_6\text{I}_3$ , 2.425. The molecular volumes of these compounds calculated from the above figures give results which agree closely with those calculated from the molecular volumes of the potassium halides. The molecular volumes of the crystallised anhydrous halides of manganese, iron, cobalt, nickel, chromium, cadmium, bismuth, iridium, thorium, and tantalum are approximately equal, irrespective of the valency of the metal, to the sum of the atomic volume of the metal and the zero atomic volume of the halogen (16.2 for chlorine, 19.2 for bromine, 24.3 c.c. for iodine). The hexammine halides of the bivalent metals follow the same law, the zero molecular volume of each ammonia group being 20 c.c. Comparison of the molecular volumes of the hexammine-cobaltous and -chromous halides with those of the corresponding luteo-cobaltic and -chromic compounds shows that the

two figures are the same within a few decimal points; e.g., the molecular volume of  $\text{Co}(\text{NH}_3)_6\text{Cl}_2$  is 156.9, that of  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  is 156.4. These compounds may therefore be called isomolar ("gleichräumig"). Hexammine-ferrous chloride is not isomolar with the corresponding ferric compound, as that is not a "luteo"-compound.

A. R. P.

**Anhyseretic Properties of Iron and Nickel.** J. R. ASHWORTH.—(See ii, 444.)

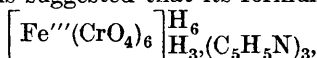
**Kinetics of the Tempering Process in Steel.** W. FRAENKEL and E. HEYMANN (*Z. anorg. Chem.*, 1924, **134**, 137—171).—The tempering of quenched carbon steels at temperatures between 78° and 360° has been followed by measuring the changes in the density and electrical resistance during the treatment. The velocity of the tempering process depends on the temperature, and the temperature coefficient is of the same order as that of a chemical reaction in a homogeneous phase. The change of electrical resistance during tempering follows the kinetic law  $-dc/dt = Kc^{10}$ , which supplies evidence for the existence of a carbide  $\text{FeC}_{8-10}$  in osmondite. The results obtained in electrolytic solution experiments suggest that the carbon in martensite exists in a state of atomic dispersion. [Cf. *B.*, 1924, 559.]

A. R. P.

**Hardness of Iron-Nickel Alloys.** H. SCHOTTKY (*Z. anorg. Chem.*, 1924, **133**, 26—28).—The maximum hardness of iron-nickel alloys depends on the co-existence of two solid solutions, viz.,  $\alpha$ -iron in  $\alpha$ -nickel and  $\gamma$ -iron in  $\alpha$ -nickel. [Cf. this vol., ii, 189.]

S. K. T.

**Ferri-chromic Acid Compounds.** R. WEINLAND and E. MERGENTHALER (*Ber.*, 1924, **57**, [B], 776—778).—Three new co-ordinated compounds are described. *Tripyridine hexachromato-ferriate*,  $\text{Fe}_2\text{O}_3 \cdot 12\text{CrO}_3 \cdot 6\text{C}_5\text{H}_5\text{N} \cdot 9\text{H}_2\text{O}$ , is obtained as an orange, microcrystalline powder on dissolving ferric nitrate and chromic anhydride in a minimum amount of water and adding pyridine. It has no odour of pyridine and loses no water in a vacuum over sulphuric acid. It is suggested that its formula is



corresponding with the class of ferromolybdates discovered by Struve (*Bull. Acad. Petersb.*, 1853, **12**, 145). On mixing solutions of ferric nitrate, chromic acid, and ammonia and heating on a water-bath, the carmine-red insoluble *ammonium dichromato-ferriate*,  $[\text{Fe}(\text{CrO}_4)_2]\text{NH}_4$ , separates. The corresponding *potassium salt* ( $+2\text{H}_2\text{O}$ ) forms a sparingly soluble, dark orange-red, microcrystalline powder.

F. A. M.

**Electromotive Behaviour of the Compound  $\text{CoSn}$ .** G. TAMMANN and A. KOCH (*Z. anorg. Chem.*, 1924, **133**, 179—186).—The crystalline substance,  $\text{CoSn}$ , shows a markedly more noble potential than either cobalt or tin, or the compound  $\text{Co}_3\text{Sn}$ , corresponding with an exceptional passivity comparable with that of

chromium and the richer chromium-iron alloys, but in spite of this the compound precipitates copper from copper sulphate solutions. The potential appears to be further lowered with increase of the oxygen content of the electrolyte, but the compound is not suitable for measurement of oxygen concentrations.

S. I. L.

**Systematic Doctrine of Affinity. XXVIII. Heats of Formation of Intermetallic Compounds. V. Cobalt-Aluminium, Copper-Zinc, and Copper-Tin Alloys.** W. BILTZ (*Z. anorg. Chem.*, 1924, **134**, 25-36).—The heats of formation of  $\text{CoAl}_5$  and  $\text{CoAl}$  were determined from the heats of solution of the component metals and metallic compound in hydrochloric acid of strength  $\text{HCl} : 8 \cdot 8 \text{H}_2\text{O}$ ; for  $\text{Cu}_3\text{Sn}$ ,  $\text{HCl} : 20 \text{H}_2\text{O}$  was used, and for  $\text{Cu}_3\text{Zn}_3$  a solution of bromine in aqueous potassium bromide was used as solvent. The results obtained were:  $2\text{Co} + 5\text{Al} = \text{Co}_2\text{Al}_5 + 86 \text{ Cal.}$ ;  $\text{Co} + \text{Al} = \text{CoAl} + 32 \text{ Cal.}$ ;  $2\text{Cu} + 3\text{Zn} = \text{Cu}_2\text{Zn}_3 + 16 \text{ Cal.}$ ;  $3\text{Cu} + \text{Sn} = \text{Cu}_3\text{Sn} + 8 \text{ Cal.}$  The solution of the metals in concentrated bromine solution results in a complicated state of equilibrium between simple and polybromides and the same state of equilibrium may not always be attained. The heat of dilution is very similar for the metallic compound and the mixture of the compound. The molecular heat of solution of a mixture  $2\text{Cu} + 3\text{Cd}$  in  $\text{HCl} : 20 \text{H}_2\text{O}$  is greater by 3 Cal. than for the compound  $\text{Cu}_2\text{Cd}_3$ , whereas in previous experiments (see this vol., ii, 18), in which bromine-potassium bromide solution was used as solvent, the heat of formation of  $\text{Cu}_2\text{Cd}_3$  was  $-1 \cdot 3 \text{ Cal.}$  It is concluded that the true value for the heat of formation of  $\text{Cu}_2\text{Cd}_3$  is 3 Cal., and not  $-1 \cdot 3 \text{ Cal.}$  as previously found. The compounds are formed in all cases with a contraction in volume.

J. B. F.

**Equilibrium of the Reduction of Nickel and Cobalt Chlorides and Bromides by Hydrogen.** G. CRUT (*Bull. Soc. chim.*, 1924, [iv], **35**, 550-584).—The reduction of nickel chloride by hydrogen is a true reversible reaction; equilibrium is reached at  $445^\circ$  when the concentration of hydrogen chloride is about 59%. No false equilibria could be detected. The equilibrium constant,  $K$ , is given by the expression  $L/4 \cdot 571T + \log p + \log [\text{HCl}]^2/[\text{H}_2]$ , where  $p$  is the equilibrium pressure and  $L$  the heat of the reaction ( $-30 \cdot 7 \text{ cal.}$  at  $15^\circ$ ). The value of  $K$  over the temperature range  $310-445^\circ$  is 11.28. The reverse reaction is very slow. Hydrogen chloride does not appear to attack nickel reduced from its chloride at  $210^\circ$  or above; the metal assumes a compact form which offers less surface to the gas. Nickel reduced from the oxide reacts readily under these conditions. The value of  $K$  for the reduction of cobalt chloride is given by a similar expression to the above ( $L = 32 \cdot 0 \text{ cal.}$  at  $15^\circ$ ); it is 10.9 at  $445^\circ$ . Special experimental precautions had to be taken with this salt and with the bromides of nickel and cobalt. For nickel bromide and cobalt bromide, respectively (at  $445-575^\circ$ ),  $K = 12 \cdot 05, 11 \cdot 87$ ;  $L$  ( $15^\circ$ )  $36 \cdot 9 \text{ cal.}, 39 \cdot 2 \text{ cal.}$ ; heat of formation from metal and gaseous bromine,

61.5 cal., 63.8 cal.; heat of solution of anhydrous salt, 18.2 cal., 17 cal.

Calorimetric determinations of the heats of solution of the anhydrous bromides gave 18.9 cal. for the nickel salt and 18.4 cal. for the cobalt salt. S. K. T.

**Stability of Chromates at High Temperatures.** M. R. NAIR and H. E. WATSON (*Proc. Asiatic Soc. Bengal*, 1922, **18**, 73).—A study of the equilibrium between chromium trioxide and bases in the presence of air. Calcium oxide and chromium trioxide yield calcium chromate slowly at 650°, but the product begins to decompose at 750°. Excess of calcium oxide increases the rate of formation and the amount of decomposition at higher temperatures. A mixture of calcium oxide, sodium carbonate, and chromium trioxide (1.7 : 0.65 : 1) gave a quantitative yield of chromate in 4 hours at 660° and in 5 minutes at 1050°. CHEMICAL ABSTRACTS.

**Plasticity. I.** O. RUFF (*Z. anorg. Chem.*, 1924, **133**, 187—192).—Plasticity arises from the possibility of displacing molecular layers or complexes of a material relatively to one another without tearing them apart. Plastic materials may be divided into those with one component, and those with several. The latter may be divided into those formed by kneading of a solid substance in a viscous fluid, and those obtained by concentration of suspensions of lyophile substances; to the latter division belong the clays. The theoretical conditions necessary for the preparation of plastic masses of this division are considered. S. I. L.

**Plasticity. II. Plastic Masses with Zirconium Dioxide.** O. RUFF and J. MOCZALA (*Z. anorg. Chem.*, 1924, **133**, 193—218).—The pure oxide, even when ground to a fineness of 0.5 $\mu$ , shows no plastic properties with pure water. In order to obtain plastic masses, the surface of the oxide must first be suitably modified by treatment with fused alkali or dilute acid, the latter giving the best results. If after the acid treatment the material is dialysed, it loses its property of becoming plastic, but regains it after further treatment. Crucibles prepared from the plastic masses after firing are highly resistant to temperature, but porous unless burned at very high temperatures; addition of thoria, yttria, and other oxides reduces the porosity. Crude oxide ores may also be employed, but yield vessels resistant only up to 1600°. S. I. L.

**Hafnium Content of Zirconium Ores.** G. HEVESY and V. T. JANTZEN (*Chem. News*, 1924, **128**, 341—342).—The hafnium content of thirteen minerals containing zirconium has been determined and, except in the case of three samples of zircon and three samples of thortveitite, the Hf : Zr ratio was found to be about 1 : 30. A blue, transparent zircon from Siam contained 3.5% HfO<sub>2</sub>, a malacon from Hitterö 5% HfO<sub>2</sub>, malacon from Madagascar 7% HfO<sub>2</sub>, together with more than 60% ZrO<sub>2</sub> in each case. Thortveitite from Befanamo, Madagascar, contains 3.2% HfO<sub>2</sub> and only

2.0%  $\text{ZrO}_2$  and is so far the only mineral found which contains more hafnia than zirconia.

A. R. P.

**Spectrum of Vanadium.** O. LAPORTE.—(See ii, 435.)

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## Mineralogical Chemistry.

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**Composition of the Interior of the Earth. II.** G. TAMMANN (*Z. anorg. Chem.*, 1924, **134**, 269—276).—Aluminium and manganese both replace iron in the silicate  $\text{FeO}, \text{CaO}, 2\text{SiO}_2$  when heated to fusion but nickel has practically no action. It would, therefore, appear that, if the centre of the earth consists of metallic iron and the outer shell principally of an iron silicate, then all metals having an oxide with a greater heat of formation than ferrous oxide will occur only in traces in the molten iron, which should contain therefore only nickel in appreciable proportions, as the oxides of zinc, cobalt, cadmium, bismuth, and lead, of which the heats of formation approach that of iron oxide, occur only in relatively small proportions in the silicate layer. Iron and iron sulphide are miscible in all proportions at temperatures above that at which iron crystals begin to form in the liquid; if, however, a layer of molten  $\text{Fe}_2\text{SiO}_4$  is maintained above the liquid mixture, separation of the metallic layer into two components, one rich and the other poor in sulphur, begins. Above a certain critical temperature, therefore, the earth's substance will consist of two layers only, but below this temperature a layer rich in sulphides will appear between the inner mass of molten iron and the outer silicate layer. A. R. P.

**Magmatic Gases of Etna Lava collected by the Method of Inhalation.** G. PONTE (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 237—241).—Although observations demonstrating a distinct reducing action of basic magma (cf. Brunn, *Bull. Soc. franç. Min.*, 1914, **37**) have led to the abandonment of the old hypothesis that flowing lava may hold water vapour in solution, experimental evidence on the latter point is lacking. The inhalation method now employed with Etna lava at  $940\text{--}945^\circ$  consists in forcing an inert gas into the lava and then withdrawing it with the exhaled gases it entrains. When dry nitrogen was used, the condensed material withdrawn contained sodium and potassium chlorides and showed lithium lines in its spectrum; the gases comprised carbon monoxide and dioxide, hydrogen, sulphur dioxide, and methane. Moist nitrogen gave similar results, except that ammonium chloride also was found and the amounts of all the gaseous components, particularly the hydrogen, were increased. These results confirm the absence of moisture from the basic magma, and the increase in the quantity of hydrogen when moisture is introduced is proof that the magma exhibits an energetic reducing action. T. H. P.

**Crystalline Magnesite of Valle della Germanasca.** E. GRILL (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 149—152).—At Prali (Valle della Germanasca) crystalline magnesite occurs abundantly in lenticular forms having marked saccharoid structure,  $d\ 3.002$ . Analysis gave  $\text{FeCO}_3$ , 3.16%;  $\text{CaCO}_3$ , 1.15%;  $\text{MgCO}_3$ , 95.69%. The compositions of magnesites from Ciappanica (Val Malenco) and Badia d'Admont (Styria) are also given. T. H. P.

**Ludwigite from Peru.** M. G. EDWARDS (*Amer. J. Sci.*, 1924, [v], **7**, 486—488).—Velvety black, finely fibrous ludwigite occurs abundantly in metamorphic limestone at a quartz-monzonite contact near the summit of the Andes in province Yauli. The mineral is opaque and has a dark-green streak. Analysis by G. PLEWS gave I, and deducting impurities II:

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MgO}$	$\text{CaO}$	$\text{MnO}$	$\text{B}_2\text{O}_3$	$\text{H}_2\text{O}$	n.d.	Total
I.	3.80	0.92	34.55	5.27	34.80	3.75	trace	14.00	0.25	2.66	100.00
II.	—	1.03	38.59	5.88	38.87	—	—	15.63	—	—	100.00

This agrees with the general formula  $4(\text{Mg},\text{Fe})\text{O},\text{Fe}_2\text{O}_3,\text{B}_2\text{O}_3$ , and corresponds with a mixture of 9 parts of magnesioludwigite ( $3\text{MgO},\text{B}_2\text{O}_3,\text{MgO},\text{Fe}_2\text{O}_3$ ) with 4 of ferroludwigite ( $3\text{MgO},\text{B}_2\text{O}_3,\text{FeO},\text{Fe}_2\text{O}_3$ ). L. J. S.

**Radioactive Chrysocoll from the Bena de Padru Mine.** E. PUXEDDU and E. MANCA (*Annali Chim. Appl.*, 1924, **14**, 123—127).—Chrysocoll occurs in the Bena de Padru mine in the Ozieri region in three different varieties: (1) A turquoise-coloured variety,  $d^{20}\ 2.40$ , forming small, compact, amorphous masses with conchoidal fracture of pale blue or green tint and of the formula  $\text{H}_2\text{CuSiO}_4,\text{H}_2\text{O}$  or  $\text{CuSiO}_3,\text{H}_2\text{O}$ . (2) An impure reddish-brown form containing a comparatively high proportion of iron and exhibiting colloidal properties. (3) A reddish-brown variety containing chalcocite and copper carbonate as impurities and having the composition  $\text{Cu}_3\text{SiO}_4$ .

All the samples examined exhibit radioactivity, but the precipitates produced by hydrogen sulphide are too feeble in dispersive power to indicate the presence of polonium. The maximum discharge is caused by the ammonium hydroxide precipitate, but all attempts to identify uranium or thorium have remained fruitless. The absence of barium excludes the presence of radium, so that the activity of these minerals is probably due to actinium.

T. H. P.

**Nephelenic Syenites of the Los Islands (French Guinea).** A. LACROIX (*Compt. rend.*, 1924, **178**, 1109—1114).—Some new analyses of syenite are given; these appear to indicate that there are two types of the mineral, the silicon, sodium, and calcium content being the factors which determine the variation in silico-zirconates. H. J. E.

**Rare Earths in Yttrofluorite from Hundholm.** T. VOGR (*Zentr. Min. Geol.*, 1923, 673—676; from *Chem. Zentr.*, 1924, i, 634).—It is shown by X-ray analysis that yttrofluorite from Hund.

holm contains yttrium, erbium, gadolinium, dysprosium, cerium, neodymium, samarium, and cassiopeium. Lanthanum is absent.

G. W. R.

**Precipitation of Manganese from Meteoric Solutions.** G. A. THIEL.—(See ii, 489.)

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## Analytical Chemistry.

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**Determination of the Temperature of Miscibility [of Liquids].** H. ROSSET (*Ann. Chim. Analyt.*, 1924, [ii], 6, 129—134).—A summary is given of the general theory of the change of miscibility of liquids with temperature. Apparatus is described suitable for determinations of critical temperatures of solution of one liquid in another and of the clouding points of mixtures of equal volumes of two liquids.  
H. C. R.

**Inexpensive Furnace for Ashing Food and Excreta in Porcelain Crucibles.** C. J. MARTIN (*Biochem. J.*, 1924, 18, 419—421).—The ashing takes place in a large crucible in presence of an adequate air supply at a uniform temperature below that sufficient to fuse the ash or the glaze or to vaporise any constituent of the ash which it is proposed to determine.  
S. S. Z.

**Micro-analysis by Pregl's Method.** A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1924, 146, 302—304).—Descriptions are given of a tap by means of which a sensitive control of the stream of carbon dioxide in the micro-Dumas method of Pregl is secured, of a new and more convenient type of micro-pipette, and of a filter on which small quantities of precipitates may be collected and weighed with an error not greater than 0.0001 mg.  
J. P.

**Thermal-conductivity Method for the Analysis of Gases.** P. E. PALMER and E. R. WEAVER (*U.S. Bur. Standards, Tech. Paper*, 1924, No. 249, 35—100).—Two similar electrically-heated wires surrounded respectively by the gas to be analysed and a reference gas of standard composition constitute adjacent arms of a Wheatstone network, and the out-of-balance condition of the bridge, produced when the composition of the gases differs, is indicated by a galvanometer or determined by a potentiometer device (cf. A., 1920, ii, 503). Results obtained in the application of the method to the determination of one constituent of a variety of gaseous mixtures are described.  
J. S. G. T.

**Applications of the Analysis of Combustible Gaseous Mixtures.** P. LEBEAU (*Bull. Soc. chim.*, 1924, [iv], 35, 489—514).—A lecture delivered at the Collège de France on Jan. 26, 1924. [Cf. B., 1924, 585.]

**Indicators. VII. Construction of Titration Curves.** A. THIEL (*Z. anorg. Chem.*, 1924, **135**, 1—20).—From any assumed degree of acidity in a mixture of an acid and a base a simple logarithmic method admits of calculation of the degree of neutralisation. If  $\phi$  express  $\alpha/(1-\alpha)$ , the proportion of dissociated to undissociated molecules, the ordinary equation for the affinity constant of the acid gives  $\log \phi = \log k - \log[H^+] = \log k + p_H$ , i.e.,  $\alpha/(1-\alpha)=1$  when  $p_H = -\log k$ . Putting  $p_{H(1/2)} = -\log k$ , then for a definite equilibrium  $\log \phi_x = p_{Hx} - p_{H(1/2)} = \Delta p_H$ . The value  $p_{Hx}$  therefore gives as a simple function the degree of dissociation, and the dissociation curve for the acid may be directly constructed from this determination,  $p_{H(1/2)} = -\log k$  being known. The method is applied to the consideration of the cases of division of a base between two or more acids, neutralisation of polybasic acids, etc. Calculations of the proportions of primary and secondary phosphates in *M*/15 solution made from the accepted values of the affinity constants for the three degrees of dissociation of the acid as given by Abbott and Bray (A., 1909, ii, 660) agree well with the proportions given by Sørensen, who determined  $p_H$  for a known series of mixtures at 18°, the variations observed being attributed to some uncertainty with regard to the second constant. S. I. L.

**Anthocyanin as an Indicator for Acidimetry.** V. MATULA (*Chem.-Ztg.*, 1924, **48**, 305—306).—Anthocyanin indicator is obtained by evaporating an aqueous extract of red cabbage to a small volume, adding a large excess of alcohol, neutralising the liquid with potassium hydroxide, and filtering. The reddish-brown solution is very sensitive to acids and bases, giving a red colour with the former and a greenish-yellow colour in alkaline solution. The neutral point is marked by a sudden change from red through lilac to greyish-blue; excess of alkali produces first a blue, then an emerald-green, and finally a yellowish-green colour. The range of usefulness of the indicator is approximately the same as that of litmus, but its sensitivity is much greater; it is therefore suitable for the titration of ammonia and of weak acids, e.g., acetic acid. A. R. P.

**[Apparatus for] Conductometric Titrations.** G. JANDER and E. MANEGOLD (*Z. anorg. Chem.*, 1924, **134**, 283—296).—Instead of the usual telephone indicator, a sensitive mirror galvanometer may be used in carrying out conductometric titrations. A 4-volt accumulator in connexion with a small inductor or buzzer provides a source of low-tension alternating current through the cell circuit. The current in the galvanometer circuit is rectified by means of a sensitive crystal of galena and is adjusted to zero by means of the sliding contact of the bridge before starting a titration. The maximum deflection of the spot of light is measured after each addition of 0.5 or 0.2 c.c. of standard solution delivered from a burette graduated in 0.01 c.c., and the square roots of these figures are plotted against the corresponding number of c.c. of solution added. The resulting points lie on two straight lines the intersecting point of which is the end-point of the titration. A. R. P.

**Direct-reading Potentiometer for Determination of Hydrogen-ion Concentration.** F. LIEBERT (*Chem. Weekblad*, 1924, **21**, 254—255).—The calibration of the instrument is described, the normal calomel electrode being connected in parallel with the electrode under examination. S. I. L.

**Determination of Halogens by Combustion in a Current of Oxygen over Platinised Asbestos.** F. ARNDT (*Ber.*, 1924, **57**, [B], 763—764).—The method of Dachlauer and Thomsen (this vol., ii, 419) for determining halogen in organic compounds is not new and possesses no advantages over the method in which the halogen is absorbed by silver powder. The latter method is applicable also to nitrogenous substances, contrary to Dennstedt's statement. Halogen and sulphur may be determined simultaneously by passing the products of combustion over sodium carbonate at 400—500° and determining the halogen in one half and the sulphur in the remainder. F. A. M.

**[Electrometric Determination of Small Quantities of Chlorine and Bromine Ions].** E. RUDBERG.—(See ii, 467.)

**Detection of Bromine and Iodine Ions in presence of other Ions giving Precipitates with Silver Nitrate.** G. P. PAMFIL (*Z. anorg. Chem.*, 1924, **133**, 263—264).—A saturated solution of silver chloride in ammonia in presence of sodium hydroxide gives precipitates with bromides or iodides only; a similar solution of silver bromide gives a precipitate with iodides only. S. I. L.

**Use of Potassium Dichromate in Iodometry.** G. JANDER and H. BESTE (*Z. anorg. Chem.*, 1924, **133**, 73—81; cf. *infra*).—Potassium dichromate is excellent for use in iodometry provided the necessary precautions are taken. In the Zulkowsky method (*J. pr. Chem.*, 1868, **103**, 351), the mixture of potassium dichromate, potassium iodide, and acid must stand, ice-cooled, for 10—15 minutes before titration. Concentrated hydrochloric acid must be used in the Bunsen distillation method. S. K. T.

**Bunsen's Iodometric Distillation Method of Determining Highly Oxidised Substances.** G. JANDER and H. BESTE (*Z. anorg. Chem.*, 1924, **133**, 46—54).—Rupp's experiments (A., 1918, ii, 369), which showed that the main error in this method arises from the reaction  $2\text{Cl}_2 + 2\text{H}_2\text{O} (\text{steam}) = 4\text{HCl} + \text{O}_2$ , have now been repeated and his results confirmed. It is proposed to hinder this reaction by using a small distilling flask (60—80 c.c.) which is connected to the absorbing vessel by as short a tube as possible. Concentrated hydrochloric acid should always be used in the distilling flask. S. K. T.

**Determination of Tetrathionate by means of Sulphite.** A. KURTENACKER (*Z. anorg. Chem.*, 1924, **134**, 265—268).—The interaction of sulphite and tetrathionate yields thiosulphate and trithionate. A solution of the tetrathionate is mixed with a solution of sodium sulphite and alcohol. After 5 minutes, formaldehyde and acetic acid are added to combine with the excess of

sulphite and the liquid is titrated immediately with 0.1*N*-iodine solution. Pentathionates may be determined in a similar manner.

A. R. P.

**Nesslerisation and Avoidance of Turbidity in Nesslerised Solutions.** O. FOLIN (*Biochem. J.*, 1924, **18**, 460—461).—  
—Polemical, in reply to Stanford (this vol., ii, 201). S. S. Z.

**Determination of the Relative Proportions of Nitric Oxide and Nitrogen Peroxide in a Mixture.** A. KLEMENC and K. MUHA (*Z. anorg. Chem.*, 1924, **134**, 208—220).—If the gas mixture contains a greater volume of nitric oxide than of nitrogen peroxide a 100 c.c. sample is shaken with concentrated sulphuric acid, which absorbs equal molecular proportions of each gas (to form nitrogen trioxide) and the excess of nitric oxide is determined in the residual gas by the bromate method (see below), an allowance of 7 c.c. being made for the solubility of nitric oxide in strong sulphuric acid. The dissolved nitrogen trioxide is determined by the usual nitrometer method. The bromate method of determining the gases consists in shaking with an acid solution of potassium bromate whereby both gases are oxidised to nitric acid, so that by determining the excess of bromate and the amount of combined nitrogen in the solution, after absorption of the gases, by Lunge's nitrometer method, the proportions of each may be calculated.

A. R. P.

**Determination of Organic Phosphorus.** E. J. BAUMANN (*J. Biol. Chem.*, 1924, **59**, 667—674).—In the usual wet ashing process, which is a preliminary to the micro-determination of organic phosphorus, some of the phosphoric acid may be lost by volatilisation and some may be converted into meta- and pyro-phosphoric acid. The use is therefore recommended of a mixture of hydrogen peroxide and sulphuric acid for the oxidation of the organic matter, by which means the ashing can be accomplished at a lower temperature.

C. R. H.

**Colorimetric Determination of Small Amounts of Phosphorus.** A. P. BRIGGS (*J. Biol. Chem.*, 1924, **59**, 255—264).—The technique previously described (A., 1922, ii, 659) is improved and procedures are given for the colorimetric determination of phosphorus in the various phosphorus compounds of blood, for the determination of calcium and magnesium, and for total base. The method is based on the formation of phosphomolybdic acid and its subsequent reduction by quinol and sulphur dioxide with the production of a stable blue colour proportional to the phosphorus present. The excess of molybdic acid is not reduced. The results obtained by this method do not give values for inorganic phosphorus higher than those obtained by other methods; thus there is very little hydrolysis of phosphorus in organic combination. To determine both the organic and inorganic phosphorus the mixture is heated in a boiling water-bath with solutions of molybdate, quinol, and sulphuric acid; after cooling, sulphite solution is added and after appropriate dilution the colour is compared with a standard. The determination of calcium as the phosphate is carried out by

first precipitating it as the oxalate, centrifuging, decomposing it with hydrochloric acid and hydrogen peroxide, precipitating in ammoniacal solution with a phosphate, and, after washing with ammoniacal alcohol, determining the phosphate colorimetrically.

D. R. N.

**Failure of the Test for Phosphorus in a Case of Phosphorus Poisoning.** F. BARTSCHAT (*Z. Unters. Nahr. Genussm.*, 1924, 47, 10).—A case of yellow phosphorus poisoning is described in which an examination of the organs, 6 days after death, by Mitscherlich's method and by Dusart and Blondel's test for phosphorous acid, and a microscopical examination of the tissues all gave negative results. Although delicate in themselves, these tests are of value only if applied almost immediately after the phosphorus has been administered.

H. C. R.

**Colorimetric Micro-determination of Phosphoric Acid.** Y. TERADA (*Biochem. Z.*, 1924, 145, 426—430).—The solution under investigation is shaken with the reagent (ammonium molybdate and strychnine nitrate in nitric acid solution) and after 1 hour the precipitate is centrifuged, washed with 5% nitric acid, dissolved in warm sodium carbonate solution, phenylhydrazine hydrochloride (in 38% acetic acid) is added, the tube is heated on a water-bath for 30 minutes at 70—80°, the contents are diluted, and the resulting wine-red colour is compared in a Duboscq colorimeter with standard solutions. The method may be used for determining phosphate in urine, muscle-tissue, etc.

J. P.

**Determination of Arsenic.** O. HACKL (*Chem.-Ztg.*, 1924, 48, 346).—Prior to the volumetric determination of arsenic, if the sulphide is to be dissolved by heating with sulphuric acid, it is preferable to collect it on glass wool. Both precipitate and wool are eventually heated with strong sulphuric acid and potassium sulphate until the arsenic sulphide has completely dissolved; if this operation is conducted in a beaker covered with a clock-glass, arsenic is lost, for minute crystals of arsenic trioxide can usually be observed on the clock-glass.

A. R. P.

**Presence of Silicon in Tissues. Micro-method for Determining Silicon.** L. ISAACS (*Bull. Soc. Chim. biol.*, 1924, 6, 157—168).—The dried material is oxidised with boric acid, calcium nitrate, and nitric acid; the residue is treated with aqueous sodium hydroxide, acidified with acetic acid, and ammonium molybdate solution added. Sodium sulphite is added to the hot solution, and the blue colour formed by reduction of the silicomolybdate is compared with that given by a standard silicate solution. If the tissue contains blood, a correction must be applied for the colour produced by the iron present. Silicon is present in small but very variable quantities in almost all organs, and in relatively much greater amounts in the brain of the dog (no figures given) and the rabbit. In man, the average content (as silica) in normal organs is 1.5 mg. per 100 g. of fresh tissue.

J. P.



**Determination of Carbon by the Wet Method.** A. FRANZ and H. LUTZE (*Ber.*, 1924, **57**, [B], 768—770).—A weighed amount of the organic substance is warmed with about three times the theoretical quantity of potassium persulphate, in aqueous solution, and the dried carbon dioxide absorbed in the usual manner. The whole process, excluding weighings, only occupies 20—25 minutes, and the results are accurate to 0.1%. With halogenated compounds, it is necessary to interpose a halogen absorption tube between the reaction vessel and the carbon dioxide absorption tube.

F. A. M.

**Volumetric Determination of Carbon.** J. F. DURAND (*Compt. rend.*, 1924, **178**, 1193—1195).—The carbon in organic substances is converted into carbon dioxide by oxidation with permanganic anhydride in sulphuric acid solution. The method is applicable to a wide range of compounds and gives accurate results. [Cf. *B.*, 1924, 581.]

H. J. E.

**Determination of Alkali Carbonate in the Presence of Alkali Hydrogen Carbonate by Warder's Method.** T. SABALITSCHKA and G. KUBISCH (*Z. angew. Chem.*, 1924, **37**, 255; cf. Treadwell, "Kurzes Lehrbuch der analytischen Chemie," 1923, 487, 488).—The volumetric determination of alkali carbonate in the presence of hydrogen carbonate by Warder's method is untrustworthy and may fail to reveal the presence of as much as 5% of the former. Winkler's method is preferable.

W. T. K. B.

**Iodometric Determination of Sodium.** M. BÁLINT and H. PETOW (*Biochem. Z.*, 1924, **145**, 242—243).—The authors have devised a micro-method for the determination of sodium similar to that of Müller (this vol., ii, 123), but imperfections still exist in both.

J. P.

**Determination of Calcium in Whole Blood.** A. C. ALPORT (*Biochem. J.*, 1924, **18**, 455—459).—The blood is received in potassium oxalate, weighed, and incinerated. The ash is dissolved in hydrochloric acid, evaporated on the water-bath, and the residue extracted with acetic acid, sodium acetate, and water. The calcium is eventually converted into the oxalate with ammonium oxalate, decomposed with dilute sulphuric acid, and the oxalic acid determined with 0.01*N*-potassium permanganate. Normal values in human blood range from 5.42 to 6.87 with an average value of 5.8 mg. of calcium per 100 c.c.

S. S. Z.

**Differentiation of Radium, Mesothorium, and Radium-thorium by  $\gamma$ -Rays.** W. BOTHE.—(See ii, 446.)

**Metallic Magnesium as a Qualitative and Quantitative Reagent in Inorganic Analysis.** G. P. PAMFIL (*Z. anorg. Chem.*, 1924, **133**, 265—266).—Magnesium is a suitable reagent for the precipitation of various heavy metals.

S. I. L.

**Precipitation of Zinc Sulphide from Sulphate Solutions.** O. HACKL (*Chem.-Ztg.*, 1924, **48**, 326).—In order to obtain complete

precipitation of zinc sulphide from faintly acid solutions, the amount of free sulphuric acid present must not exceed 0.18 g. per 100 c.c. To adjust the acidity of an unknown solution to this strength, it should be evaporated to a small volume, rendered alkaline with ammonia, treated with sulphuric acid until acid to Congo paper, again made just alkaline, and then treated with the requisite quantity of acid. A control is made with a solution containing an amount of ammonium salts approximately equal to that in the assay.

A. R. P.

#### Potentiometric Titration of Zinc with Ferrocyanide.

E. J. A. H. VERZIJL and I. M. KOLTHOFF (*Rec. trav. chim.*, 1924, **43**, 380—388; cf. Kolthoff, A., 1922, ii, 580).—In consequence of the favourable results obtained by Müller (A., 1923, ii, 879), the authors have reinvestigated the conditions under which zinc can be titrated potentiometrically with potassium ferrocyanide. Using  $M/40$  solutions of ferrocyanide, at room temperature, the results obtained by the procedure already described (Kolthoff, *loc. cit.*) are 1% too low. When, however, about 20 g. of ammonium sulphate are added per 100 c.c. of solution, substantially accurate results are obtained. The presence of large quantities of sodium, magnesium, calcium, and aluminium salts causes the results to be low. Manganese, cadmium, and copper should not be present, but ferric compounds are rendered harmless by the addition of ammonium fluoride and sulphuric acid. The potassium ferrocyanide should contain 1% of ferricyanide. This renders it more sensitive to decomposition by light, but the solution can be kept indefinitely in dark brown glass bottles.

E. H. R.

#### Titration of Zinc by Ferrocyanides of Different Metals.

I. M. KOLTHOFF and E. J. A. H. VERZIJL (*Rec. trav. chim.*, 1924, **43**, 389—393).—Of a number of ferrocyanides examined, only the potassium salt is suitable for the potentiometric titration of zinc. The composition of the precipitate is  $K_2Zn_3[Fe(CN)_6]_2$ . In presence of a caesium salt, the precipitate has the composition  $ZnCs_2Fe(CN)_6$ , but the caesium salt polarises the electrode, causing a considerable fall of potential, and the end-point is not sharp (cf. Treadwell and Chervet, A., 1922, ii, 786; 1923, i, 764). Contrary to the statement of these authors, rubidium has no influence on the composition of the precipitate. Titration with ammonium ferrocyanide or ferrocyanic acid follows a similar course to that with potassium ferrocyanide. Titration of a zinc salt with sodium, magnesium, or calcium ferrocyanide gives a precipitate of zinc ferrocyanide,  $Zn_2Fe(CN)_6$ , which forms a double salt with excess of the reagent. With barium ferrocyanide, pure zinc ferrocyanide is obtained, but no double salt.

E. H. R.

**Separation of Cadmium from Zinc by Precipitation as Sulphide in Potassium Cyanide Solution.** K. CHALUPNY and K. BREISCH (*Chem.-Ztg.*, 1924, **48**, 349—351).—The solution is neutralised with potassium hydroxide solution and potassium cyanide is added until the precipitate first formed just redissolves, a

definite excess of both reagents then being added. The liquid is boiled with the addition of thiocarbamide, the cadmium being completely precipitated as sulphide in a form which filters readily. The precipitate is washed once by decantation with an alkaline cyanide solution, then with ammonium nitrate water, and dissolved in hydrochloric acid. The process is repeated using only a small quantity of cyanide in a small volume of solution. The second precipitate is dissolved in hydrochloric acid, the solution is boiled to expel hydrogen sulphide, neutralised with potassium hydroxide, and treated with cyanide to dissolve the precipitate first formed, and the cadmium is deposited electrolytically. [Cf. *B.*, 1924, 580.] A. R. P.

**Sensitive Reactions for Copper.** R. FLEMING (*Analyst*, 1924, 49, 275).—(1) A deep blue precipitate insoluble in the usual organic solvents is obtained when 3–4 drops of a dilute solution of ammonium or potassium thiocyanate and a few drops of a 1% alcoholic solution of benzidine (sensitiveness 1 in  $10^6$ ) or 0.5% alcoholic guaiacum resin (sensitiveness 1 in  $10^7$ ) are added to the copper solution. (2) On heating the dilute copper solution with a few drops of 0.5% alcoholic guaiacum resin a deep blue colour is formed, the resulting compound being soluble in chloroform and the reaction sensitive to 1 part of copper in  $2 \times 10^8$ . The colour given by strong solutions of iron with guaiacum resin is not stable on heating. D. G. H.

**Electrometric Titration of Mercury with Ammonium Thiocyanate.** R. MÜLLER and O. BENDA (*Z. anorg. Chem.*, 1924, 134, 102–104).—In order to obtain a sharp potential difference at a point corresponding with the theoretical value, in the electrometric titration of mercury with ammonium thiocyanate, mercury ions must be absent from the solution. Hence strongly acid solutions show a more definite potential difference than slightly acid solutions. Thus in the case of mercuric nitrate the indefinite end-point in neutral or weak acid solutions is due to hydrolysis, which is suppressed by the presence of a large excess of nitric acid. In such a strongly acid solution the transition point lies very near to the theoretical value and nearer than that obtained by indicators.

J. B. F.

**Analytical Methods for certain Metals including Cerium, Thorium, Molybdenum, Tungsten, Radium, Uranium, Vanadium, Titanium, and Zirconium.** R. B. MOORE, S. C. LIND, J. W. MARDEN, J. P. BONARDI, C. W. DAVIS, and J. E. CONLEY (*U.S. Bur. Mines, Bull.* 212, 325 pages).—A critical review of known methods, with suggested modifications.

**Separation of Aluminium and Iron from Zinc, Manganese, and Nickel by the Basic Acetate Method.** A. KLING and (MME.) A. LASSIEUR (*Compt. rend.*, 1924, 178, 1551–1552).—For the complete precipitation of aluminium the hydrogen-ion concentration of the solution must be at least  $p_H$  5.2, but with this acidity filtration of the precipitate is impossible unless filter-paper be added before precipitation. To 350 c.c. of the liquid are added methyl-red ( $p_H$  5.2–5.6) and 20 c.c. of a 10% solution of sodium acetate

followed by sodium hydroxide solution until the indicator is just affected. After addition of a small quantity of filter-paper the liquid is boiled for 2 minutes, the precipitate filtered, washed with a 1% solution of ammonium nitrate, ignited, and weighed. The precipitation of manganese commences at  $p_H$  6.5 and a single precipitation effects complete separation if the above procedure be followed. With zinc, precipitation begins at  $p_H$  6.0, so that separation is possible if the acidity is strictly  $p_H$  5.2, the addition of a large quantity of sodium chloride being necessary to make filtration of the precipitate possible. Reprecipitation of the aluminium is thus rendered necessary. Although for the precipitation of nickel the acidity must be  $p_H$  6.1, much is carried down with the aluminium and separation by this method is impossible. Precipitation of iron is complete at  $p_H$  4.1, so that separation from zinc is readily possible. The impossibility of the use of an indicator makes the separation of nickel untrustworthy, and the method is not advisable when iron and aluminium are together present.

J. W. B.

**Standardisation of Permanganate with Ferrous Ammonium Sulphate.** I. M. KOLTHOFF (partly with J. C. VAN DIJK) (*Pharm. Weekblad*, 1924, **61**, 561—566).—Commercial samples of Mohr's salt, even after recrystallisation, contain zinc, manganese, magnesium, etc. The pure salt may be obtained by reduction of ferric ammonium sulphate with hydrogen sulphide; it is more suitable than oxalic acid for the standardisation, since the reaction weight is so much greater, and the titration proceeds smoothly at the ordinary temperature.

S. I. L.

**Colorimetric Determination of Iron.** D. VON DESEÖ (*Biochem. Z.*, 1924, **146**, 323—327).—The influence of phosphates and various concentrations of hydrochloric acid on the micro-method of Autenrieth and Funk (*Münch. med. Woch.*, 1912, **59**, 765) for the determination of iron has been investigated, with the view of applying the method to the analysis of pigmented bones. Satisfactory results are obtained if the complex ferri-phosphates be decomposed by preliminary heating in the presence of acid on the water-bath.

J. P.

**Micro-analytical Separation of Iron and Phosphoric Acid.** G. FONTÈS and L. THIVOLLE (*Bull. Soc. chim.*, 1924, [iv], **35**, 641—644).—The iron in acid solutions containing 0.1 to 1.5 mg. of the metal may be determined by adding alcoholic dimethylaminoazobenzene, very nearly neutralising with ammonia, and then adding sodium hyposulphite followed by a solution of  $\alpha$ -nitroso- $\beta$ -naphthol in acetic acid, until the precipitate of the complex ferro-nitroso- $\beta$ -naphthol is obtained. The latter is washed with acetic acid and treated as previously described (A., 1923, ii, 583). Copper, nickel, and cobalt must be absent, but fairly large quantities of phosphoric acid may be present.

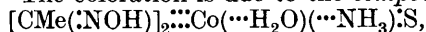
S. K. T.

**Determination of Metals of the Ammonium Sulphide Group by Hydrogen Sulphide under Pressure.** L. MOSER and M. BEHR (*Z. anorg. Chem.*, 1924, **134**, 49—74).—The solubilities of

the sulphides of cobalt, nickel, zinc, iron, manganese, and thallium were determined in sulphuric acid of various degrees of normality. Zinc is quantitatively precipitated from solution by hydrogen sulphide under pressure; the precipitate is dense and easily filtered. Manganese is quantitatively separated from zinc in *N*/16-sulphuric acid solution. Iron and cobalt are quantitatively separated from zinc in *N*/16-sulphuric acid solution only when the iron or cobalt is not greater than 0.1 of the zinc. Nickel in a similar proportion is quantitatively separated in *N*/8-sulphuric acid solution. Molybdenum is precipitated quantitatively only in *N*-sulphuric acid solution if the concentration of the molybdenum does not exceed 0.1 g MoO<sub>3</sub> per 100 c.c. It is also quantitatively separated from zinc, nickel, cobalt, and iron only in 5*N*-, from iron in 2.5*N*-, and from aluminium in *N*-sulphuric acid solution, when not more than 0.1 g. MoO<sub>3</sub> per 100 c.c. is present. The separation of molybdenum from uranium gives good results over wide limits of metal concentrations. A quantitative separation of thallium and zinc was not obtained; the precipitate in sulphuric acid solution of various strengths consisted of zinc sulphide associated with a double sulphide of thallium and zinc.

J. B. F.

**Colour Reaction between Cobalt Salts and Dimethylglyoxime in the Presence of Sulphides.** F. FEIGL and L. VON TUSTANOWSKA (*Ber.*, 1924, 57, [B], 762—763).—Cobalt may readily be detected even in the presence of nickel by treatment of the acid solution with sodium acetate and alcoholic dimethylglyoxime, filtration of eventually precipitated nickel dimethylglyoxime, and addition of dilute sodium sulphide solution to the filtrate. A violet coloration develops, the intensity of which depends on the quantity of cobalt present. If the solution is acidified with acetic acid and extracted with amyl alcohol, the latter is coloured dark violet to pale wine-red. The reaction is sensitive to 1 part in 830,000 parts. The coloration is due to the *compound*,



or its dimeride.

H. W.

**Compounds of Quadrivalent Nickel with Dimethylglyoxime and a Sensitive Test for Nickel.** F. FEIGL (*Ber.*, 1924, 57, [B], 758—761).—When nickel chloride dissolved in warm water is treated successively with sodium hydroxide solution (30%), a hot, saturated alcoholic solution of dimethylglyoxime, and lead dioxide a red solution is obtained from which, after cautious neutralisation with dilute acid, a dark red *compound*,  $[\text{CMe}(\text{N} \cdot \text{OH}) \cdot \text{CMe} \cdot \text{NO}]_2 \text{NiO}$ , is precipitated. The quadrivalency of nickel in the substance is demonstrated by its ability to liberate iodine from acidified potassium iodide solution. When treated with iodine and potassium iodide in alkaline solution, it yields the *compound*,  $[\text{CMe}(\text{N} \cdot \text{OH}) \cdot \text{CMe} \cdot \text{NO}]_2 \text{Ni}(\text{OK}) \cdot \text{I} \cdot 2\text{H}_2\text{O}$ . For the detection of nickel the solution is treated with concentrated ammonia, lead dioxide, a few drops of dilute sodium hydroxide solution, and alcoholic dimethylglyoxime, boiled for a short time, and filtered; the filtrate is dark red to reddish-yellow in colour, according to the

quantity of nickel present. The sensitiveness of the test is about four times as great as that of Tschugaev. H. W.

**[Analysis of] Complex Compounds of Platinum and Palladium with Organic Sulphides.** L. TSCHUGAEV (compiled by E. FRITZMANN) (*Z. anorg. Chem.*, 1924, **134**, 277—282).—An introductory paper to the study of complex platinum and palladium compounds with organic sulphides and thioethers. Owing to the great volatility of many of these compounds, the ordinary methods for the determination of the sulphur and chlorine content are not available. To determine the sulphur, a mixture of the substance with potassium nitrate and sodium carbonate is placed in a hard glass test-tube between two layers of the fusion mixture, the upper layer being covered with sodium carbonate. The tube is heated in a horizontal position, beginning at the sodium carbonate layer and heating towards the closed end. After 2 hours, the mass is allowed to cool and dissolved in hydrochloric acid. Nitrogen compounds and silica are removed as usual by evaporation and the sulphuric acid is precipitated with barium chloride. For the determination of chlorine a mixture of the substance with freshly-burnt lime is heated between two layers of lime in a manner similar to that described above, except that a nickel tube is used. The chlorine is determined gravimetrically in the usual way. A. R. P.

**Quantitative Separation of Platinum and Iridium.** S. AOYAMA (*Z. anorg. Chem.*, 1924, **133**, 230—244).—Separation is effected by (1) precipitation of the metal from an acid solution of the chloride by means of metallic copper, which precipitates platinum completely, but iridium to the extent of 1—3% of the total present only, (2) dissolving the precipitate and reducing again with magnesium to remove copper, and (3) igniting in a stream of hydrogen and treating the metal with aqua regia, which dissolves platinum but does not attack iridium after this treatment. An alternative method is to effect the first reduction with magnesium, which precipitates both metals completely, and separate after ignition in hydrogen by means of aqua regia. S. I. L.

**Determination of Organic Vapours in Gas Mixtures by means of Active Charcoal, particularly of Benzene in Illuminating and Coke Oven Gas.** E. BERL and E. WACHENDORFF (*Z. angew. Chem.*, 1924, **37**, 205—206; cf. Fischer and Zerbe, *B.*, 1924, 43).—When benzene which has been adsorbed by active charcoal is expelled by means of steam at 130°, there is a certain loss, which is constant for a given set of conditions, due to adhesion in the condenser and receiver, uncondensed vapour, and retention of a small quantity of benzene by the charcoal. This benzene, together with moisture, is removed by subsequent evacuation of the adsorption tube. Charcoal which is used for the first time retains a considerable amount of benzene, but the loss in subsequent experiments is constant. Allowing for this, an average recovery of 99.6% is obtained by expulsion with steam at 130° for 1 hour.

W. T. K. B.

**Micro-determination of Methyl Alcohol in Blood.** N. V. BILDSTEN (*Biochem. Z.*, 1924, **146**, 361—369).—The micro-method of Widmark (*ibid.*, 1922, **131**, 473) for the determination of ethyl alcohol in blood has been adapted, with a few modifications in detail, for determining methyl alcohol (cf. Nicloux, *Compt. rend. Soc. Biol.*, 1912, **70**, 59). The rate of disappearance of methyl alcohol from the blood of rabbits which had received intravenously 0.8 g. of the alcohol per kg. body-weight, has been followed by this method. In general, the curves are broken by a temporary increase of concentration which appears from 4 to 6 hours after the injection.  
J. P.

**Application of the Biochemical Method of Characterising Dextrose to the Detection of Maltase in Malt.** M. BRIDEL (*Compt. rend.*, 1924, **178**, 1636—1637).—Maquenne (A., 1923, i, 442) found that a cold-water extract of malt containing maltose undergoes gradual increase in reducing power. That this change is, as Maquenne suggested, due to hydrolysis of the maltose present by maltase contained in the malt extract is now shown by determining the dextrose in the solution, before and after digesting it for 16 days, by the method involving combination of this sugar with methyl alcohol under the influence of emulsin.  
T. H. P.

**Optical Determination of Starch in Technical Starch Products and in Parts of Plants by means of the Interferometer.** O. WOLFF (*Z. angew. Chem.*, 1924, **37**, 206—207).—Two equal quantities of the starchy material are mixed with equal quantities of water, and one is boiled to gelatinise the starch whilst the other is kept at the ordinary temperature. To each is then added a diastase solution and, after an hour, equal quantities of kieselguhr. After filtration, the two clear solutions are compared in the interferometer. Fibrous vegetable material must be thoroughly disintegrated by grinding it with purified sand before the above treatment. In each case, the interferometer is previously calibrated by carrying out the above operations with known quantities of pure starch. The method gives lower results than chemical methods involving treatment with acids, the difference probably being due to hydrolysis of hemicellulose, as well as of starch, in the latter process.  
W. T. K. B.

**Oxidation of Tartaric Acid by Potassium Permanganate and Hydrogen Peroxide.** W. MEIGEN and I. SCHNERB (*Z. angew. Chem.*, 1924, **37**, 208).—In the quantitative oxidation of dilute solutions of tartaric acid by potassium permanganate in the presence of a sufficient quantity of sulphuric acid no precipitate of manganese dioxide is formed, so that the addition of excess of oxalic acid and subsequent titration back are unnecessary. Greater accuracy is obtained by standardising the permanganate solution with pure potassium hydrogen tartrate rather than with oxalic acid. Crude potassium hydrogen tartrate contains organic impurities and cannot be directly titrated with permanganate. The tartrate should first be separated by precipitation from alcoholic solution. Traces of organic impurities which are precipitated at the same

time are oxidised in acid solution by cold permanganate; this does not affect the tartrate, which is subsequently titrated hot. The oxidation of tartaric acid by hydrogen peroxide in the presence of an iron salt or, better, of a copper salt, is of value for removing it in cases where its presence prevents the precipitation of metallic hydroxides. Thus, in qualitative analysis tartaric acid is removed after the hydrogen sulphide group by boiling the filtrate with copper sulphate and hydrogen peroxide, the copper being then removed by precipitation with hydrogen sulphide. In quantitative analysis, iron and aluminium may be determined in presence of each other by precipitating the former with ammonium sulphide in the presence of tartaric acid, filtering, heating the filtrate with copper sulphate and hydrogen peroxide, removing the copper with hydrogen sulphide, and finally precipitating the aluminium with ammonia. Further applications of a similar nature occur in the separation of zirconium or titanium from iron, and of molybdenum from tungsten.

W. T. K. B.

**Bromometric Determination of Iodine Values.** W. MANCHOT and F. OBERHAUSER (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 261—263).—Excellent agreement with iodine values determined by Hübl's method for substances of iodine value varying from that of oleic to that of linolenic acid was obtained by using solutions of bromine in hydrochloric or acetic acid with chloroform, or in acetic acid without chloroform. [Cf. *B.*, 1924, 564.] H. C. R.

**Fatty and Resin Oxy-acids and their Analytical Separation.** H. WOLFF (*Chem. Umschau*, 1924, **31**, 87—89).—Fatty and resin oxy-acids can be separated by Wolff and Scholze's method (*A.*, 1914, ii, 393). Five to 6% of the fatty oxy-acids remain unesterified in this process and an almost equal proportion of resin oxy-acids is esterified, so that if the amounts of each of these acids present are equal, the errors so caused cancel out. The total amount of oxy-acids present rarely exceeds 20%, so that the maximum error can only amount to 1.0—1.2%. Gladding's method (Holde, "*Unters. der Kohlenwasserstofföle und Fette*," 5th ed., p. 638) involves an error of about the same magnitude in the determination of fatty oxy-acids, but the error involved in the determination of resin fatty acids amounts to 65%, so that this method cannot be used when resin fatty acids are present. The refractive indices of alcoholic solutions of resin and fatty oxy-acids (1 : 3) differ, but not sufficiently to afford a practical method of analysis.

H. C. R.

**Quantitative Aspects of the Kreis Test.** II. G. E. HOLM and G. R. GREENBANK (*Ind. Eng. Chem.*, 1924, **16**, 518).—The oxidation products of linoleic, linolenic, and ricinoleic acids, as well as of oleic acid, give the Kreis test (cf. *ibid.*, 1923, **15**, 1051). Linoleic and ricinoleic acids, however, gave but faint tallowy odours even when relatively large amounts of oxygen had been absorbed. Linolenic acid produced no tallowy odour on oxidation. The product of the number of c.c. of oxygen absorbed per 100 g. of fatty acid and the amount (g.) of oxidised acid necessary to give an equivalent colour intensity in the Kreis test is greater in the case of



the above three acids than in that of oleic acid. The colour given by oxidised ricinoleic acid in the Kreis test is entirely different from that given by oleic, linoleic, and linolenic acids; the relative proportion of colour is small and the rate of oxygen absorption slow. Oleic acid is evidently the main constituent of fats and oils concerned in the production of tallowiness or rancidity, and the olfactory sense gives no true criterion of how highly oxidised a fat or oil may be.

H. C. R.

**Determination of the Free Fatty Acids of Blood.** A. VON SZENT-GYÖRGYI and T. TOMINAGA (*Biochem. Z.*, 1924, **146**, 226—238).—The gravimetric method involves dehydration of the blood in acetone and simultaneous treatment with a barium chloride-acetic acid mixture, extraction with alcohol and removal of hæmatin, extraction with light petroleum, removal of acetone-soluble phosphatides, conversion of the fatty acids into the corresponding sodium soaps, removal of cholesterol, its ester, and neutral fat by light petroleum, liberation of the acids from the soaps, reprecipitation of the acids from light petroleum as the sodium soaps, washing, liberation of the acids, repeated extraction with acetone, and finally drying and weighing of the resulting fatty acids.

J. P.

**Detection of Higher Multiple Unsaturated Free Fatty Acids in Blood.** A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1924, **146**, 239—244).—Two methods are described for the quantitative detection of unsaturated fatty acids in blood, which involve a modification of the method used for determining the free fatty acids (cf. preceding abstract), and the formation of bromine additive products precipitable by ether and so separable from the saturated acids.

J. P.

**Chemistry of Jaffé's Reaction for Creatinine. A Red Tautomeride of Creatinine Picrate.** I. GREENWALD and J. GROSS (*J. Biol. Chem.*, 1924, **59**, 601—612).—The red colour produced in Jaffé's reaction for creatinine (A., 1886, 1056) is due to the formation of a tautomeric form of creatinine picrate. It is obtained as a red powder on the addition of hydrochloric acid to a mixture of creatinine, sodium picrate, and sodium hydroxide in excess. On prolonged heating in a vacuum at 139°, this red powder is converted into creatinine picrate. The reaction is not given by other nitro-compounds related to picric acid.

C. R. H.

**Detection of Urobilin in the Duodenal Fluid.** L. GRIMBERT and G. POIROT (*J. Pharm. Chim.*, 1924, [vii], **29**, 169—172).—In order to separate urobilin from bilirubin, the presence of which interferes with the characteristic fluorescence given by the former substance with zinc acetate, the duodenal fluid is acidified with hydrochloric acid, a drop of hydrogen peroxide is added, and the liquid is heated in boiling water for 2 minutes. The bilirubin is oxidised to biliverdin, which is insoluble in chloroform. The solution is then cooled and extracted with chloroform, the chloroform solution is dehydrated with anhydrous sodium sulphate and treated with 2 c.c. of a saturated solution of anhydrous zinc acetate in chloroform. A green fluorescence indicates the presence of urobilin.

H. C. R.

## General and Physical Chemistry.

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**Quantum Theory of Radiation.** N. BOHR, H. A. KRAMERS, and J. C. SLATER (*Z. Physik*, 1924, **24**, 69—87; cf. this vol., ii, 433).—A discussion of the application to problems of the quantum theory, such as the Compton effect, of an idea introduced by Slater (*Nature*, 1924, **113**, 307) to reconcile the continuous and discontinuous features of radiation phenomena. S. B.

**Duration of Molecules in Upper Quantum States.** R. C. TOLMAN (*Physical Rev.*, 1924, **23**, 693—709).—A full account of work previously published (cf. this vol., ii, 362).

**Possible Explanation of the Behaviour of the Hydrogen Lines in Giant Stars.** K. T. COMPTON and H. N. RUSSELL (*Nature*, 1924, **114**, 86—87).

**Light emitted from Solid Nitrogen when bombarded with Cathode Rays and its Bearing on the Auroral Spectrum.** L. VEGARD (*Proc. K. Akad. Wetensch.*, 1924, **27**, 113—126).—A detailed account of work reported previously (cf. this vol., ii, 436), including a description of the apparatus employed. T. H. P.

**Spectrum of Ionised Lithium.** M. MORAND (*Compt. rend.*, 1924, **178**, 1701—1704; cf. this vol., ii, 437).—Several new lines have been found. A very feeble ray, 4501, is thought to belong to the spectrum of the doubly-charged lithium ion. By analogy with helium, it is considered probable that the rays 2934 and 7600 belong to the spectra of singly-charged ortholithium and paralithium, respectively, the two orbital electrons of the ortholithium being in a less stable state than those of the paralithium ion. Calculation shows that the potential of transformation of paralithium into ortholithium is 44.8 volts, and this actually represents the minimum potential difference necessary to excite the ray 2934 in lithium vapour (Mohler, *Science*, 1923, **58**, 468). This forms a fresh confirmation of the principle of spectroscopic displacement. The second ionisation potential of lithium appears to be in the neighbourhood of 65 volts, and Mohler (*loc. cit.*) finds that the ray 2934 only reaches its maximum intensity for a potential of about 60 volts. It is suggested that 4678 and 4664 are the first terms of the Bergmann series for para- and ortho-lithium. M. S. B.

**Spectrum of Mercury below the Ionisation Potential.** J. A. ELDRIDGE (*Physical Rev.*, 1924, **23**, 685—692).—The results obtained by a photoelectric method by Franck and Einsporn, who showed that  $2p_2$  and  $2P$  are not the only orbits to which electrons could be directly displaced by collision, have been confirmed spectroscopically by minimising the effect of space charge. The

development of the mercury spectrum has been followed and the appearance of new lines at 7, 8.4, 8.9, 9.9, and 10.4 volts (the ionising potential) takes place in the stages predicted by theory. It is suggested, but not proved, that a displacement of an electron from the normal (1S) orbit to any other is possible when the energy of an impacting electron equals or exceeds the energy of that orbit. It is considered likely that other energy levels, observed only by the photoelectric method, are real, but that the corresponding orbits are incapable of functioning in spectroscopic emission, since transitions both to and from them violate the selection principle.

A. A. E.

**Analysis of Arc Spectrum of Titanium.** C. C. KIESS and H. K. KIESS (*J. Opt. Soc. Amer.*, 1924, **8**, 607—645; cf. A., 1923, ii, 596).—Approximately 400 lines of the arc spectrum of titanium have been classified as belonging to multiplets of the triplet and quintet series systems, or to intercombinations of these systems. A few lines have also been selected as probable members of the singlet series system. The structures of the multiplets are in accordance with the selection principle. New arc lines of titanium are incidentally recorded.

S. B.

**Theory of Band Spectra.** P. TARTAKOVSKY (*Z. Physik*, 1924, **24**, 98—116).—A consideration of the maximum value of the oscillation quantum number, according to the author's theory of band spectra (*ibid.*, 1923, **15**, 153).

S. B.

**Structure of the Second Positive Group of Nitrogen Bands.** R. MECKE and P. LINDAU (*Physikal. Z.*, 1924, **25**, 277—278).—The structure of the spectrum of the second positive group of the nitrogen bands has been, to a considerable degree, elucidated according to the principle of combination. Certain disturbing elements affecting the co-ordination both of the lines of various bands and of the various series within one band have to be taken into account. Nine out of the total 44 bands have been investigated and, with one exception, all the terms up to  $n = 5$  have been determined. The lines can be classified into two groups of three branches, denoted by  $R_1$ ,  $R_2$ ,  $R_3$ , and  $P_1$ ,  $P_2$ ,  $P_3$ , respectively. The  $R_1$  and  $P_1$  branches consist of doublets, the members of the  $R_2$  and  $P_2$  branches are simple, but every second line is displaced, and the  $R_3$  and  $P_3$  branches are simple and not displaced.

L. J. H.

**Ultra-violet Emission Bands of Oxygen.** R. C. JOHNSON (*Proc. Roy. Soc.*, 1924, **A**, 105, 683—691).—Measurements have been made of bands of the oxygen emission spectrum in the region 2300—4400 Å. It has been found that the main band system in this region can be completely represented by a Deslandres formula,  $v = 1620$  or  $1420, +16.945p^2 - 13.37m^2$ . The observed values of  $p$  were 55—47, and of  $m$ , 25—34. A weak emission of bands found in absorption in ozone was also observed, and as these ozone bands bear no apparent relation to the main band system studied, it is concluded that the latter is not due to ozone, contrary to Stark's opinion, but to some other oxygen molecule, probably  $O_2$ .

S. B.

**Quartz Spectrograph.** E. O. HULBERT (*J. Opt. Soc. Amer.*, 1924, **8**, 707—709).—A description of a Littrow mounting of a 30° quartz prism. The reflecting surface at the back of the prism is provided by a layer of mercury. S. B.

**Stark Effect in Hydrogen and Helium.** J. S. FOSTER (*Physical Rev.*, 1924, **23**, 667—684).—Using Lo Surdo's method with a rotating cathode, Stark effect measurements were made for hydrogen and helium lines in fields 1 to 38 kv./cm. The known effect for the Balmer hydrogen series is supplemented by observations on the changes in relative intensities of the components with increasing field, particularly with  $H_\gamma$  and  $H_\epsilon$ , at low fields. With parhelium, measurements were made for the groups near the *D* lines and 3614 Å., which were also measured. The number of lines in each group increases with the order. Combination series are suggested which include these lines and the components of Stark's "diffuse principal" series, and fit the scheme proposed by Tschulanowsky. With orthohelium, measurements are given for groups 3820 and 3705 Å. and observations for 4026 Å. A. A. E.

**Relativity Doublets in X-Ray Spectra.** A. LANDÉ (*Z. Physik*, 1924, **24**, 88—97).—Recent measurements of the separations of optical doublets of ionised atoms have supported the view that  $\Delta\nu = k \cdot (Z-s)^4$  for optical doublets as well as for X-ray doublets. For this and for other reasons, Sommerfeld's relativity theory of X-ray doublets is abandoned in favour of an explanation analogous to that accorded optical doublets (see *ibid.*, 1923, **16**, 391, and A., 1923, ii, 709). This relation governing doublet separations is one of the outstanding difficulties of the Bohr theory. S. B.

**Apparatus for X-Ray Research.** S. K. ALLISON and G. L. CLARK (*J. Opt. Soc. Amer.*, 1924, **8**, 681—691).—An account is given of technical improvements in X-ray spectrometers. S. B.

**Double Refraction in Moving Fluids.** E. KRUEGGER (*Z. physikal. Chem.*, 1924, **109**, 438—452).—The apparatus consisted essentially of an inner cylinder, which could be rotated up to 6000 revs. per min., surrounded by one only slightly larger, which was stationary. The liquid under investigation was contained between the two cylinders and was brought into rapid movement by the rotation. Polarised light was passed through the liquid, parallel to the axis of rotation, and examined for double refraction. All the liquids which showed the phenomena were optically heterogeneous, but the converse did not hold. Increased temperature usually diminished the double refraction and some substances, *e.g.*, olive oil, showed a definite transition temperature, but the value of this differed according to whether the liquid was being heated or cooled. Quantitative results varied considerably with the previous history, *e.g.*, with the age (particularly in the case of lactic acid), and with the temperature immediately previous to a determination; thus, previously warmed 0.4% gelatin solution, on cooling to 20°, showed for some time an abnormally small double refraction.

L. J. H.

**Structure of Molecules in Relation to their Optical Anisotropy.** C. V. RAMAN (*Nature*, 1924, **114**, 49—50).—It is suggested as a working hypothesis that the optical anisotropy of molecules is chiefly due to the mutual influence of the electric doublets induced by the external field in its constituent atoms, the latter individuals being isotropic. This view is receiving support from experiments in progress.  
A. A. E.

**Rotatory Dispersion of Crystals.** L. LONGCHAMRON (*Compt. rend.*, 1924, **178**, 1828—1831; cf. A., 1922, ii, 603).—A more sensitive test of the relations previously observed between optical rotatory powers in the solid and the liquid or dissolved condition is afforded by the investigation of the coloured salt potassium rhodium oxalate (Jaeger, A., 1918, i, 3), which shows a high rotation and anomalous dispersion in solution. The salt is laevorotatory for light of more than 6000 Å. and dextrorotatory for less than 5900 Å. whatever the concentration of the solution. The crystals show a rotation of  $-9.5^\circ$  per mm. for 6400 Å., this being the only light which is transmitted by thick crystals. The rotations of the crystalline and dissolved substances were compared over the range 4900 to 7000 Å. The dispersion is similar, but the point of inversion in the solid occurs at 5190 as compared with 5970 Å. in solution. Since the symmetry of the crystal is precisely that required by Werner's stereochemical formula, there cannot be a rotation due to crystal structure, superposed on the molecular activity: the observed rotations are due solely to molecules arranged parallel to one another. The observed figures are satisfactorily interpreted in terms of Drude's theory, the coloured salt having, in addition to absorption bands in the ultra-violet, one at least in the visible region.  
G. M. B.

**The Rotation Dispersion of Camphor.** F. BÜRKL.—(See this vol., i, 753.)

**Infra-red Absorption Spectra of Organic Compounds. Isomerism and Homology.** J. LECOMTE (*Compt. rend.*, 1924, **178**, 1698—1701).—Continuation of previous work (cf. this vol., ii, 439) on the variations in the infra-red absorption spectra of isomerides, and of members of homologous series. In isomeric compounds, the influence of the form of the carbon chain, that is, whether straight or branched, is small, down to a limit of  $\lambda=10\mu$  for saturated alcohols,  $9\mu$  for mixed ketones, and  $11.5\mu$  for aliphatic esters. Esters of different acids, however, have variable absorption bands beyond  $7\mu$ . Different types of homologous series have been studied. In a simple series such as the primary alcohols,  $C_nH_{2n+1}OH$ , all the compounds show the same bands up to limits varying from  $7\mu$  to  $10\mu$ . In series of compounds containing the same characteristic group twice, the position of the absorption maximum is practically constant, provided the two groups maintain the same distance apart.

The positions of absorption bands, calculated from dispersion formulæ, agree very well with the results of experiment for rock salt, sylvine, etc., but not for organic compounds. Better agreement in the latter case is found by application of the quantum

theory. Since it is only for wave-lengths greater than from  $7\mu$  to  $11.5\mu$  that isomerides and homologues show differences in absorption, absorption bands in this region probably arise from molecular rotation.

M. S. B.

**Infra-red Absorption of Carbon Monoxide.** E. F. LOWRY (*J. Opt. Soc. Amer.*, 1924, **8**, 647—658).—The absorption band of carbon monoxide, with maxima at  $4.60$  and  $4.73\mu$ , has been examined under the dispersion of a grating of 2887 lines per inch. No evidence of fine structure was obtained, but slight minima are present, one on each side of the band centre. From the positions of the maxima, the moment of inertia and the distance  $l$  between the atomic centres in the carbon monoxide molecule are calculated. The value for  $l$ ,  $1.15 \times 10^{-8}$  cm., agrees with that given by Eucken (*Z. Elektrochem.*, 1920, **26**, 377).

S. B.

**Absorption of Ultra-violet Rays by Acraldehyde.** V. HENRI (*Compt. rend.*, 1924, **178**, 844—847).—The spectrum of acraldehyde in solution varies with the nature of the solvent; in hexane, it resembles that exhibited by the substance in the state of vapour. Two series of bands were observed, five of increasing intensity between  $4150 \text{ \AA.}$  and  $2780 \text{ \AA.}$ , and a region between  $2450 \text{ \AA.}$  and  $1980 \text{ \AA.}$  When the acraldehyde is in a state of vapour, the former group may be resolved into a large number of lines. Evidence is adduced to show that the former series is due to the carbonyl group, whilst the latter originates in the ethylenic bond. This is confirmed by comparison with the spectra of propaldehyde,  $\beta$ -methyl- $\Delta^8$ -butylene, and acrylic acid.

H. J. E.

**Absorption Spectrum of Naphthalene Vapour.** V. HENRI and H. DE LAZLÒ (*Proc. Roy. Soc.*, 1924, **A**, **105**, 662—682; cf. this vol., ii, 367).—When radiation is absorbed by a molecule, changes may occur (1) in the energy of the electrons in the molecule, (2) in the vibratory energy of the component atoms, and (3) in the rotational energy of the molecule as a whole. Three types of molecular absorption spectra may therefore be expected: (a) in which all three of the above energy changes are quantised, (b) in which only changes (1) and (2) are quantised, and (c) in which only (1) is quantised. Spectra of type (a) will consist of groups of band series with a fine structure. Type (b) will have groups of band series in which the individual bands have no fine structure and are  $5$ — $10 \text{ \AA.}$  wide. Type (c) will consist of continuous absorptions over regions  $100$ — $300 \text{ \AA.}$  wide. Examples are quoted of each type of absorption (cf. this vol., ii, 4).

The absorption of naphthalene vapour has been examined. The saturated vapour was maintained in a jacketed quartz cell  $30$  cm. long, between temperatures of  $20^\circ$  and  $150^\circ$ . The cell was previously evacuated. An absorption of type (a) was observed in the region  $3200$ — $2820 \text{ \AA.}$  and one of type (b) in the region  $2820$ — $2500 \text{ \AA.}$  The three branches caused by a positive, negative, and zero change in the rotational quantum number were analysed in the absorption of type (a); constant frequency differences were detected in the

type (*b*) absorption. The authors conclude that in general the absorption of a molecule evolves from type (*a*) through (*b*) to (*c*) with increase in the frequency of the absorbed light. They suggest a connexion between this transition and intramolecular changes of structure. The value for the moment of inertia of the naphthalene molecule deduced from the constants of the absorption spectrum is much smaller than that obtained by Bragg from the difference in length of the unit cells of naphthalene and anthracene crystals.

S. B.

**Effect of Viscosity on Fluorescence.** F. PERRIN (*Compt. rend.*, 1924, 178, 2252—2254).—The fluorescence of a dissolved substance decreases exponentially as the concentration of the solution decreases, and since a molecule in the critical state (*i.e.*, one which has absorbed a quantum of the exciting radiation) returns to the normal state immediately another molecule of the same substance approaches sufficiently near, the constant will depend on the coefficient of diffusion of the dissolved substance and therefore on the viscosity of the solution. This has been verified for solid solutions of fluorescent-blue and eosin in fused dextrose. When the fluorescence only decreases appreciably at high concentrations the substance exhibits fluorescence in the pure solid state, *e.g.*, acid quinine sulphate and phenanthrene. The viscosity also affects the duration of the critical state of the molecules and therefore the rate of disappearance of the luminescence. Short periods of phosphorescence have been observed with some of the solid solutions employed, especially with rhodamine (which decreases to one-half in  $\frac{3}{4}$  second), with eosin, erythrosin, and rhodamine in ordinary glycerol, and with eosin (0.001 second), in 70% glycerol solution. The duration of the critical state also diminishes as the concentration of the solution increases.

J. W. B.

**Application of Fluorescence Phenomena to the Identification of Medicaments.** E. BAYLE and R. FABRE.—(See ii, 574.)

**Phosphorescence and Photoelectric Effect.** M. CURIE (*Compt. rend.*, 1924, 178, 2244—2246).—The influence of varying concentrations of bismuth on the intensity of the photoelectric effect and on the fluorescence and phosphorescence of calcium sulphide is investigated, all the specimens containing 1% of sodium chloride. The conclusion of Lenard (*A.*, 1909, ii, 283) that calcium sulphide free from bismuth shows no photoelectric effect is confirmed. The photoelectric effect appears with the introduction of the phosphorescent substance but does not depend appreciably on its concentration and is not a consequence of luminescence.

J. W. B.

**Conservation of Momentum in Exciting and Ionising Collisions.** G. JOOS and H. KULENKAMPFF (*Physikal. Z.*, 1924, 25, 257—263).—The principle of conservation of momentum is combined with that of the conservation of energy for collisions resulting in excitation or ionisation, and the results are applied to

various limiting cases. For the case where particles of atomic mass collide at low velocities, as in slow canal rays, the total mass of both is taken into account and the velocity of impact necessary to produce excitation must be at least twice that required for the same process if the impinging particle be an electron. This is in accordance with the limited experimental data available. For greater velocities, the mass of the atom struck does not enter, but only that of the electron displaced. On this assumption, the calculated velocity for  $\alpha$ -particles at the end of their effective path is of the right order of magnitude.

L. J. H.

**Explanation of Abnormal Low-voltage Arcs.** K. T. COMPTON and C. H. ECKART (*Nature*, 1924, **114**, 51).—Experiments with low-voltage arcs in argon and mercury indicate that there is always a sufficient cathode drop to produce ionisation. A. A. E.

**Temperature Coefficients of Electrical Conductors.** W. BILTZ (*Z. anorg. Chem.*, 1924, **133**, 306—311; cf. this vol., ii, 184, 552).—Fused salts may be divided into two classes as regards the temperature coefficients of their electrical conductivity: (1) salts, such as silver chloride, which are good conductors in the fused state, and have positive temperature coefficients which are less when the salt is fused than when it is in solution; and (2) salts such as aluminium chloride, which are poor conductors in the fused state, and have positive temperature coefficients comparable with or greater than those of the salt in solution. The temperature coefficients of all substances are determined almost entirely by the absolute value of the conductivity, the greater the conductivity the less being the temperature coefficient. This rule is unaffected by the nature of a particular substance, and by its presence in the liquid, amorphous, or crystalline state. At the one end of the series are the pure metals which have very high conductivity and negative temperature coefficients, whilst at the other extreme are insulators such as crystalline sodium chloride with low conductivity and large positive temperature coefficients.

W. H.-R.

**Dielectric Constants and Chemical Constitution of Organic Liquids.** E. H. L. MEYER (*Z. Physik*, 1924, **24**, 148—152).—Organic liquids containing a carbon atom which has at least two valencies attached to atoms other than carbon, or which contain electronegative inorganic groups, are all dipolar liquids, and possess a high dielectric constant, with a large temperature coefficient.

S. B.

**$\gamma$ -Rays of Very High Frequency, Emitted by Radium.** J. THIBAUD (*Compt. rend.*, 1924, **178**, 1706—1709).—Since  $\gamma$ -rays, and the  $\beta$ -rays excited by them, bear the same energy relations to one another as X-rays and the resulting corpuscular radiation, that is, the energy of the  $\beta$ -ray is equal to the difference between the energy of the exciting  $\gamma$ -ray and the energy necessary to drive out the electron from the atom (Ellis, A., 1921, ii, 422; 1922, ii, 339), the wave-lengths of  $\gamma$ -rays may be determined by studying the secondary  $\beta$ -rays excited by them in a heavy element.



The author has measured the secondary  $\beta$ -ray emission from lead excited by the  $\gamma$ -radiation from radium. The first four lines in the magnetic  $\beta$ -ray spectrum obtained correspond with those measured by Ellis (*loc. cit.*) and by de Broglie and Cabrera (A., 1923, ii, 109), and with the natural spectrum of radium-B. Four others, with double the energy, are new, and correspond with the  $\beta$ -particles emitted from the *K* and *L* levels of radium-B and -C. From the energies required to remove an electron from these levels and the energies of the  $\beta$ -radiation, calculations of the  $\gamma$ -radiation are made. The values 1123 and 605 kilovolts, obtained for the natural spectrum of radium-C, are identical with those obtained for the natural spectrum of radium from the results of Rutherford and Robinson (A., 1913, ii, 899). Ellis's rule (*loc. cit.*) therefore applies to  $\gamma$ -rays of very high frequency, and the energies thus calculated for the  $\gamma$ -rays indicate that, within the nucleus, there may be differences of energy corresponding with potentials exceeding a million volts. The results have been checked by using platinum and uranium radiators.  $\beta$ -Ray velocities up to 0.974 of the velocity of light have been examined by a modification of de Broglie and Cabrera's method (*loc. cit.*).  
M. S. B.

**Structure of Selenium.** H. COLLINS (*Chem. News*, 1924, 128, 408—411; cf. this vol., ii, 381).—Numerical considerations lead the author to write the formula  $\begin{smallmatrix} \text{Na} \\ \text{Na} \end{smallmatrix} > \text{Na}-\text{H}-\text{H}_3-\text{H}-\text{H}_3-\text{H}$  for the atom of selenium, and it is further stated that "Se equals  $\text{Na}_2\text{S}$ ."

A. A. E.

**Atomic Models of the Alkali Metals.** R. B. LINDSAY (*J. Math. Phys.*, 1924, 3, 191—236).—An attempt is made to calculate the orbits of the electrons of these atoms based on the Bohr theory. To allow for the mutual action of one electron on another, it is assumed that each electron will influence the others as a continuous distribution of electricity the density of which is uniform over every spherical surface around the nucleus, and of such a magnitude that the total charge between two such surfaces is equal to the fraction of the electron charge corresponding with the fraction of time which the electron spends between these surfaces. As a first approximation, Keplerian orbits are used, and what appear reasonable values for the effective nuclear charge and the effective quantum number are selected. From these the energy and the dimensions of the orbit are calculated and these values substituted in the fundamental quantum equation  $\oint p_r dr = (n-k)h$ . The resulting divergence of the value of  $(n-k)$  from its true integral value is thus determined and indicates the direction in which the assumed values for the effective charge and quantum number were in error. A second approximation is then made and so on until satisfactory agreement is obtained. In this way, the dimensions of the orbits of the various electrons in lithium, sodium, potassium, rubidium, and caesium are calculated and the orbits plotted. The effective quantum numbers for the outermost electron are all greater than those measured from spectrum observations, although the variation from

atom to atom is very similar. The dimensions of the ions thus obtained are in fair agreement with those deduced from crystal data. The author also deals with the effect of the existence of phase relations between electrons travelling in similar orbits and the polarisation effect induced by the outermost electron on the others. The latter effect is shown to be capable of explaining the discrepancy between the values for the effective quantum numbers found in the earlier part of the paper and those determined by spectrum measurements in the case of lithium and sodium. G. S.

**Systematic Doctrine of Affinity.** W. BILTZ.—(See this vol., ii, 482, 487, 491.)

**The Increased Valency-affinity,  $\sqrt{A}$ , of the Metallic Ion in Fused Salts.** J. J. VAN LAAR (*Chem. Weekblad*, 1924, 21, 339—341).—The value of  $\sqrt{A}$  for metals can be calculated from the vapour pressure of the fused metal; this value is found to be identical with the value for the metal in the fused salts. From the values for the vapour pressures of fused lead chloride,  $10^2\sqrt{A_0}=37$ ; for metallic lead  $10^2\sqrt{A_0}=26$ , whilst the residual affinity for  $2\text{Cl}=2\times 5.4=11$ . Calculations for the halides of the alkali metals lead to the same conclusion. It follows that the metals in fused salts must be entirely in the free condition. S. I. L.

**Explanation of the Theory of the Rotation of the Atomic Nucleus. VI—VII.** H. HENSTOCK (*Chem. News*, 1924, 128, 257—260, 277—278, 405—408; cf. A., 1923, ii, 400, 477, 679, 845; this vol., ii, 296).—An extension of the author's theory to explain many of the difficulties arising in the application of the theory of alternate polarity to carbon compounds. It is suggested that the bonds, instead of the atoms, should be labelled positive or negative, and that atoms are always united by bonds of opposite weak alternate polarity. Ammonium and alkylammonium compounds, compounds containing double bonds, the oximes, and ring compounds are considered. A. A. E.

**Relations between the Atomic Concentration and the Mechanical, Thermal, and Optical Constants of the Elements.** P. LASAREFF (*Compt. rend.*, 1924, 178, 1716—1718).—A mathematical paper in which the relationships between  $N$ , the atomic concentration of an element, and the modulus of elasticity, the latent heat of fusion, and the infra-red frequency, respectively, and also the relationship between the amorphous and crystalline states of the same element, are deduced. It is shown that a positive thermal effect should be obtained whenever an amorphous substance crystallises. M. S. B.

**The Crystal-molecule. X-Ray Spectroscopy and Constitution.** A. SCHLEICHER (*J. pr. Chem.*, 1924, [ii], 107, 225—231).—A theoretical discussion, in which crystallographic considerations are applied to molecular structure, using a principal valency direction as an axis.

W. A. S.  
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**Liquid Crystals. Soap Solutions and X-Rays.** J. W. McBAIN (*Nature*, 1924, **114**, 49).—When examined in slightly convergent light between crossed Nicols, soap solutions clearly exhibit a fan-like structure composed of focal lines. Every aqueous soap may be prepared in each of the forms, hexagonal crystals, curd fibres, anisotropic and isotropic liquids. Soap curds should not be classified as "smegmatic" (cf. Friedel, A., 1923, ii, 223, 224), since that state ("liquide à conique") is filled by the transparent conic liquid soaps. A. A. E.

**"Fibre" Structure of Electrolytically Prepared Metals.** R. GLOCKER and E. KAUPP (*Z. Physik*, 1924, **24**, 121—139).—A "fibre" structure, or one in which the crystallographic axes of all the component crystals are parallel, has only been observed previously in metals which have been mechanically worked. A similar structure has now been detected by the X-ray method in many electrolytically deposited metals. The "fibre axis" is always identical with the direction of the stream lines during electrolysis. Crystallographically, the direction of the "fibre axis" may vary with the composition of the electrolytic bath. It is concluded that the axis always represents the direction in the crystal in which the velocity of deposition is a maximum, under the imposed conditions. If the current density during deposition is too high the crystals lose all regular orientation. S. B.

**Isotherms of Hydrogen between  $-104^{\circ}$  and  $-244^{\circ}$ .** H. K. ONNES and F. M. PENNING (*Arch. Néerland.*, 1924, III, A, **7**, 157—165).—Measurements of the pressure volume relations for hydrogen at very low temperatures have been rendered possible by recent improvements in the hydrogen-vapour cryostat. The measurements were made in a piezometer and the procedure is described.

So far as possible, at each temperature, determinations of pressure were made at densities  $d_A=60, 70, 80$ , and  $90$ . The percentage variation in the values of  $pv_A$  from those recorded by Onnes and Braak (*ibid.*, 1924, III, A, **6**, 1), is quite small, and, in general, corresponds with a variation in temperature of less than about  $0.014^{\circ}$ . M. S. B.

**Isotherms of Helium between  $-205^{\circ}$  and  $-258^{\circ}$ .** F. M. PENNING and H. K. ONNES (*Arch. Néerland.*, 1924, III, A, **7**, 166—171; cf. previous abstract).—Experiments have been made with the object of determining the form of the isochores for helium between densities  $d_A=165$  and  $185$ , data at these low temperatures being very scanty (cf. Onnes, *Comm. phys. lab. Leiden*, Nos. 102A, 102c, 119; Holborn and Schultze, A., 1915, ii, 743; Holborn and Otto, A., 1922, ii, 737). The values of  $pv_A$  are tabulated and represented by a formula which shows them to be in good accord with previous determinations at higher temperatures. M. S. B.

**Isochores of Air and of certain other Gases.** F. M. PENNING (*Arch. Néerland.*, 1924, III, A, **7**, 172—206).—In general, the

isochores of gases and liquids do not deviate greatly from straight lines, but it is important for the formulation of the equation of condition to know whether isochores are straight lines or curves. The author has therefore examined the isochores of air at temperatures between  $-145^{\circ}$  and  $-70^{\circ}$  for  $d_A=80, 90$ , and  $100$ , of hydrogen at temperatures  $-103^{\circ}$  to  $-244^{\circ}$  for  $d_A=70, 80$ , and  $90$  (cf. preceding abstract), and of helium (cf. preceding abstract) at temperatures  $-205^{\circ}$  to  $-259^{\circ}$  for  $d_A=175$  and  $185$ . The isochores are found to be represented by curves which deviate perceptibly from straight lines.

M. S. B.

**Boiling Points and Heats of Evaporation of Salts.** R. LORENZ and W. HERZ.—(See ii, 549.)

**Vapour Pressure of Solid Carbon.** J. J. VAN LAAR (*Compt. rend.*, 1924, **178**, 2250—2252).—A restatement of the results of previous calculations (cf. A., 1921, ii, 17, and Wertenstein and Jedrzejewski, A., 1923, ii, 632).

J. W. B.

**Vapour Pressures of Alkaline-earth Metals.** O. RUFF and H. HARTMANN.—(See this vol., ii, 481.)

**Measurements of Gaseous Diffusion.** J. M. MULLALY (*Nature*, 1924, **113**, 711—712).—The method of measurement is illustrated by placing mercury and iodine at the opposite ends of a straight, sealed glass tube containing helium or nitrogen, and determining the gradient of flow from the composition of the deposit and the amount of vapour precipitated in unit time.

A. A. E.

**Determination of the Density of Gases.** F. POLLITZER (*Z. angew. Chem.*, 1924, **37**, 459—461).—An apparatus is described in which the weight of a long column of the gas is compared with that of a similar column of a gas of known density by means of a manometer. Two vertical tubes 10 m. long are soldered together lengthwise and bent horizontal at their upper ends which connect with a pressure-equalising chamber. The lower ends may be put into communication with a source of gas or with the manometer by means of 3-way cocks. The manometer consists of a vessel filled with petroleum and connected with a tube inclined at a small angle to the horizontal and provided with a scale for measuring the height of the liquid. The scale is calibrated by comparing two gases of known density, and an analysis is conducted by comparing the unknown gas with one of the standards.

A. R. P.

**Equation of State of a Gas.** J. E. JONES (*Proc. Camb. Phil. Soc.*, 1924, **22**, 105).—A mathematical discussion of the effect on the perfect gas law of intramolecular fields. The resulting equation is of the usual type,  $pv=kNT+B/v$ , but the method of deduction gives to  $B$  a physical meaning. In the interior of the gas  $B/v^2$  is shown to be the stress across unit area due to the interaction of the gas on the two sides of the area. It is a statical stress which exists apart from the motion of the gas. From a consideration of the statistical distribution of the molecules it is shown that  $B$  can be

calculated as a function of the temperature. The pressure at the boundary is calculated for a more general molecular model than that assumed by van der Waals. The same expression is found for  $B/v^2$ , but in this case  $B/v^2$  denotes the diminution of the momentum pressure at the boundary as distinct from the static stress which it represents in the interior of the gas. G. S.

**Dielectric Constant and Volume of the Molecule.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, **135**, 370—371).—The results of Grimm and Patrick (this vol., ii, 86) for the dielectric constants of organic liquids at the boiling point have been used to confirm the authors' previous deduction, that the quotient  $\psi$ , of molecular refractive power by molecular volume, for all substances should be  $\psi_s=0.331$  at the b. p. (cf. A., 1923, ii, 801) except for dipolar molecules. The values of  $\psi_s$  for benzene, toluene, *m*-xylene, *p*-cymene, carbon tetrachloride, and carbon disulphide are of the order 0.3, in agreement with theory. The remaining substances, which probably consist of dipolar molecules, have considerably larger values of  $\psi_s$ . W. H.-R.

**Comparison of Molecular Volume Numbers.** I. R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, **135**, 372—373).—The molecular volumes at absolute zero have been calculated for a number of substances from their refractive indices (A., 1923, ii, 801), and also from the equation of state, by a method due to van Laar (see Lorenz, "Raumerfüllung und Ionenbeweglichkeit," 1922, p. 102). The numbers obtained by the optical method are always much the smaller. The closest agreement between the values calculated by the two methods is shown by carbon disulphide, for which the ratio is 1.22, and the greatest difference by hydrogen, for which the ratio is 2.63. W. H.-R.

**Attempt to include Transition Temperatures in the Law of Corresponding States.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, **135**, 374—379).—An attempt to extend the previous work of the authors connecting various physical constants of substances with the law of corresponding states. The m. p. and transition temperatures of a large number of substances (metals, simple compounds, and minerals) have been tabulated. If  $T_u$  is the transition temperature, and  $T_e$  the m. p., the ratio  $T_u/T_e$  varies between 0.252 and 0.978, but by far the greater proportion of substances give values between 0.6 and 0.9. Approximately,  $T_u/T_e=0.8$ , but many exceptions are shown. W. H.-R.

**Properties of Powders. VIII. Influence of Velocity of Compression on Apparent Compressibility of Powders.** E. E. WALKER (*Trans. Faraday Soc.*, 1924, **19**, 614—622).—When a column of powder is compressed in a cylinder under constant load, the relation between the volume  $V$  (ratio of apparent volume of powder/actual volume of solid particles) and time is given by  $V_1 - V_2 = 10K'(t_2^{1/10} - t_1^{1/10})$ , where  $K'$  is the velocity coefficient and  $t$  is time. This equation holds for all powders for which  $V=C-K \log R$  (cf. Part VI, *ibid.*, p. 79), where  $R$  is the resistance of the

powder to steady loads. When  $V$  approaches unity,  $K'$  and  $K$  are no longer constant, but diminish with time, but the ratio  $K'/K$  remains constant. An expression for the resistance to impact in terms of the resistance to constant load has been derived. The shrinkage of ammonium nitrate pellets in the presence of traces of moisture is explained by the high value of  $K'$  for this substance, which is great enough to allow of comparatively rapid contraction under small loads, such as those produced by capillary forces. S. S.

**Criterion of Gas Evolution from Powdered Substances.**

G. TAMMANN and H. DIEKMANN (*Z. anorg. Chem.*, 1924, **135**, 194—196).—The temperature at which a mercury drop (0.3—0.8 cm. diameter), supported on a dry, powdered substance, sinks through the powder increases with the density of the latter. When adsorbed gases are evolved on warming, the compactness of the powder is destroyed and the mercury sinks through more readily. Reduction of external pressure produces the same effect. When the powder grains are 0.2—1.0 mm. in diameter the drop will not sink on heating or on reducing the pressure. S. K. T.

**Potentiometric Determination of the Velocity of Diffusion of Metals through Mercury.**

E. COHEN and H. R. BRUINS (*Z. physikal. Chem.*, 1924, **109**, 397—421).—A method of measuring the rate of diffusion of metals through mercury is described which may be employed over a wide range of temperature and pressure. It has been used to determine the coefficient of diffusion of cadmium in mercury at 20° and 1 atm., the value  $1.520 \times 10^{-5}$  sq. cm./sec. being obtained. A mercury surface in a tube of known area was covered with cadmium sulphate solution and converted into very dilute amalgam by electrolysis with a cadmium anode, employing a constant current for a known time. The reduction in the cadmium concentration at the surface, due to diffusion, is followed by a change in potential as measured against an amalgam of constant composition (heterogeneous) immersed in the same electrolyte. Great difficulties were introduced by the curvature of the surface. This, of itself, makes the calculated area too small, and, during electrolysis, causes more rapid exhaustion of the electrolyte near the walls of the tube than elsewhere, with a correspondingly lower concentration of deposited cadmium, introducing an error equivalent to the calculated area being too large. By regulating the strength of the electrolysing current, compensation of these two opposing errors can be secured, especially when the edge is shielded by a rubber ring. In these circumstances the calculated diffusion coefficient is independent of the time. The particular current strength which gives this result depends on the concentration of the cadmium sulphate solution. The reproducibility of the results is about 0.5%.

L. J. H.

**Piezo-chemistry. Influence of Pressure on the Velocity of Diffusion of Metals through Mercury.** E. COHEN and H. R. BRUINS (*Z. physikal. Chem.*, 1924, **109**, 422—430).—With the method and apparatus previously described (cf. preceding abstract) the diffusion coefficient of cadmium through mercury at 20° and

1500 atm. was found to be  $1.446 \times 10^{-5}$  sq. cm./sec., a decrease of about 5% on the value obtained at the same temperature and 1 atm.

L. J. H.

**Viscosity Coefficients of Nitric Oxide and Propane and their Mixtures with Hydrogen.** A. KLEMENC and W. REMI (*Monatsh.*, 1924, **44**, 307—316).—The viscosities were determined by Rankine's method (A., 1910, ii, 188, 409, 829; 1911, ii, 87). The following values were found: carbon dioxide  $\eta_0 = 138.2 \times 10^{-6}$ ,  $C = 263.4$  ( $C$  = Sutherland's "attraction constant"), hydrogen  $\eta_0 = 84.9 \times 10^{-6}$ ,  $C = 90.7$ ; nitric oxide  $\eta_0 = 179.7 \times 10^{-6}$ ,  $C = 162.2$ ; propane  $\eta_0 = 75.2 \times 10^{-6}$ ,  $C = 323.7$ . For mixtures of nitric oxide and hydrogen, the viscosity increases continuously with increase in the nitric oxide concentration. For mixtures of propane and hydrogen the viscosity increases to a maximum value  $\eta_0 = 97 \times 10^{-6}$  with 15% propane; the observed values do not agree satisfactorily with those calculated from Puluj's formula (*Wien Akad. Ber.*, 1879, **79**, 97, 745).

F. A. M.

**Hydrotropic Phenomena. II.** R. TAMBA (*Biochem. Z.*, 1924, **145**, 415—421).—The miscibility of various liquids such as amyl and benzyl alcohols, quinoline, aniline, cyclohexanone, cyclopentanol, nitrobenzene, benzaldehyde, and ethyl acetate, with 50% solutions of the potassium or sodium salts of isobutyric, *n*-valeric, *n*-hexoic, *n*-heptoic, palmitic, stearic, oleic, trichloroacetic, copaibic, and abietic acids has been investigated with reference to the question of hydrotropism (Neuberg, A., 1916, ii, 555).

J. P.

**Volumes Occupied by the Solute Atoms in certain Metallic Solid Solutions and their consequent Hardening Effect.** A. L. NORBURY (*Trans. Faraday Soc.*, 1924, **19**, 586—600).—Density determinations have been made of pure copper and of solid solutions in copper of aluminium, silicon, manganese, nickel, zinc, silver, and tin. When the thickness of the specimen was reduced 50% or more by cold hammering, small blow-holes were eliminated and consistent measurements were obtained. When the difference between the Brinell hardness numbers for copper and a 1 at.-% solution is plotted against the difference of the corresponding mean atomic volumes, all the points lie on a smooth curve except in the case of silicon. In general, the hardening effect is therefore proportional to the distortion of the copper lattice by the added element, but in the case of silicon the chemical affinity is great enough to form a compound which still further distorts the space lattice and gives a very hard alloy. Similar curves are afforded by the data of Goebel (*Z. Metallk.*, 1922, **14**, Sept.-Dec.) for solid solutions in lead. S. S.

**Specific and Latent Heats of Iron and Steel.** A. MALLOCK (*Nature*, 1924, **113**, 566—567).—Cooling curves obtained with iron and steel wires show that as the carbon content of the steel is increased, the temperature at which recalescence occurs is lowered, and that the specific heat of iron and steel at the ordinary temperature is about three times as great as at temperatures above the

point of recalescence. No sudden change in the coefficient of expansion or specific heat between  $1400^{\circ}$  and  $1500^{\circ}$  was observed.

A. A. E.

**Thermo-electric Properties of Bismuth Alloys with Special Reference to the Effect of Fusion. Note on Thermo-electric Inversion.** C. R. DARLING and R. H. RINALDI (*Proc. Physical Soc.*, 1924, **36**, 281—287).—The thermo-electric effect of copper-bismuth alloys, and of alloys of bismuth with lead or tin, were measured over a range of temperature (at the hot junction) which included the m. p. With pure bismuth a sharp break in the *E.M.F.*-temperature curve occurs at the point of fusion. The addition of lead (up to 30%) to the bismuth lowers the *E.M.F.*, but further addition gives a progressive, although slight increase. The addition of 10% of tin reverses the sign of the *E.M.F.*, but larger quantities reduce this negative value, so that with 60 or 70% of tin and high temperature it becomes positive again. The authors report two breaks in the cooling curves of these alloys (cf. A., 1902, ii, 145). It would seem that, whenever solidification is accompanied by considerable expansion, marked breaks occur in the *E.M.F.*-temperature curve, but not when there is contraction.

Iron and an alloy of 60% bismuth and 40% tin show re-inversion. With the cold junction at  $0^{\circ}$  the *E.M.F.* is zero when the hot junction is at  $0^{\circ}$ ,  $200^{\circ}$ , or  $350^{\circ}$ , negative (max. 0.5 mv.) for the first interval, positive (max. 0.13 mv.) for the second, and increasingly negative above  $350^{\circ}$ .

L. J. H.

**Study of Diffusion in Liquids by an Optical Method.** B. W. CLACK (*Proc. Physical Soc.*, 1924, **36**, 313—335).—A glass cell contains solution which is kept saturated at the bottom, and at constant, very small concentration at the top by means of a special streaming device. When a steady state of diffusion had been attained, the refractive index of the line  $\lambda = 5461$  was measured at different levels. The total weight of salt passing out of the cell per unit time and the variation of refractive index with concentration were determined. From these data, and the densities of the solutions, the coefficients of diffusion of sodium chloride, potassium chloride, and potassium nitrate in 0.05—5*N* solution have been calculated. The two former show a minimum of diffusivity at about 0.3 and 0.4*N*, respectively, but with the latter no minimum occurs up to about 2.3*N*. The results with the chlorides agree with the theory of Arrhenius (*ibid.*, 1921, **3**, 263), and for all three the coefficient tends towards the limiting value at infinite dilution deduced by Nernst. It is claimed that the measurements are as accurate for dilute solutions as for those of much greater concentration.

L. J. H.

**Extinction Coefficients of some Acids and their Salts in the Ultra-violet.** J. C. GHOSH and S. C. BISVAS (*Z. Elektrochem.*, 1924, **30**, 97—103).—The extinction coefficient in the ultra-violet has been determined by a modification of Henri's method for a number of strong and weak acids and their salts. Strong acids



and their salts have practically identical absorption coefficients, but there is a marked difference between weak acids and their salts. This is ascribed to a difference in the constitution of the acids and salts respectively (cf. A., 1918, ii, 299). H. T.

**Empirical Calculation of the Activity-coefficient of Simple Ions.** L. EBERT (*Z. Elektrochem.*, 1924, 30, 65–66).—Using the data for the osmotic coefficient determined by Debye and Hückel (A., 1923, ii, 459) it is shown that the activity-coefficient for uni- and bi-valent ions can be calculated from the expression  $\log f_a = -k\sqrt{C_{\text{ion}}}$  (cf. Bjerrum, A., 1919, ii, 9). This expression holds for values of  $C$  from 0 to 0.12 with univalent and from 0 to 0.05 for bivalent ions. H. T.

**Density and Temperature.** IV. W. HERZ (*Z. Elektrochem.*, 1924, 30, 62–64).—The coefficients of expansion of organic liquids and saturated vapours at equally reduced temperatures have been calculated from known data. For liquids the coefficient decreases with increase of molecular weight and increases with the temperature; for saturated vapours, the coefficient decreases with increasing molecular weight and with increasing temperature. For homologous series of organic liquids, the molecular coefficient of expansion increases with increase of molecular weight. H. T.

**Hydration of Univalent Ions.** E. SCHREINER (*Z. anorg. Chem.*, 1924, 135, 333–369).—The electrolytic theory of Bjerrum (A., 1919, ii, 9; *Z. anorg. Chem.*, 1920, 109, 275) has been used to determine the degree of hydration of univalent ions. The author's previous results for the hydration of hydrogen ions (*Z. anorg. Chem.*, 1922, 121, 321) have been corrected in order to allow for the effect of salts on the unsaturated quinhydrone electrode. The corrected hydration numbers for the hydrogen ion in a 0.005*M*-solution of hydrochloric acid in the presence of varying quantities of potassium chloride, correspond approximately with  $m=11$ . Closely agreeing numbers varying from 9.5 to 10.5 were obtained by direct measurements with saturated hydro-quinhydrone and quino-quinhydrone electrodes (cf. Büllmann and Lund, A., 1922, ii, 111). The results of Bates and Kirschmann (A., 1920, ii, 88) for the vapour pressures of solutions of hydrochloric acid have been used to calculate the hydration numbers of the ions by an extension of Bjerrum's theory, according to which, in solutions containing 0–5 mol. of hydrogen chloride in 1000 g. water, the total hydration numbers of both ions  $m+n=10-11$ . The hydration numbers become smaller at higher concentrations and in 10*M*-solution,  $m+n=5$ . Similar results are obtained in the case of hydrobromic acid. The hydration numbers of hydrogen ions in 0.005*M*-hydrochloric acid in the presence of dextrose and sucrose had a mean value of  $m=11.3$ . The hydration number of the chlorine ion calculated from the results of Corran and Lewis (A., 1922, ii, 691) is  $n=2.6$ . For the lithium ion,  $m=6.5-7.5$ , and for the hydroxyl ion,  $n=6.5-7$ , calculated from the *E.M.F.* and freezing-point data, and for fluorine the number is about 6.5. The ionic product  $[H^+][OH^-]$  of water is raised to a maximum by increas-

ing quantities of dissolved electrolytes, whilst non-electrolytes lower the ionic product. This effect has been calculated for solutions of sucrose, potassium chloride, and magnesium sulphate.

The hydration numbers are statistical and have no real meaning, but the size of the imaginary hydrated ion can be calculated if it is assumed that the water of hydration forms a spherical shell round an ion, the radius of which can be obtained from the results of Bragg (A., 1920, ii, 537). When the imaginary radii of the hydrated ions are calculated in this way, it is found that the sums of the radii for cations and anions bear a constant ratio to the minimum distances between ions in electrolytes calculated by Bjerrum. The hydration numbers obtained by the static thermodynamic method of Bjerrum do not in general agree with those predicted by the kinetic method.

W. H.-R.

**Vapour Pressure and the Law of Equilibrium for Electrolytes.** K. JABŁCZYŃSKI (*Rocz. Chem.*, 1923, 2, 467—473).—The ionisation constant for various electrolytes is calculated from vapour-pressure data, applying the formula  $N^{4/3}/N_0 = K_1$  of Jabłczyński and Wisniewski (A., 1922, ii, 190). For sodium and potassium chlorides at 100° the constancy of  $K_1$  is very satisfactory; it is rather less so for lithium chloride. The hydration of the ions in solution is also taken into account and the figures obtained are in good agreement with the ebullioscopic measurements of Jabłczyński and Kon (T., 1923, 123, 2953). On the strength of these facts it is possible to calculate the depression of the vapour pressure of water at various temperatures due to the dissolution of the above salts; the figures so obtained are in excellent agreement with the experimental values found by Tammann (Landolt-Börnstein, Tables, 4th ed., p. 418).

G. A. R. K.

**Electrical Conductivity of certain Univalent Salts of the Higher Fatty Acids in Non-aqueous Solutions and in the Fused State.** S. S. BHATNAGAR and M. PRASAD (*Kolloid-Z.*, 1924, 34, 193—196).—The electrical conductivities of sodium and potassium palmitate, oleate, and stearate in the fused state, and also in solution in ethyl, propyl, butyl, and amyl alcohols, have been examined. The conductivity in the fused state is electrolytic, and the increase with rise of temperature is ascribed to increased dissociation, and not to greater mobility of the ions. The conductivity in amyl alcohol is too low to be determined, but in the other alcohols it follows the Nernst-Thomson rule. If the equivalent conductivities of the soap solutions are plotted against the conductivities per litre, straight lines are obtained, in contrast to the results of McBain and Martin (T., 1914, 105, 957) for aqueous solutions of sodium palmitate. The alcoholic soap solutions do not obey Ostwald's dilution law.

M. S. B.

**Electrolytic Conductivity of Molten Chlorides.** A. VOIGT and W. BILTZ.—(See ii, 552.)

**Inductor for Conductivity Determinations for Use with Continuous Current.** F. SCHEMINZKY (*Z. physikal. Chem.*, 1924, 109, 435—437).—The apparatus consists of a condenser in

series with a commercial glow lamp. This is essentially a Geissler tube and allows current to pass only when a definite potential has been attained. The oscillating current thereby produced in the primary coil of a transformer (also in series with the lamp) induces a sine-wave current in the secondary coil. L. J. H.

**Electrolytic Capacity and Resistance of a Platinum-Rhodamine-B-Platinum Cell.** K. F. SUN (*Physical Rev.*, 1924, **23**, 617—630).—The phase angle method of measurement shows that the resistance is constant but the capacity increases with *E.M.F.* above 0.4 volt and varies inversely as the square root of the frequency for 10 to 70 cycles. Increase of concentration and temperature increases the capacity and decreases the resistance. Solutions of rhodamine-B in ethyl alcohol were employed. A. A. E.

**Determination of the Potential of the Alkali Metals.** G. TRÜMLER (*Z. Elektrochem.*, 1924, **30**, 103—109).—By means of the chain  $\text{Na}|\text{solid sodium salt}|\text{saturated solution of sodium salt}|\text{NKClHg}_2\text{Cl}_2|\text{Hg}$ , the normal potential of sodium has been determined and found to be 2.72 volts. As guard electrolytes (solid sodium salt in the above chain) sodium chloride and Thüringer glass were used. The former is a good insulator and on this account not very suitable; the latter behaves, however, towards saturated sodium chloride as an ideal sodium electrode. H. T.

**Oxidation Potentials of Molybdenum and Tungsten Octacyanides.** O. COLLEBERG (*Z. physikal. Chem.*, 1924, **109**, 353—374).—Tungsten and molybdenum both form two stable complex cyanides of the type  $\text{K}_3\text{M}(\text{CN})_8$  and  $\text{K}_4\text{M}(\text{CN})_8$ , in which the metal is respectively quinque- and quadri-valent. The oxidation potentials of mixtures of the two tungsten complex ions may be represented, at 0°, by the formula  $E = E_0' + 0.0541 \log C_5/C_4$ , where  $C_5$  and  $C_4$  are, respectively, the total concentrations of the complex ions in which the metal has the valency indicated by the suffix, and  $E_0'$  is a constant so long as  $C_4 + C_5$  is constant. The author assumes arbitrarily that the activity coefficients, (*f*), of the salts may be represented by equations of the type  $\log f = -k\sqrt[3]{C}$ , where  $C = C_5 + C_4$  (cf. A., 1919, ii, 9; 1923, ii, 459, 724; this vol., ii, 386). This leads to a formula for the potential of the type  $E = 0.504 + 0.0541 \log C_5/C_4 + 0.1429\sqrt[3]{C_5 + C_4}$  which holds for  $C = 0.002$ — $0.1$  mol. per litre. Addition of potassium chloride increases the potential, and theoretical considerations similar to the above lead to a formula of the type  $E = E_0 + k\sqrt[3]{C_5 + C_4 + [\text{KCl}]} + 0.0541 \log C_5/C_4$ , where  $E_0 = 0.5155$  and  $k = 0.08167$ . This was confirmed experimentally at 0° for the case where  $C_5 + C_4$  was kept constant (approximately 0.01*M*) while  $C_5/C_4$  and  $[\text{KCl}]$  varied, the latter from 0—1 mol.

With  $C_5 + C_4 = 0.106M$  the temperature coefficient of the cell composed of the normal calomel electrode and the complex tungsten cyanide electrode is negative, and the heat of reaction at 25° is 16860 cal. Similar experiments were made with the corresponding molybdenum compounds. L. J. H.

**Membrane Potentials and their Relation to Anomalous Osmosis.** F. E. BARTELL (*Colloid Symposium Monograph, Univ. Wisconsin*, 1923, 120—144; cf. A., 1923, ii, 221, 298, 384).—The general gas law  $PV=nRT$  should apply (substituting  $\pi$ =osmotic pressure for  $P$ ) to a system where a semi-permeable membrane separates solution and solvent, providing the membrane is strictly semi-permeable. Anomalous osmotic effects are believed to be caused primarily by electric forces due to electrolytes in the solution. One set of these forces operates between the two faces of the membrane, giving a membrane potential; the second set operates along the pore walls of the membrane in the form of an electrical double layer, giving a capillary potential. Therefore change in pore diameter changes the shape of the osmosis curve. Furthermore the nature of the charge on the capillary walls influences both the intensity and direction of the osmosis, this electrical effect being superimposed on the ordinary normal osmosis. The theory explains: (1) anomalous osmosis with such different membranes as porcelain, parchment paper, gold beater's skin, bladder and collodion; (2) potential changes; (3) abnormal swelling or shrinking of colloids.

CHEMICAL ABSTRACTS.

**Potential of Poisoned Electrodes.** N. ISGARISCHEV and E. KOLDAEWA (*Z. Elektrochem.*, 1924, 30, 83—86).—The influence of potassium cyanide, arsenious oxide, hydrogen sulphide, brucine, and quinine on the potentials of the hydrogen and oxygen electrodes has been investigated. In the case of the hydrogen electrode, these substances reduce the potential, which, however, rises to its true value after several hours. The poisoned oxygen electrode shows little tendency to return to its normal value. These effects cannot be explained by a depolarising action, and are attributed to combination between the platinum and the added poisons with the formation of compounds which have lower potentials. These compounds are unstable in acid solution and the poison is carried off in the stream of hydrogen.

H. T.

**Influence of Fluoride on Overvoltage.** N. ISGARISCHEV and D. STEPANOV (*Z. Elektrochem.*, 1924, 30, 138—143).—Investigations have been made of the influence of fluorides on overvoltage in acid and alkaline solutions, with platinum gold, silver, and graphite electrodes. A maximum overvoltage is obtained for a certain fluoride concentration, viz., 5—10 g. of sodium fluoride per litre in alkaline and 35 g. of ammonium fluoride in acid solutions. The increase in overvoltage is ascribed to the formation of oxyfluorides at the electrode surface. These oxyfluorides as well as the oxides of platinum are dissolved when the concentration exceeds the above values. Similar results were obtained from a study of the discharge curves with polarised anodes.

H. T.

**Hydrogen Overvoltage of Metals and their Characteristic Properties. II. Overvoltage and Melting Points.** E. J. WEEKS (*Chem. News*, 1924, 129, 17; cf. this vol., ii, 457).—Fifteen metals are tabulated in two groups, those of comparatively low

m. p. ( $-38^{\circ}$  to  $+630^{\circ}$ ) having a hydrogen overvoltage in acid solution of 0.5–0.7, and those of m. p. 960–3000° having an overvoltage of zero–0.35. A. A. E.

**Cathodic Behaviour of Alloys. I. Iron-Nickel Alloys.** S. GLASSTONE (*Trans. Faraday Soc.*, 1924, **19**, 574–585).—The ratio iron : nickel in iron-nickel alloys prepared by electro-deposition from solutions of ferrous and nickel sulphates is always greater than that in the solution. At all current densities between 0.005 and 0.12 amp./cm.<sup>2</sup> nickel-iron alloys have a smaller negative deposition potential than either pure iron or pure nickel. Similar curves exhibiting shallow minima were found when the hydrogen and oxygen overvoltages are plotted against composition. The cathodic behaviour of the alloys in the presence of potassium chlorate, alkaline benzaldehyde, and alkaline and acid nitrobenzene was investigated. In all cases pure iron forms the most efficient reducing cathode. The effect of the addition of nickel is most marked with potassium chlorate as depolariser, whilst in acid nitrobenzene solutions all the alloys give 100% reduction. S. S.

**Electromotive Force of Filtration.** L. RIÉTY (*Compt. rend.*, 1924, **178**, 2246–2247; cf. A., 1911, ii, 575).—With concentrated saline solutions a difference of potential is produced between the ends of a capillary tube through which the solution is made to flow under high pressure. This is positive for copper sulphate and negative for copper nitrate solution. Prolonged flow (several days) causes the electromotive force to tend towards a limit, decreasing in the first case and increasing in the second. The electromotive force is proportional to the pressure and inversely proportional to the concentration of the solution. J. W. B.

**Electrolytic Crystallisation of Lead.** V. KOHLSCHÜTTER and F. UEBERSAX (*Z. Elektrochem.*, 1924, **30**, 72–83).—The electro-deposition of metals has been further studied on the lines devised by G. Schulze (*ibid.*, 1922, **28**, 119). Measurements of the velocity of growth with varying current densities do not support the view that growth takes place in three directions. In the deposition of lead from lead nitrate or perchlorate solutions at small current densities, massive pointed or leaf-like crystals were obtained, crystal chains being formed only at higher current densities. The velocity of chain growth depends on the lead ion and the hydroxyl ion concentrations; it increases with increase in the hydroxyl ion concentration and diminishes with increase in the lead ion concentration. Owing to the complexity of the phenomena, no explanation of crystal growth is put forward. H. T.

**Electrical Double Layer on the Surface of Solid and Liquid Bodies. II. Surface Tension.** J. FRAENKEL (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 5–20; cf. *ibid.*, **49**, 87).—Since atoms consist of a positive nucleus surrounded by electrons, every solid or liquid substance may be considered to be bounded by an electrical double layer. The thickness of this is equal to the diameter of the orbits of the external electrons. The surface tension of fused

metals can be interpreted in terms of the electrostatic energy of the double layer, whilst the radii of the atoms and the internal potentials of many metals can be calculated from the corresponding values of surface tension. The figures for internal potentials thus obtained vary from 2—6 volts, that for platinum being 5.1 volts, which fully agrees with the figure obtained from its thermionic effect. The metals can be arranged on this basis in a series which is very much like the series of Volta. The surface tension of dielectric liquids can be explained similarly. The internal pressure of liquids is determined by the normal force with which the external double layer of electricity attracts the internal one. Between the internal pressure and surface tension there is a relation which allows the magnitudes of the molecules to be calculated. For water, alcohol, and ether the molecular diameter is equal to 1.7, 3.0, and  $3.6 \times 10^{-8}$ , respectively. S. P. S.

**Heat of Evaporation and Tension of Saturated Steam at Temperatures Close to Absolute Zero.** A. BRANDT (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 1—5).—The deductions of Ariès (A., 1917, ii, 192) are inconsistent with the fact that the internal heat of vaporisation is equivalent to the work which must be done to overcome the internal forces of molecular attraction. S. P. S.

**Activity of Surface Layers of Fluids.** L. GURWITSCH (*Z. physikal. Chem.*, 1924, **109**, 375—377).—Solids partly immersed in liquids are dissolved more rapidly at the (air) surface layer of the liquid than elsewhere, even although the resulting solution has a lower specific gravity and higher surface tension than the solvent.

L. J. H.

**Surface Tension of Oil-in-water and Water-in-oil Emulsions.** S. S. JOSHI (*Kolloid-Z.*, 1924, **34**, 197—201).—Experiments have been carried out to test Quincke's conclusion that the surface tension of emulsions is less than that of pure water. Surface tension measurements on emulsions of castor, olive, and kerosene oil in water, and of olive oil in sodium oleate solution, have been made by the capillary rise and drop weight methods, and also by Ferguson's method (*Phil. Mag.*, 1913, [vi], **25**, 507). The last gave lower results than the other two methods. It has been found that, if all non-emulsified oil be completely removed, the emulsion has the same surface tension as the pure dispersive medium, but the presence of non-emulsified oil or other immiscible impurity results in a lowering of the surface tension. M. S. B.

**Preliminary Measurement of a Primary Gas-grown Skin.** J. J. MANLEY (*Proc. Physical Soc.*, 1924, **36**, 288—290).—A portion of the air absorbed on a glass surface is evolved on repeated evacuation and standing. This is regarded as having come from a "secondary" skin. When all this is evolved—no more being set free on keeping for three years in the highest vacuum of a Töpler pump—a further amount, regarded as coming from the "primary" skin, is given off by the action of the glow discharge between the mercury and an external electrode. From the known surface area

and the volume of gas evolved, this primary skin must be at least 20 mols. thick, assuming the absorbed molecules to have the same diameter as in the gaseous state.

L. J. H.

**Removal of Gas-grown Skins from a Sprengel Pump.** J. J. MANLEY (*Proc. Physical Soc.*, 1924, **36**, 291—293).—A pump is described having two vacuum tubes interposed between the cistern and the fall tube. These are fitted with external electrodes and by means of the glow discharge (cf. preceding abstract) both the glass surface and the mercury may be freed from absorbed gases.

L. J. H.

**Heterogeneous Equilibria. I. Conditions at the Boundary Surface of Crystalline Solids and Application of Statistical Mechanics.** J. A. V. BUTLER (*Trans. Faraday Soc.*, 1924, **19**, 659—665).—A theoretical paper in which, by the application of the methods of statistical mechanics to the equilibrium between a crystal surface and a saturated solution, it is shown that  $\log_e c = Q_v/RT - \log_e (AN_0/1000A'N)$ , where  $c$  is the solubility,  $Q_v$  the limiting heat of formation of the saturated solution,  $N_0$  the Avogadro number, and  $N$  the number of molecules per unit area of crystal surface. This equation has the same form as the familiar Le Chatelier-van't Hoff expression but defines the integration constant in terms of  $N$ ,  $N_0$ ,  $A = \sqrt{R/2\pi M}$ , where  $M$  is the molecular weight, and  $A = \nu\sqrt{R/W_2}$ , where  $\nu$  is a characteristic frequency for the crystal and  $W_2$  the work done in transferring 1 g.-mol. from the crystal to the point at which the attraction of the crystal and that of the solvent are in equilibrium. Taking for  $\nu$  the frequency of the "Reststrahlen" and for  $W_2$  the total heat of solution or the latent heat of fusion, it is found in the case of the alkali chlorides that the second term of the above equation gives a value for the integration constant of the right order of magnitude.

S. S.

**Liesegang's Phenomenon.** K. JABŁCZYŃSKI (*Rocz. Chem.*, 1923, **3**, 228—235).—The formation of rings of silver chromate in the Liesegang experiment is shown to be dependent on the rate of diffusion of the silver nitrate. The rate of formation can be expressed by  $(v_2^3 - v_1^3)/(t_2 - t_1) = 3kDc_0/\pi s = A$ , where  $s$  is the thickness of the gelatin layer,  $c_0$  the concentration of the silver salt, which is assumed to be constant, and  $D$  is the coefficient of diffusion of the salt in the medium. Measurement shows that  $A$  is constant within the limits of experimental error. It is also found that the ratio of the areas bounded by the rings (including the intervals between them) is a constant  $(\pi v_3^2 - \pi v_2^2)/(\pi v_2^2 - \pi v_1^2) = (v_3^2 - v_2^2)/(v_2^2 - v_1^2) = B$ . It has been suggested by Küster that there is a connexion between Liesegang's phenomenon and the formation of annular rings in tree trunks. Measurements were carried out on sections of oak and laburnum, but the values for  $A$  and  $B$  were found to be variable. The ring-like pattern observed in agate, on the other hand, is very probably due to a process related to Liesegang's phenomenon.

G. A. R. K.

**Investigation of Smoluchowski's Equation as applied to the Coagulation of Gold Hydrosol.** L. ANDERSON (*Trans. Faraday Soc.*, 1924, **19**, 623—634).—The rate of coagulation of gold hydrosols by hydrochloric acid, potassium chloride, barium chloride, and aluminium chloride has been measured colorimetrically, using the method of Hatschek. Smoluchowski's equation is found to hold for the region of rapid coagulation but not for the slower coagulation obtained with more dilute electrolytes. S. S.

**Method of Measuring the Rate of Coagulation of Colloidal Solutions over Wide Ranges.** H. H. PAINE and G. T. R. EVANS (*Trans. Faraday Soc.*, 1924, **19**, 649—658).—The coagulation of copper hydrosol by potassium sulphate has been followed over a wide range of velocities by adding starch to reduce the rate of coagulation by more concentrated electrolytes. The influence of the starch on the speed of the coagulation was allowed for by a transformation factor, which was found to be given by the relation  $\log F = k(s - s_0)$ . Here  $F$  is the transformation factor by which the observed rate must be multiplied to give the rate of coagulation in the absence of starch,  $s$  the starch concentration, and  $k$  and  $s_0$  are constants determined by experiment for the colloid and starch used.

The rate of coagulation of copper sols determined in this manner varies with the concentration of electrolyte in accordance with the equation of Freundlich (A., 1919, ii, 52). The results confirm the existence of a maximum rate of coagulation. S. S.

**Effect of Sucrose on the Rate of Coagulation of a Colloid by an Electrolyte.** L. ANDERSON (*Trans. Faraday Soc.*, 1924, **19**, 635—648).—The coagulation of gold sols at 25° by hydrochloric acid, barium chloride, and potassium chloride, in the presence of varying amounts of sucrose, has been studied. In general, it is found that the coagulating power of an ion is determined by its "activity" and not by its concentration. Sucrose not only increases the "activity" of the coagulating ion, but has a definite peptising action on the gold sol and in the case of barium and hydrogen ions produces a specific increase in coagulating power over and above that due to increased "activity." S. S.

**Rate of Formation of Precipitates. Precipitation in a Colloidal Medium. Liesegang's Phenomenon.** K. JABŁCZYŃSKI and (MLLE.) A. KLEIN (*Rocz. Chem.*, 1923, **2**, 479—490).—The rate of precipitation of silver chloride has been measured under different conditions in the presence of gelatin. The precipitation is shown to proceed in the same way as in pure water (Jabłczyński and Lisiecki, *Spraw. Tow. Nank. Warsz.*, 1917, **10**, 124). This supports the authors' explanation of the process of precipitation based on diffusion as against a purely mechanical explanation. Other arguments in favour of this view are the considerable time required for the formation of some precipitates in dilute solution and the behaviour of multivalent ions. The mechanical explanation does, however, apply to the precipitation of completely insoluble



colloids (such as sols of gold and platinum which are called colloids of the first order); the diffusion theory explains the behaviour of soluble colloids (colloids of the second order) such as silver halides.

Experiments with solutions of silver nitrate and ammonium dichromate in the presence of gelatin give results comparable with those referred to above. The formation of larger grains of solid at the expense of smaller ones by a process of diffusion affords an explanation of the formation of Liesegang's rings (*Phot. Archiv*, 1896, 321; *Z. physikal. Chem.*, 1897, 23, 365; A., 1907, ii, 533). The gradual increase in distance between successive rings is attributed to the diminishing concentration of silver ions with increasing distance from the centre. It is shown that the formula of Morse and Pierce (A., 1904, ii, 14) can be readily deduced from the diffusion theory, which also explains the constant value of  $h/h_1$  expressing the increase in thickness of the successive rings. G. A. R. K.

**General Colloid Chemistry. X. Chemical Behaviour and Colour of the Ionogen Complexes of Arsenic Trisulphide Sols.**

A. SEMLER (*Kolloid-Z.*, 1924, 34, 209—213).—The colour of arsenic sulphide sols varies from the orange-red of the coarser suspensions to the pure citron-yellow of the finely divided sols which show only a slight milkiness by transmitted light. Flocculation by an acid or a neutral salt gives a citron-yellow precipitate, but by drying at 100° the product precipitated by barium or calcium chloride it becomes red. When heated, this red product behaves similarly to realgar, but its behaviour with water shows that its colour is probably due to the presence of barium thioarsenite. In the same way, other coagula have a colour approaching that of the thioarsenites of the precipitating metallic ion. On this fact is based a theory of the formation of arsenic trisulphide sol through the production and subsequent decomposition of unstable thioarsenious acid. M. S. B.

**General Colloid Chemistry. XI. Analysis and Constitution of Silver Sols. II.**

A. ERLACH and W. PAULI (*Kolloid-Z.*, 1924, 34, 213—224).—The conditions of formation and the composition of silver sols produced by Kohlschütter's method (A., 1908, ii, 182), that is, by the reduction of a silver oxide sol by hydrogen at 60°, have been studied. The presence of alkali is necessary, either as sodium hydroxide, sodium carbonate, or ammonia. If the hydrogen is prepared by the action of sulphuric acid on zinc the sol always contains sulphur. The sols are negatively charged. On purification by dialysis, the electrical conductivity may be reduced to  $3.5 \times 10^{-6}$  mho. This is due to the presence of free hydrogen ions. The purified sol still contains varying quantities, up to 20%, of silver oxide. This may be removed by reduction with hydrogen in a platinum dish, the silver being precipitated whilst the remaining silver sol is unaffected in colour and stability. Between 10 and 30 atoms of silver appear to be associated with one electric charge. Very variable colours are obtained, yellowish-red, greenish-yellow, greyish-blue, and black with bluish-green reflections.

The nature of the ionogen complexes associated with the colloidal particles is discussed. In the formation of a sol it is supposed that  $[\text{AgO}]\text{Na}$ , or some similar complex, plays a part; but once the sol is formed sodium may be replaced by hydrogen without affecting the stability. The attachment of the silver oxide molecules to the sol is connected with the fact that silver compounds readily form complex salts.

M. S. B.

**Production of Metal Sols.** R. FÜRTH (*Kolloid-Z.*, 1924, **34**, 224—227).—Colloidal solutions of silver, gold, platinum, and copper in water, have been obtained by first reducing the metal to a fine powder by means of the electric arc in air between two electrodes of the same metal, and mixing this with water. Satisfactory silver and platinum sols have been obtained, but only a very dilute gold sol, a large proportion of the powder falling to the bottom of the vessel in the latter case. This is probably due to the tendency of gold sols to crystallise. The copper sol contained chiefly a coagulated copper hydroxide sol. No silver sols could be obtained in ethyl alcohol and benzene, and in glycerol the particles were not apparently so highly charged as in water. This behaviour is attributed to the differences between the dielectric constants. The lower the dielectric constant of the dispersive medium, the smaller the charge which it can give to the metal powder, and hence the less the tendency to sol formation. Organo-sols prepared by Bredig's or Svedberg's method are already electrically charged by the powdering process.

M. S. B.

**Possibility of a Connexion between the Protective and Elastic Properties of Hydrophilic Sols.** H. FREUNDLICH and L. F. LOEB (*Kolloid-Z.*, 1924, **34**, 230—233).—The protective action of certain hydrophilic colloids has been ascribed to their adsorbability, but other factors come into play, and a comparison has been made between the protective action of different colloids and their elasticity, since it is possible that the protection is due to the formation of a strong, viscous coating round the particles of sol. Sodium oleate, which has no elasticity, has, however, a much smaller protective power than the elastic sodium stearate. Gelatin, which is very elastic, is also a good protective agent, yet dextrin and starch, which are fairly strong protective colloids, are quite inelastic, and the very elastic agar sol exerts no protective action.

M. S. B.

**Behaviour of Ferric Hydroxide, Manganese Dioxide, and Humus Sols towards Carbonate, Hydrogen Carbonate, and Clay.** H. UDLUFT (*Kolloid-Z.*, 1924, **34**, 233—237).—Dolomite adsorbs ferric hydroxide sol but not manganese dioxide, whereas clay adsorbs both. Manganese dioxide and ferric hydroxide sols exert a protective action on one another. Humus, however, precipitates ferric hydroxide but not manganese dioxide. The hydrogen carbonate ion precipitates ferric hydroxide when unprotected, but not manganese dioxide and humus sols. The importance of these results is discussed from the geological point of view. [Cf. *B.*, 1924, 595.]

M. S. B.

**Coagulation of Dispersoid Solutions on the Surfaces between Contiguous Phases.** A. JANEK (*Ann. Ecole Sup. Mines de l'Oural*, 1918—1919, **1**, [i], 45—58).—The coagulation of both negative ( $\text{Au}_2\text{S}_3$ ,  $\text{ZnS}$ ,  $\text{CuS}$ ) and positive [ $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ ] colloids was observed when the colloidal solutions were either (1) shaken in sealed tubes with an organic liquid practically insoluble in water such as xylene, or (2) added to a clear mixture of chloroform, water, and alcohol (1:3:6) or a mixture consisting of benzene, water, and alcohol (3:1:6). The addition of the colloidal solution to such a mixture causes the formation of an emulsion followed by the separation of two layers and the precipitation of the disperse phase at the junction of these layers. It was found that the negative colloidal solutions were coagulated under these conditions in a few minutes although differences were observed according to the nature of the dispersoid and the organic liquid used; the positive solutions were more resistant. Experiments were also made in which measured quantities of positive and negative colloid were mixed before adding to the mixture of liquids and it was found that the completeness of the coagulation was inversely proportional to the "life" or stability of the colloid; within certain limits it was also inversely proportional to the rate of coagulation, so that there exists a direct proportionality between the life and the rate of coagulation of a colloid. Some mixtures of positive and negative colloids exhibit the phenomenon of fractional coagulation; positive dispersoids when shaken in contact with the experimenter's finger instead of in sealed tubes were found to coagulate as readily as the negative solutions. G. A. R. K.

**Rate of Formation of Precipitates. V. Ter- and Quadri-valent Ions. The Change of Mercuric Iodide from Yellow to Red.** K. JABŁCZYŃSKI and J. LISIECKI (*Rocz. Chem.*, 1923, **2**, 474—477).—Previous experiments (Jabłczyński and others, *Spraw. Tow. Nauk Warsz.*, 1917, **10**, 106, 122, 461; 1918, **11**, 333) which included uni- and bi-valent ions have now been extended to ter- and quadri-valent ions, namely, ferri- and ferro-cyanide ions, using the same method as before (A., 1913, ii, 203). The results are in complete agreement with those previously obtained.

The authors' diffusion theory (*loc. cit.*) explains Ostwald's rule relating to the precipitation of the least stable and therefore most soluble form of a compound, and the subsequent change to the less soluble stable modification. The rate of change depends on the solubility of the unstable form. All factors tending to decrease this solubility will therefore retard the change, and it is now shown that the presence of excess of mercuric ions actually has such a retarding influence on the change of the yellow modification of mercuric iodide to the yellow. G. A. R. K.

**Composition of Micelles. Colloidal Chromium Oxide.** R. WINTGEN and H. LÖWENTHAL (*Z. physikal. Chem.*, 1924, **109**, 378—396).—A continuation of previous work (A., 1923, ii, 78;

this vol., ii, 156). Chromic oxide sols, prepared by the action of ammonium hydroxide on chromic chloride solutions followed by dialysis, were studied in the same manner as previously. The electrolyte absorbed, and that in the inter-micellar liquid, is essentially ammonium chloride. Electrolytes are more efficiently removed by continuous dialysis than by repeated changes of water at intervals, as the latter method leads to a greater loss of chromium. The nature of the sol is determined by the ratio of chlorine to chromium. In a typical case the micelle may be represented by  $(\overline{20.82 \text{ Cr}_2\text{O}_3; 1.073 \text{ NH}_4\text{Cl}; x\text{H}_2\text{O}})\text{CrO}^+_n + n\text{Cl}'$ . The sols present special difficulties in ultramicroscopic study and “ $n$ ” cannot be determined. The ratio of chromic oxide to chlorine in the sols is not appreciably affected by ultra-filtration, and the same is true of the general composition and equivalent aggregation. This shows that the filtrate is identical with the inter-micellar liquid. Even on repeated ultra-filtration, taking up the residue each time with water, only a small change is found. This depends mainly on the fact that only a small proportion of the total chlorine is present in the inter-micellar liquid, the rest being associated with the colloidal particles.

L. J. H.

**Mechanism of Reciprocal Precipitation of Colloids.** R. WINTGEN and H. LÖWENTHAL (*Z. physikal. Chem.*, 1924, **109**, 391—396).—On the theory of micelle structure developed by the authors (cf. preceding abstract and references) reciprocal precipitation of oppositely charged colloids should be a maximum when their respective concentrations, expressed in gram equivalent aggregates per litre, are the same. (An “equivalent aggregate” is the weight of a particle divided by the number of its charges.) This was tested in the case of stannic oxide, peptised with alkali, and chromic oxide sols. The equivalent aggregation of each sol was determined as previously described and mixtures in various proportions taken, the total volume always being the same. Precipitation occurred only within narrow limits and with a pronounced maximum; this maximum was accurately indicated by the absence of the “Tyndall beam” effect in the final solution. Whatever the dilution of the sols before mixing, the maximum precipitation occurred when the proportions agreed with the calculated values. In many cases, reactions between the peptising electrolytes may introduce disturbing effects. Complications may also arise from the small micelles of a highly dispersed colloid penetrating those of one with larger particles and being precipitated by the electrolyte there present. This may occur in the precipitation of very highly dispersed colloidal dyestuffs by chromium oxide sols.

L. J. H.

**Formation of Inorganic Jellies.** H. B. WEISER (*Colloid Symposium Monograph, Univ. Wisconsin*, 1923, 38—61; cf. A., 1923, ii, 765).—Jellies of chromic, stannic, cupric, and aluminium oxides, ferric, manganese, and zinc arsenate are considered, with particular reference to the formation of hydrous jellies. If mixing

can be effected sufficiently rapidly, such jellies may be made by metathesis.

CHEMICAL ABSTRACTS.

**Gels and Theory of Adsorption.** N. E. GORDON (*Science*, 1923, **58**, 495—497).—The adsorption of the cation of potassium hydrogen phosphate and other salts increases with an increase in the values of  $p_H$ , but the negative adsorption of the anions was irregular. Although this result would be expected from Helmholtz's double layer theory, and Hardy's work, the anticipated change in sign of the charge on the gel at about  $p_H$  7 was not realised. The fact that, on addition of sodium hydroxide to silica gel, part of the sodium is found in the solution with its attending ultramicros, and part in the proximity of ultramicros which have too great a mass to migrate, supports the theory of surface ionisation. There appear to be four different types of adsorption from solution: (a) chemical adsorption, which follows the mass law, (b) exchange adsorption, where one ion is adsorbed by replacement of a second ion, (c) partition ratio adsorption, obeying Henry's law, (d) electro-ionic adsorption, where the adsorbed material is held by a secondary valency.

A. A. E.

**Formation of Manganese Arsenate Jellies.** E. O. KRAEMER (*Colloid Symposium Monograph*, Univ. Wisconsin, 1923, 62—74).—There is no sharp line of demarcation between a precipitate and a jelly. Starting with a definitely crystalline precipitate it is possible to pass through a series of solvated gelatinous precipitates through weak, "mushy" jellies to clear, firm, and elastic ones. In these experiments the time of setting was fixed by whirling the mixture of manganese sulphate and alkali arsenate in the reaction beaker, and observing when the motion of included bubbles, etc., stopped abruptly. The following variable factors are considered: (1) concentration of reacting materials, (2) cation effect, (3) anion effect, (4) influence of acids, (5) influence of non-electrolytes, and (6) temperature. Jellies with an excess of manganese salt show strong syneresis, whilst excess of arsenate stabilises. Jelly formation appears to begin with the formation of nuclei; these grow, then aggregate.

CHEMICAL ABSTRACTS.

**Ageing Phenomena in Silica Gels.** R. SCHWARZ and F. STÖWENER.—(See ii, 547.)

**Colloid Chemical Characteristics of Technical Clays and Kaolins.** I. W. OSTWALD and F. PIEKENBROCK.—(See ii, 555.)

**Reversible Colloid of Iron.**—A. F. G. CADENHEAD and W. H. VINING.—(See ii, 557.)

**Heat of Coagulation of Sulphur Hydrosols.** F. L. BROWNE (*Colloid Symposium Monograph*, Univ. Wisconsin, 1923, 7—19; cf. A., 1923, ii, 218, 244).—Variation in the heat of coagulation of a sulphur hydrosol with the coagulant and its concentration is ascribed to the heats of mixing of the coagulants with polythionic acids in the sols, as well as to incidental changes in ion adsorption.

Sulphur in the coagulum appears to be in the same allotropic state as in the sol.

CHEMICAL ABSTRACTS.

**Heat of Adsorption of Oxygen by Charcoal.** E. A. BLENCH and W. E. GARNER (*J. Chem. Soc.*, 1924, **125**, 1288—1295).—The initial heat of adsorption of oxygen by purified vegetable charcoal ("Norite") rises from 60 to 220 cal./mol. of oxygen as the temperature of absorption rises from 18° to 450°, and above 200° it is greater than the heat of formation of carbon dioxide. The heat of adsorption decreases rapidly as the surface becomes saturated. At low temperatures, oxygen is adsorbed without chemical change and oxygen is given off on evacuation. At higher temperatures chemical combination occurs with the formation of groups  $C_xO_y$  on the surface (cf. Rhead and Wheeler, T., 1913, **103**, 461). At a given temperature some of these groups are stable and others unstable. The adsorbed gas can only be removed by evacuation at 900° and is given off in the form of oxides of carbon. The heat of formation of the stable groups increases with rise of temperature.

W. H.-R.

**Calculation of Heats of Formation and Interpretation of some Exceptions to the Law of Maximal Work.** C. HENRY (*Compt. rend.*, 1924, **178**, 2248—2250).—A mathematical paper in which new formulæ, based on the radiation hypothesis, are derived for the calculation of heats of formation. The law of maximal work is a direct deduction from the application of the radiation hypothesis to instantaneous reactions and exceptions to this law are discussed.

J. W. B.

**Thermal Method for the Study of Gaseous Systems.** G. PICCARDI (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 287—290).—Theoretical.

T. H. P.

**Dissociation under a Temperature Gradient.** P. A. M. DIRAC (*Proc. Camb. Phil. Soc.*, 1924, **22**, 132).—A mathematical discussion of the equilibrium in a partly dissociated gas when subjected to a temperature gradient. Under these conditions there will be a flow of undissociated molecules from the cold to the hot end where they dissociate and flow back. This involves a transfer of energy in addition to that of the thermal conduction. In the resulting equilibrium, there is an excess of concentration of double molecules at the hot end over that which would occur if there were no temperature gradient and a corresponding deficiency at the cold end. The temperature gradients at the two ends will be greater than in the centre. The mathematical equations for the equilibrium state are deduced and it is shown that observations of the concentrations or the temperature gradients at the ends would enable the velocity of dissociation to be calculated in terms of other physical constants.

G. S.

**Reactions occurring during the Discharge of the Oxygen-Hydrogen Cell.** F. FISCHER and W. KRÖNIG.—(See ii, 542.)

**Periodic Catalytic Decomposition of Hydrogen Peroxide.** E. S. HEDGES and J. E. MYERS.—(See ii, 542.)

**Catalytic Decomposition of Hydrogen Peroxide Solutions by Blood Charcoal.** J. B. FIRTH and F. S. WATSON.—(See ii, 542.)

**Silent Discharge involving Catalysis.** F. O. ANDEREGG and E. H. BOWERS.—(See ii, 545.)

**Periodic Phenomena during the Electrolysis of Chromic Acid.** J. E. LIEBREECH (*Z. Elektrochem.*, 1924, **30**, 186—187).—A reply to the criticisms of Kleffner and Oyabu (*ibid.*, 1923, **29**, 208). H. T.

**Effect of Intermediate Oxides on the Electrolytic Short-circuiting Effect.** C. F. HOLMBOE (*Z. Elektrochem.*, 1924, **30**, 88—90).—Data are given for the rates of discharge when iron, iron-alkali, and iron-nickel-alkali batteries are short circuited. The considerable amount of energy associated with the current flow in the former case is attributed to the adhesion of anions to the iron anode. By coating the latter with nickel to a depth of 0.05 mm. the effect almost completely disappears, although the "intake" capacity of the cells is unaffected. The results show that the iron anode is only converted at the most into superoxide at the surface, the main crystal structure being unaffected, since the nickel layer eliminates the whole of the polarisation. H. T.

**Dissolution of Lead in Alkaline Liquids by Alternating Currents.** F. JIRSA and J. FABINGER.—(See ii, 554.)

**Ultra-microscopic Electrode Phenomena.** V. KOHL-SCHÜTTER (*Z. Elektrochem.*, 1924, **30**, 164—180).—Micro-observations have been made on the processes which occur at the electrodes during electrolysis. With copper electrodes in a dilute copper sulphate solution, a blue zone of positively charged copper hydroxide containing copper can be observed at the cathode followed by a dark space, and then a yellow zone of minute negatively charged hydrogen bubbles. The formation of the copper hydroxide is probably due to the discharge of cuprous ions at the electrode,  $2\text{Cu}^+ \rightarrow \text{Cu} + \text{Cu}^{2+}$ , and subsequent hydrolysis of the cupric solution. In the hydrolysis copper particles are encased in the hydroxide. The yellow zone is due to the discharge of the hydrogen ion and repulsion of the minute hydrogen bubbles. Similar phenomena were observed with silver electrodes in silver nitrate solution. With copper electrodes in water at the anode, colloidal particles of copper hydroxide are formed. These are cataphoretically carried to the cathode where they discharge the negatively charged hydrogen mist, with the formation of a dark zone. With higher potentials it is possible to get negatively charged hydrogen bubbles adhering to the cathode. The hydrogen in the mist becomes surrounded by positively charged hydroxide and becomes attracted in consequence. With silver electrodes in water, silver peroxide is formed at the anode. This

breaks down forming an oxygen mist and silver particles. Both are negatively charged and are held at the anode. "Black" copper observed during electrolysis consists of copper particles surrounded by copper hydroxide as a protective colloid and always contains hydrogen due to the method of formation. The observed phenomena are expected to throw light on overvoltage and show that electrode processes are much more complicated than is indicated by the schemes  $M^+ + \ominus \rightarrow M$  and  $M - \ominus \rightarrow M'$ . H. T.

**Influence of Colloids on the Rate of Reactions Involving Gases. II. Decomposition of Hydrogen Peroxide and of Nitrosotriacetoneamine.** A. FINDLAY and W. THOMAS (*J. Chem. Soc.*, 1924, **125**, 1244—1252).—Using sols of gelatin, starch, dextrin, albumin, and peptone, the influence of colloids on the velocities of reactions have been studied. In the decomposition of hydrogen peroxide by fuller's earth, of nitrosotriacetoneamine in the presence of hydroxyl ion, and of hydrogen peroxide in the presence of iodide ion, the velocity coefficients, determined from the rate of gas evolution, have a relatively high initial value which decreases rapidly to a constant value. This decrease is due to the influence of the reactants on the colloid and is reduced if the colloid is left for some time in contact with the catalyst before the reaction is started. On the other hand, except in the case of peptone, which behaves abnormally, the velocity coefficients for the third reaction determined by titration with permanganate show that the colloid has no influence on the velocity of the reaction, indicating that in homogeneous systems the colloid affects only the rate of escape of gas and not the chemical action itself. In the first reaction the colloid, however, affects both the rate of the chemical reaction and the rate of escape of gas. The relative effects of different colloids depend on the reaction and on the concentration.  
W. H.-R.

**Rate of Photochemical Change in Solids.** E. J. BOWEN, H. HARTLEY, W. D. SCOTT, and H. G. WATTS (*J. Chem. Soc.*, 1924, **125**, 1218—1221).—Using filtered light of known spectral range, photochemical change in solid crystals has been studied in the case of (1) the isomeric change of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid (cf. Lobry de Bruyn, *Rec. trav. chim.*, 1903, **22**, 298); and (2) the photochemical transformation of cinnamylidenemalononic acid (cf. Riiber, A., 1902, i, 617). If the change does not proceed too far, the products of decomposition remain in solid solution in the original crystals. Within the limits of experimental error, the absorption of each quantum of energy corresponds with the transformation of one molecule. The effect of plane polarised light is the same as that of ordinary light of the same intensity, and, taking into account the work of Padoa (A., 1920, ii, 143), it is considered that both the ordinary and extraordinary rays are photochemically effective, but that their absorption coefficients are different. Since each quantum of absorbed energy is effective it would seem that the electron which is transferred from the normal to a higher orbit is very rarely



deactivated before the photochemical change occurs. The time of the primary reaction is therefore small compared with the probable time of rearrangement of the atoms in the molecule.

W. H.-R.

**Photochemistry of the Halogen Hydrides.** E. J. BOWEN (*J. Chem. Soc.*, 1924, 125, 1233).—The complex photochemical relationships of the hydrogen halides are discussed with reference to (1) the theory that dissociation into atoms occurs, *e.g.*,  $\text{Cl}_2 + h\nu = \text{Cl} + \text{Cl}$ , or  $\text{HI} + h\nu = \text{H} + \text{I}$ ; and (2) the theory that active molecules are produced. It is shown that the dissociation theory affords a quantitative explanation of all the experimental observations, if due consideration is given to the heats of reaction, and if it is assumed that a large heat evolution favours spontaneous reaction, whilst heat absorption has the opposite tendency. This explanation is not possible on the basis of the activation theory.

W. H.-R.

**Photochemical Decomposition of Silver Chloride.** R. SCHWARZ and P. GROSS.—(See ii, 550.)

**Automatic Töpler Pump.** F. PORTER (*Ind. Eng. Chem.*, 1924, 16, 731—732).—The pump described evacuates an apparatus and delivers the gas into a collecting tube, as is required, especially in connexion with analyses for helium in low-temperature work. The pear-shaped pump chamber with top and bottom side connexions is alternately filled with mercury and emptied by means of a levelling bulb. This is connected to a manometer and to a 4-way valve the other connexions of which lead to air at 15 lb. pressure, the suction of a good water jet pump, and the atmosphere. This valve is electrically operated by means of solenoids and a 110 volts direct current circuit system operated through contacts at different parts of the mercury column. The glass apparatus is simple in construction.

C. I.

**Condenser for Distilling Oils of Wide Boiling Range.** H. N. CALDERWOOD, jun. (*Ind. Eng. Chem.*, 1924, 16, 576—577).—A condenser suitable for the condensation of distillates of b. p. 35—268° in one distillation consists of a tube 1100 mm. long fitted with three Liebig jackets each 250 mm. long, the top one being air cooled and the bottom one cooled by tap water. The inlet connexion of the middle jacket is coupled to the lower end of the coil of a Liebig coil condenser placed vertically with the adapter end upwards, the outlet connexion being coupled to the upper end. The coil condenser is air cooled if necessary and the water circulates at about 90°. Cooling is thus performed in three stages with reduced risk of breakage.

C. I.

**Apparatus for Fractional Distillation under Reduced Pressure.** K. WURTH (*Z. angew. Chem.*, 1924, 37, 226—227).—The side tube of a distillation flask is bent upwards and connects with the lower end of a vertical fractionating column containing a number of perforated glass basins filled with glass beads and con-

nected with each other by **U**-tubes: the column is also provided with a jacket. The upper end of the column connects with a short condenser, and this in turn with a compartment receiver; a side tube on the latter is connected with a pressure gauge, a valve for regulating the pressure, and a pump. A receiver for distillates which solidify readily consists of a wide tube constricted at points along its length so as to form a number of bulbs which are also connected with each other by side tubes. The first portion of the distillate is run into the lowest bulb by heating the upper bulbs; the constriction above the lowest bulb is then cooled and the solidified substance seals off the lowest bulb so that the next quantity of distillate can be collected in the next higher bulb, and so on.

W. P. S.

**Apparatus for Determining the Heat of Evaporation of Liquids of High Boiling Point.** J. H. AWBERY and E. GRIFFITHS (*Proc. Physical Soc.*, 1924, **36**, 303—312).—Two new forms of apparatus for determining the heat of evaporation of liquids of high boiling point (about 400°) are described and their relative merits briefly discussed. In one, the heat evolved by the condensation of a measured quantity of liquid is determined by a continuous flow calorimeter, a determination of the specific heat of the liquid being also necessary. This apparatus can also be used to measure the quantity of vapour evolved from the liquid, at its boiling point by a given quantity of energy, but specially determined corrections for radiation must be introduced. The second apparatus employs this same principle, but reduces radiation losses to zero by special jacketing.

L. J. H.

**Calorimetric Apparatus for the Measurement of Heats of Reaction at High Temperatures.** J. D. DAVIS (*Ind. Eng. Chem.*, 1924, **16**, 726—730).—An adiabatic twin calorimeter is described, suitable for the determination of the heat of carbonisation of coal at temperatures up to 650°. The two exactly similar calorimeter bombs are symmetrically set in a common water jacket and, by the aid of various precautions to secure uniform conditions, the heat of carbonisation of a coal sample when carbonised at 500° in an atmosphere of nitrogen can be determined with an error not exceeding about 4%.

C. I.

**Method of Drawing Metallic Filaments; their Properties and Uses.** G. F. TAYLOR (*Physical Rev.*, 1924, **23**, 655—660).—The melted metal is drawn while enclosed in a glass tube of suitable composition; the glass may be removed from the filament with hydrofluoric acid, leaving a metallic wire of diameter down to 0.00002 cm. or less. The method has been applied to lead, antimony, bismuth, gold, silver, copper, iron, tin, thallium, cadmium, cobalt, gallium, indium, and their alloys. The filaments are very pliable and have high tensile strength; the temperature coefficients of resistance do not differ markedly from those of the metals in bulk, and are more constant.

A. A. E.

**Intense Lithium Flame for Polarimetric Use.** H. HUNTER  
(*J. Chem. Soc.*, 1924, **125**, 1401).—An oxy-hydrogen flame is used,  
the hydrogen being passed through a layer of solid lithium carbonate  
before being mixed with the oxygen. S. K. T.

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## Inorganic Chemistry.

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**Reactions Occurring during the Discharge of the Oxygen-Hydrogen Cell.** F. FISCHER and W. KRÖNIG (*Z. anorg. Chem.*, 1924, **135**, 169—176).—The yield of hydrogen peroxide produced by short-circuiting for 3 hours a Grove cell containing 2*N*-sulphuric acid and 1% titanium sulphate (the latter to stabilise the peroxide) was 17% referred to the current consumption. This yield was increased by enclosing the hydrogen electrode in a porous cell; by feeding the oxygen electrode with oxygen instead of air (cf. A., 1913, ii, 285) and by feeding it through two jets instead of one; by prolonged heating to redness of the platinised electrodes (*i.e.*, decreasing their surface); and by reducing the current, the time of the experiment, and the temperature. A 79% yield was obtained by electrolysing 0.5*N*-sulphuric acid containing titanium sulphate at 0°, using a current of 2 milliamp. It is concluded that, at the ordinary temperature at least, the *E.M.F.* of the Grove cell is mainly influenced by the combination of hydrogen and oxygen to form, not water, but hydrogen peroxide, which, under normal conditions, is catalytically decomposed. S. K. T.

**Periodic Catalytic Decomposition of Hydrogen Peroxide.** E. S. HEDGES and J. E. MYERS (*J. Chem. Soc.*, 1924, **125**, 1282—1287).—The periodic decomposition of hydrogen peroxide by mercury is considered not to be due to the formation of a film of oxide (cf. this vol., ii, 325). Periodic catalytic decomposition of hydrogen peroxide solution at 35° is brought about by metals (*e.g.*, silver reduced by hydrazine or hydroxylamine sulphates; freshly prepared colloidal platinum, silver, and gold), alloys (*e.g.*, copper-aluminium, after previous melting in air; cf. *loc. cit.*), metallic couples (*e.g.*, magnesium-copper), amalgams (*e.g.*, magnesium), freshly precipitated metallic oxides (*e.g.*, barium peroxide), etc. Decomposition is steady with silver reduced with Rochelle salt, electrolytic copper, stale colloidal platinum, coconut charcoal, platinum black, manganese dioxide, silver amalgam, etc. S. K. T.

**Catalytic Decomposition of Hydrogen Peroxide Solutions by Blood Charcoal.** J. B. FIRTH and F. S. WATSON (*Trans. Faraday Soc.*, 1924, **19**, 601—613).—Blood charcoal dried at 120° decomposes hydrogen peroxide solutions. Prolonged extraction with aqua regia and with bromine lowers the percentage of ash

(chiefly iron oxide) and gives an activity which decays less rapidly. Activation by heat treatment or by sorption and removal of iodine gives charcoals which decompose hydrogen peroxide much more vigorously. Two types of reaction are found with these activated charcoals, an  $\alpha$ -activity which causes a rapid initial decomposition of the peroxide with appreciable rise in temperature, but decays in a few minutes, and a  $\beta$ -activity which produces a slower decomposition persisting for several hours. The amount of decomposition depends on the concentration of peroxide as well as on the activity of the charcoal. The activity of sugar charcoal is markedly increased by the incorporation of 9% of iron oxide and subsequent heat treatment whilst the ash alone from blood charcoal has very little action on the peroxide. S. S.

**Landolt's Reaction: Its Acceleration by Bromide and Chloride.** A. SKRABAL [in part with R. RIEDER] (*Z. Elektrochem.*, 1924, 30, 109—124).—Together with the direct reduction of iodic acid by sulphurous acid, six further simultaneous reactions enter into the reduction, the rate of the reaction being represented by

$$-d[\text{IO}_3']/dt = k_1[\text{IO}_3'][\text{H}'][\text{SO}_3''] + k_2[\text{IO}_3'][\text{H}]^2[\text{I}']^2 + k_3[\text{IO}_3'][\text{H}]^2[\text{I}'][\text{Br}'] + k_4[\text{IO}_3'][\text{H}]^2[\text{I}'][\text{Cl}'] + k_5[\text{IO}_3'][\text{H}]^2[\text{Br}']^2 + k_6[\text{IO}_3'][\text{H}]^2[\text{Br}'][\text{Cl}'] + k_7[\text{IO}_3'][\text{H}]^2[\text{Cl}']^2.$$

Up to the reversal of the reaction these reaction products oxidise sulphurous acid practically instantaneously to sulphuric, so that the formula reaction is  $\text{IO}_3' + 3\text{SO}_3'' = \text{I}' + 3\text{SO}_4''$ . The values of  $k_3$ ,  $k_4$ ,  $k_5$ ,  $k_6$ , and  $k_7$  have been determined and the validity of the complete equation has been demonstrated. The kinetics of the halide-halogenate reaction can in general be represented by  $-d[\text{IO}_3']/dt = k[\text{IO}_3'][\text{H}]^2[x][y']$ , where  $x$  and  $y$  can be the same or different halogens. H. T.

**Ultra-violet Emission Bands of Oxygen.** R. C. JOHNSON.—(See ii, 510.)

**Ozone in Flames.** W. MANCHOT and E. BAUER (*Z. anorg. Chem.*, 1924, 133, 341—360).—Ozone was detected by means of the silver test (A., 1909, ii, 993) in flames of hydrogen, hydrogen-oxygen mixture, carbon monoxide, coal gas, methane, ethylene, acetylene, and cyanogen, but not in the flame of an ordinary Bunsen burner. Elongated flames contain more ozone than thick, wide flames, and the quantity of ozone is affected by conditions such as the pressure of gases supplied to the burner, shape of the burner, etc. The ozone is chiefly confined to the hottest parts of the flame and is completely destroyed on diffusing through the cooler zones to the surrounding air. Ozone is almost instantaneously destroyed at 300°. The oxy-hydrogen flame contained about 0.1% of ozone at 1500—1600°, whilst the acetylene blowpipe flame contained about 1% at a higher temperature. These quantities are too high to be accounted for by purely thermal formation, according to Nernst's heat theorem, and experiment showed that, if oxygen is heated at 1600°, no detectable ozone is produced. The quantities of ozone in flames of carbon monoxide and cyanogen showed no diminution when the gases were dried over phosphorous pentoxide, 21\*

indicating that the ozone in flames is not produced from hydrogen peroxide as was suggested by Wartenburg (A., 1921, ii, 107). The formation of ozone is possibly due to the action of free electrons in the flame. The lowest temperature at which ozone was detected was  $900^{\circ}$ , and the temperature of its formation is estimated as about  $1400^{\circ}$ . Carbon monoxide when carefully dried over phosphorous pentoxide is still inflammable, but the flame is very sensitive to pressure variations (cf. Dixon, A., 1905, ii, 577). W. H.-R.

**Structure of Selenium.** H. COLLINS.—(See ii, 515.)

**Tellurium Monoxide.** J. J. DOOLAN and J. R. PARTINGTON (*J. Chem. Soc.*, 1924, **125**, 1402—1403).—Tellurium monoxide is obtained as a grey powder by heating tellurium sulphoxide,  $\text{TeSO}_3$  (cf. Divers and Shimosé, T., 1883, 319; *Ber.*, 1883, **16**, 1004), in a vacuum at  $180$ — $225^{\circ}$ , the product being washed with sodium carbonate solution, hot water, and finally alcohol. S. K. T.

**Tellurous Acid as a Base.** J. KASARNOWSKY (*Z. physikal. Chem.*, 1924, **109**, 287—301).—The concentrations of tellurous ions in solutions containing increasing amounts of hydrochloric acid have been determined by potential measurements with a tellurium electrode, and the total tellurium contents of the solutions have been determined chemically. It is found that the value of the concentration of the tellurium ions increases as the fourth power of that of the hydrogen ions, showing that tellurous acid acts as a weak base. Numerically,  $[\text{Te}^{4+}][\text{OH}^{-}]^4/[\text{H}_2\text{TeO}_3]=1.5 \times 10^{-46}$ . S. B.

**Relationship between some Oxygen Compounds of Nitrogen.** A. SANFOURCHE (*Ann. Chim.*, 1924, [x], **1**, 5—93).—An amplification of previously published work (A., 1922, ii, 454, 762; 1923, ii, 84). The rate of oxidation of nitric oxide was measured at temperatures ranging from  $0^{\circ}$  to  $525^{\circ}$ ; the reaction appears to be of the second order. The fact that the temperature coefficient is less than unity is explained by the hypothesis that nitrous anhydride is first formed and then decomposed in part, the undecomposed portion undergoing further oxidation. The formation of nitric acid from nitrous fumes under the conditions which obtain in industry was studied; as the nitric acid first formed acts as an oxidising agent towards the less oxidised compounds, it is unusual to obtain in this manner acid of concentration greater than 50%. Nitric oxide reduces nitric acid, producing, with acid of 10% or lower concentration, nitrous acid only ( $2\text{NO} + \text{HNO}_3 + \text{H}_2\text{O} \rightarrow 3\text{HNO}_2$ ); when the concentration of the nitric acid is in the neighbourhood of 20% a second reaction ( $\text{NO} + 2\text{HNO}_3 \rightarrow \text{H}_2\text{O} + 3\text{NO}_2$ ) also occurs. The latter predominates with increasing concentration of the acid; with 70% acid the former ceases. Nitrous anhydride, or the gaseous mixture of the same composition which reacts as the anhydride, acts on water with production of nitrous acid, which decomposes, yielding two-thirds of the original nitrogen in the form of nitric oxide. Dilute nitric acid behaves towards the anhydride in a similar manner to water, but acid of

50% and greater concentration is reduced with formation of nitrogen peroxide, which dissolves in the acid. Both reactions take place simultaneously with acids of intermediate concentrations. Nitrogen peroxide originally forms with water or dilute nitric acid equimolecular quantities of nitrous and nitric acids; the subsequent decomposition of the nitrous acid thus formed is complete only when the concentration of the nitric acid does not exceed 20%; beyond this, the oxidising action of the nitric acid on the nitric oxide formed in the decomposition was observed, whilst with 70% nitric acid simple solution of the peroxide takes place. H. J. E.

**Absorption of Nitric Oxide by Solutions of Ferrous Sulphate and Sodium Sulphite.** L. MOSER and R. HERZNER (*Z. anal. Chem.*, 1924, **64**, 81—89).—An investigation of the absorptive power of solutions in the system ferrous sulphate-sulphuric acid-water for nitric oxide showed that the most efficient mixtures were a saturated neutral solution of ferrous sulphate and a solution containing 15% of ferrous sulphate, 20% of sulphuric acid, and 65% of water. In practice, however, the most satisfactory solution contains 15% by weight of anhydrous ferrous sulphate and 15% of 64% sulphuric acid. The relative absorption of nitric oxide by alkaline solutions of sodium sulphite in general increases with a decrease of concentration of sulphite and increases at first with the concentration of free alkali, then decreases when this exceeds a certain limit; the best mixture appears to consist of 11—15% of anhydrous sodium sulphite, 1% of sodium hydroxide, and 88—84% of water. A. R. P.

**Silent Discharge involving Catalysis.** F. O. ANDEREGG and E. H. BOWERS (*Proc. Indiana Acad. Sci.*, 1922, 181—186).—The yields of ozone and nitrogen pentoxide in air are much more dependent on the nature and extent of the surface than on the amount of inductive capacity of the various materials placed in the discharge space (cf. McEachron and George, *Bull. Purdue Univ.*, 1922, **6**, 1); glass wool is particularly active. Increase of voltage is accompanied by increased formation of ozone, followed by that of nitrogen pentoxide, a high concentration of which lowers the yield of ozone. Thus the concentration of the latter reaches a first, second, and sometimes a third maximum. Similar experiments were conducted with carbon monoxide. CHEMICAL ABSTRACTS.

**Fog Formation in Air which has passed through a Silent Discharge.** F. O. ANDEREGG and K. B. MCEACHRON (*Proc. Indiana Acad. Sci.*, 1922, 175—177; cf. Anderegg, McEachron, and others, *A.*, 1918, ii, 42; 1921, ii, 450; *Trans. Amer. Electrochem. Soc.*, 1920, **37**; and preceding abstract).—The fog formed when ozonised air is passed through an absorbent solution is due chiefly to hygroscopic nitrogen pentoxide. CHEMICAL ABSTRACTS.

**Thermal Decomposition of Salts of Hydroxylamine and Hydrazine.** K. A. HOFMANN and F. KROLL (*Ber.*, 1924, **57**, [B], 937—944).—The slow thermal decomposition of hydroxylamine

hydrochloride at about  $150^{\circ}$ , takes place in accordance with the equations:  $3\text{NH}_2\cdot\text{OH}=\text{N}_2+\text{NH}_3+3\text{H}_2\text{O}$  and  $4\text{NH}_2\cdot\text{OH}=\text{N}_2\text{O}+2\text{NH}_3+3\text{H}_2\text{O}$ . The addition of basic substances represses the second in favour of the first change to an extent which is less than would be expected, whereas acidic substances displace the action in the contrary direction. Nitrous acid or nitrite is produced by the acid or alkaline fusion of hydroxylamine. It is therefore probable that hydroxyhydrazine is produced initially from 2 mols. of hydroxylamine and subsequently converted into the diamide of nitrous acid,  $\text{OH}\cdot\text{N}(\text{NH}_2)_2$ ; this is hydrolysed to ammonia and nitrous acid (or nitrosyl acid in concentrated acid solution) which, with unchanged hydroxylamine, yields nitrous oxide. Confirmation of this hypothesis is found in the observation that nitrous oxide is not formed in the presence of sufficient alkali or of carbamide. In alkaline solution (cf. first equation) the diamide of nitrous acid suffers mainly intramolecular decomposition,  $\text{OH}\cdot\text{N}(\text{NH}_2)_2=\text{N}_2+\text{NH}_3+\text{H}_2\text{O}$ , accompanied by the subsidiary change:  $\text{OH}\cdot\text{N}(\text{NH}_2)_2+\text{NaOH}=\text{NaNO}_2+2\text{NH}_3$ .

Hydrazine hydrochloride decomposes above  $200^{\circ}$  into ammonium chloride, nitrogen, and hydrogen chloride. In the presence of hydroxylamine hydrochloride, reaction occurs at about  $150^{\circ}$  and, with suitable proportions of the reactants, follows the course:  $2\text{NH}_2\cdot\text{OH}+\text{N}_2\text{H}_4\cdot 2\text{HCl}=2\text{NH}_4\text{Cl}+\text{N}_2+2\text{H}_2\text{O}$ . The absence of nitrous oxide from the products indicates the quantitative participation of hydroxylamine in the change and the probable preliminary formation of a very unstable salt of diaminohydrazine.

The oxidising or reducing action of hydroxylamine depends largely on the conditions; in feebly acid solution hydroxylamine and ferric chloride give ferrous chloride and nitrous oxide, whereas in concentrated sulphuric or phosphoric acid solution hydroxylamine and ferrous sulphate yield ferric and ammonium sulphates. Hydroxylamine is oxidised by iodine in acetic acid but not in mineral acid solution; in concentrated hydrochloric acid solution hydroxylamine liberates iodine from hydrogen iodide. H. W.

**Density of Graphite.** E. RYSCHKEWITSCH and E. KÖSTER-MANN (*Z. Elektrochem.*, 1924, **30**, 86—88).—The density of graphite prepared by fusion and subsequent solidification, determined by the flotation method, is sharply defined at  $d^{16} 2.232\pm 0.0013$ . This value is in agreement, within the limits of experimental error, with that calculated from the lattice spacing by Debye and Scheerer. H. T.

**Action of Permanganic Anhydride on the Varieties of Pure Carbon.** J. F. DURAND (*Compt. rend.*, 1924, **178**, 1822—1824; cf. this vol., ii, 500).—Diamond, graphite, and acetylene black were treated with the green solution of permanganic anhydride in concentrated sulphuric acid. The action was rapid in the cold, all three being quantitatively converted into carbon dioxide, but the vigour of the reaction was unequal in the three cases. G. M. B.

**Infra-red Absorption of Carbon Monoxide.** E. F. LOWRY. —(See ii, 512.)



**Ageing Phenomena in Silica Gels.** R. SCHWARZ and F. STÖWENER (*Koll. Chem. Beihefte*, 1924, **19**, 171—202).—It has been shown previously (A., 1920, ii, 689, 690; 1921, ii, 260) that the ageing of silica gels is closely connected with the changes in conductivity of solutions of the gel in 3*N*-ammonia. For a number of gels the authors have determined the conductivity, and amounts of silica in solution in the colloidal and crystalloidal states after prolonged contact with 3*N*-ammonia. The results are expressed in terms of a "*Q* value" giving the ratio of the increase of conductivity to the amount of silica in a molecular state of dispersion. With normal ageing the *Q* value falls from  $75 \times 10^{-4}$  to about  $25 \times 10^{-4}$ . This behaviour is so well established that any anomalous conductivity can safely be referred to an anomalous behaviour of the gel. In this way it is found that gels prepared from silicon tetrachloride at either 0° or 100° and partially purified by dialysis show no alteration, but that normal ageing takes place when these gels are more carefully purified by repeated decantation and shaking with water. Gels from sodium silicate and acetic acid after dialysis show normal ageing, which is markedly retarded by small quantities of sodium chloride, carbamide, tartaric acid, or dextrose. Cases are recorded where normal ageing occurs in gels kept under water, so that the drying, which generally accompanies ageing, determines only the rate of the process. The authors conclude that the process of ageing consists of a dehydration of the primary particles which originally hold much water, and that it is probable that dehydration, in a strictly chemical sense, or polymerisation, also occurs. E. M. C.

**Preparation of Potassium Antimonate.** S. A. SCHOU (*Z. anorg. Chem.*, 1924, **133**, 404—410).—Grey antimony ore ( $\text{Sb}_2\text{S}_3$ ) is boiled with potassium hydroxide solution, cupric oxide is added, and the whole stirred and boiled for  $\frac{1}{2}$  hour, and then filtered. The filtrate (which should be quite free from sulphur and give a pure white precipitate with lead acetate solution) is evaporated to one-tenth of its original volume and treated with alcohol. The precipitated potassium antimonate is filtered off, washed with 50% alcohol, left for 24 hours, and then ground in a mortar and dried on filter paper. This method gives a yield of 90% of the theoretical, whilst a yield of 98% can be obtained if very finely divided antimony trisulphide, prepared by the careful ignition of the pentasulphide, is used instead of the ore. The antimony trisulphide and potassium hydroxide react to form a mixture of antimonite and thioantimonite, which are then oxidised by the cupric oxide with the formation of an intermediate oxysulphide,  $\text{K}_3\text{SbO}_3\text{S}$ , which cannot be isolated. The reactions may be expressed by the equations (1)  $\text{Sb}_2\text{S}_3 + 6\text{KOH} = \text{K}_2\text{SbO}_3 + \text{K}_3\text{SbS}_3 + 3\text{H}_2\text{O}$ ; (2)  $\text{K}_3\text{SbS}_3 + 3\text{CuO} = \text{K}_3\text{SbO}_3 + 3\text{CuS}$ ; (3)  $\text{K}_3\text{SbO}_3 + 2\text{CuS} = \text{K}_3\text{SbO}_3\text{S} + \text{Cu}_2\text{S}$ , (4)  $\text{K}_3\text{SbO}_3\text{S} + \text{CuO} = \text{K}_3\text{SbO}_4 + \text{CuS}$ . W. H. R.

**Spectrum of Ionised Lithium.** M. MORAND.—(See ii, 509.)

**Formation of Double Salts in the Solid State in the System Lithium Chloride-Calcium Chloride.** G. GRUBE and W. RÜDEL (*Z. anorg. Chem.*, 1924, **133**, 375—388).—The system lithium

chloride-calcium chloride has been investigated, in both the solid and liquid states, by thermal analysis. The two salts are totally miscible in the liquid state, the freezing-point curve being of the simple eutectic type, with an eutectic point at  $496^{\circ}$  and 38 mols. % of calcium chloride. The constituents separating from the liquid are solid solutions, the limits of solubility in the solid state at the eutectic temperature being 0—16 mols. % of calcium chloride, and 0—20 mols. % of lithium chloride. The limits of solid solubility decrease rapidly as the temperature is lowered. All binary mixtures on cooling show a thermal arrest in the solid state at  $441^{\circ}$ , due to the formation of the double salt  $\text{LiCl}\cdot\text{CaCl}_2$ , the reaction  $\text{LiCl} + \text{CaCl}_2 \rightleftharpoons \text{LiCl}\cdot\text{CaCl}_2$  being reversible and exothermic from left to right. If finely powdered lithium and calcium chlorides are mixed and heated together, they react in the solid state to form the double salt, the action beginning at about  $170^{\circ}$ . The double salt is completely decomposed above  $441^{\circ}$ .  
W. H.-R.

**Molten Electrolytes, Born's Grating Forces, and the Constitution of Salts.** W. BILTZ (*Z. anorg. Chem.*, 1924, **133**, 312—324).—The author's work on the electrolytic conductivity and other properties of fused salts is discussed and general conclusions are drawn with regard to fused chlorides. The majority of fused chlorides are either good conductors or very poor conductors. Out of 61 chlorides examined, 31 are good conductors in the fused state ( $\kappa$  of the order 0.1 to 1.0), 11 have  $\kappa$  of the order  $10^{-6}$ , and 15 are non-conductors, leaving only 4 with moderate conductivity. These four are the chlorides of zinc, beryllium, and mercury, and the so-called tellurium dichloride. In any group or series of the periodic table, there is a sudden jump from an element of which the chloride is practically a non-conductor in the fused state to the next element of which the chloride is a good conductor. In group I this change occurs between hydrogen chloride and lithium chloride. In group II, the change is between beryllium and magnesium; in group III between aluminium and scandium; in group IV between titanium and zirconium; and in group V between antimony or tantalum and bismuth. In this way it is possible to divide the periodic table into halves corresponding with those elements of which the chlorides do and do not conduct electricity in the fused state; a few exceptions are, however, shown, particularly in group VIII. When an element forms two chlorides, the lower chloride is always the better conductor, whilst, generally speaking, a high m. p. corresponds with good conductivity and vice versa (cf. A., 1922, ii, 370). Chlorides which are good conductors are not found with a valency higher than four, all pentachlorides examined being non-conductors. These facts are then discussed in the light of Born's theory of the crystal grating (A., 1919, ii, 188, 424, 453) and the work of Kossel (A., 1916, ii, 243). Assuming that transference of electrons occurs in mono-, di-, tri-, and tetra-chlorides, the attraction between the oppositely charged ions will become greater as the charge on the metal atom increases, and the dissociation in the fused state will become correspondingly less, and the conductivity will decrease.

This accounts for the fact that lithium chloride is a good conductor and beryllium chloride a poor conductor in the fused state. At the same time, according to Born, a repulsion exists between two oppositely charged ions, owing to the action of the shells of electrons. This repulsion favours easy dissociation, and increases as the inner shells of electrons become greater. Thus in group I, the hydrogen ion possesses no shells of electrons and consequently the attractive forces prevail and hydrogen chloride is a non-conductor. In lithium chloride, however, the repulsive forces produced by the shells of electrons opposes the electrostatic attraction of the ions, and lithium chloride is a good conductor in the fused state. In group IV, where the metal ion has four charges, the electrostatic attraction is so much greater that it is only in the case of thorium chloride that the numerous shells of electrons produce a repulsive force sufficient to cause dissociation in the fused state. In this way, the opposing effects of (1) electrostatic attraction, and (2) the repulsion due to the shells of electrons, give an explanation of the conductivity of the fused chlorides of the different elements. W. H.-R.

**Boiling Points and Heats of Evaporation of Salts.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, **133**, 380—384).—The experimental results of Wartenburg (A., 1922, ii, 739) have been used to determine the molecular heat of evaporation  $\lambda$ , the boiling point  $T_b$ , and the Trouton ratio  $\lambda/T_b$  for the alkali halides, cuprous, thallos, and lead halides, and for silver chloride, tin tetrachloride, and sodium and potassium hydroxides. If the total heats of evaporation are taken, the Trouton ratio for the majority of these salts is of the order 20—23, whilst if the internal heat of evaporation (cf. Wartenburg, *loc. cit.*) is taken, the ratio is of the order 20—22 in the case of most of the alkali halides. Exceptions are presented by the cuprous halides for which the ratio  $\lambda/T_b$  is of the order 11—12, and by thallos fluoride (about 44). Slight irregularities are also shown by some of the lithium and sodium halides and by sodium hydroxide. The experimental values for the internal heat of evaporation of the different salts are higher than the value calculated by the equation of Nernst ("Lehrbuch," 7th ed., 294), and lower than those calculated from the equation of Gruneisen (A., 1912, ii, 534), whilst the equation of Wartenburg (*Z. Elektrochem.*, 1914, **20**, 444) gives results which are on both sides of the experimental values. The general agreement with all three equations is good except for the cases mentioned above. W. H.-R.

**Orientation of Ammonium Iodide Crystals by Cleavage Planes of Micas.** P. GAUBERT (*Compt. rend.*, 1924, **178**, 856—858).—The effect of different varieties of mica on the orientation of ammonium iodide crystals allowed to form in contact with them appears to depend on their composition, being related to the potassium content. When changes have taken place in mica involving loss or replacement of the potassium, the directing power with respect to deposited crystals is not apparent, although the optical properties may remain unchanged. Heating to redness, or

exposure to the action of hydrochloric acid, causes mica to lose the power of orientation. The author suggests that the potassium atoms exert a directing influence on the potassium atoms or ammonium groups in the iodides, and states that such action on these iodides affords a method of distinguishing micas from each other.

H. J. E.

**Properties of Ammonium Nitrate. VIII. Analysis of Crystalline Deposits from Solution in Fused Ammonium Nitrate.** E. P. PERMAN and D. R. DAWKINS (*J. Chem. Soc.*, 1924, 125, 1239—1244).—The deposits formed on cooling fused salts may be separated by filtration through a Gooch crucible, the residue being freed from mother liquor by repeated pressing in a special press. The method is applied to the reciprocal salt pairs previously investigated (cf. this vol., ii, 255), the results confirming the conclusions arrived at from a consideration of the m. p. curves.

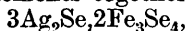
S. K. T.

**Photochemical Decomposition of Silver Chloride.** R. SCHWARZ and P. GROSS (*Z. anorg. Chem.*, 1924, 133, 389—403).—The action of panchromatic light on silver chloride has been investigated by a method similar to that used by the authors for silver bromide (A., 1923, ii, 815), the decomposition being measured by direct determination of the chlorine evolved. The silver chloride was prepared by precipitation of solutions of silver nitrate and sodium chloride in the presence of dilute nitric acid. Owing to adsorption the results are frequently affected by the presence of excess of silver salt or of chloride during the precipitation. In the moist state specimens prepared with excess of either salt show little difference. Drying over phosphorus pentoxide has little effect on specimens prepared with excess of chloride, but reduces the photochemical decomposition to about one-half in the case of specimens with excess of silver salt, this smaller decomposition being regarded as due to the masking of the surface chlorine atoms by the adsorbed positive silver ions. Colour tests indicated that dry silver chloride is darkened more strongly than dry silver bromide, and that, in both cases, specimens prepared with excess of halide are more sensitive than those with excess of silver salt. This is contrary to photographic practice in which excess of silver salt is always employed, indicating that "photographic sensitivity" (short exposures) is not identical with sensitivity to photochemical decomposition. Freshly-prepared dried silver chloride is slightly less sensitive to photochemical decomposition than specimens dried after keeping for some time under water, the sensitivity rising to a maximum after keeping for 50 hours, then decreasing slightly up to 150 hours, and then increasing again. Curves have been drawn representing the effect of light intensity and time on the decomposition of silver chloride.

W. H.-R.

**Double Selenides.** J. MEYER and H. BRATKE (*Z. anorg. Chem.*, 1924, 135, 289—312).—Double selenides containing two different

heavy metals could not be prepared; naturally occurring eucairite,  $\text{Ag}_2\text{Se}, \text{Cu}_2\text{Se}$ , is the only such selenide known with certainty. By fusing the appropriate elements together a substance,



was obtained, which may be either a double selenide or a mixture. The double *potassium iron selenide*,  $\text{K}[\text{FeSe}_2]$ , was obtained as dark violet crystals, fairly stable in air, by fusing together iron, selenium, and potassium carbonate. Replacement of the latter by potassium cyanide yielded a new *iron selenide*,  $\text{Fe}_3\text{Se}_4$ , or  $\text{Fe}[\text{FeSe}_2]_2$ . New *selenides of cobalt*,  $\text{Co}_5\text{Se}_6$ , or  $\text{Co}_3[\text{CoSe}_3]_2$ , and *nickel*,  $\text{Ni}_5\text{Se}_6$ , or  $\text{Ni}_3[\text{NiSe}_3]_2$ , were prepared similarly, using potassium cyanide and carbonate, respectively, in the fusion mixture. Potassium manganese selenide was probably formed in a fusion of manganese, selenium, and potassium carbonate, but it was very unstable in air and towards water and acids. By using sulphur in place of selenium, crystals of uncertain composition were obtained, probably  $\text{K}_2[\text{Mn}_3\text{S}_4]$ .  
S. K. T.

**Solubility of Calcium Carbonate in Water containing Carbon Dioxide under High Pressures. Properties of the Solutions obtained.** O. HAEHNEL (*J. pr. Chem.*, 1924, [ii], 107, 165—176).—The solution obtained by treating an aqueous suspension of calcium carbonate with carbon dioxide under 56 atm. pressure at  $18^\circ$  contains 0.393% of calcium carbonate, corresponding with 0.637% of calcium hydrogen carbonate. This figure is considerably higher than any found by earlier investigators (cf. McCoy and Smith, A., 1911, ii, 380). Both prepared and natural (Iceland spar) calcium carbonate gave the same result. At first the experiments were carried out in an apparatus so fitted that after treatment the suspension could be filtered while still under pressure but later this was found to be unnecessary as the solutions obtained were fairly stable. Thus, even after standing exposed to the air at room temperature for 24 hours, the solution still contained 0.30% of calcium carbonate; it could be shaken, filtered through paper, or even gently warmed without appreciable precipitation taking place. A determination of the carbon dioxide evolved on boiling showed that calcium hydrogen carbonate was actually present. Attempts to isolate this compound in the solid form gave promising but unsatisfactory results. When the above solution was evaporated to dryness at  $10^\circ$ , anhydrous crystals of calcium carbonate were obtained, not the hexahydrate described by Johnstone and others (A., 1916, ii, 433). The solubility of calcium carbonate depends on the pressure of carbon dioxide to which the mixture is subjected. It reaches the above maximum at about 40 atm., not at 16 atm. as stated by McCoy and Smith (*loc. cit.*). The curve obtained by the author agreed well with that obtained for low pressures by Engel (A., 1886, 120). With rise in temperature (at 56 atm.), the solubility increases slightly, to 0.40%  $\text{CaCO}_3$  at  $25^\circ$ , to fall off rapidly until it is 0.26% at  $55^\circ$ . The conductivity of the solution, saturated at  $18^\circ$  [0.64%  $\text{Ca}(\text{HCO}_3)_2$ ] is  $3605 \times 10^{-8} \text{ cm.}^{-1}\omega^{-1}$ .  
W. A. S.

**Reactions of Chromates at High Temperatures. I. Synthesis and Decomposition of Calcium, Sodium, and Magnesium Chromates in Air.** M. R. NAYAR, H. E. WATSON, and J. J. SUDBOROUGH (*J. Ind. Inst. Sci.*, 1924, 7, 53—70; cf. this vol., ii, 492).—Calcium and chromic oxides begin to interact in the presence of air to form calcium chromate at 650°; at 700° a 95% yield of chromate is obtained with mixtures containing 2 equivalents of calcium oxide to 1 of chromic oxide and a 60% yield when the ratio is 1 : 1. In the presence of excess of calcium oxide, equilibrium is attained at about 800°, although pure calcium chromate does not begin to decompose until 1000° is reached. No basic salts of definite composition are obtained by heating pure calcium chromate. Sodium carbonate and chromic oxide readily interact to form chromate at temperatures below 660°; the salt melts at 800° and remains undecomposed after prolonged heating at 1000°. Ferric oxide and, to a greater extent, calcium oxide accelerate the formation of chromate in mixtures of sodium carbonate and chromic oxide by preventing the mass from fusing and thus allowing better access of air. Magnesium chromate decomposes completely at 650° into a mixture of chromites from which  $5\text{MgO} \cdot 4\text{Cr}_2\text{O}_3$  may be obtained as an insoluble residue after extraction of the mass with hydrochloric acid. Magnesium oxide and chromic oxide in equimolecular proportions give very little chromate below 600° and at higher temperatures yield only the chromite  $6\text{MgO} \cdot 5\text{Cr}_2\text{O}_3$ . A. R. P.

**Electrolytic Conductivity of Molten Chlorides.** A. VOIGT and W. BILTZ (*Z. anorg. Chem.*, 1924, 133, 277—305).—The conductivities of a number of molten chlorides have been determined with precautions to avoid the presence of moisture which greatly affects the results. The chlorides were prepared in glass or silica vessels and distilled into the conductivity apparatus. The following values (amongst others) were found for the specific conductivities at different temperatures. Beryllium chloride: 451°, 0.00319; 472°, 0.00868. Uranium tetrachloride: 570°, 0.34; 620°, 0.48. Thorium tetrachloride: 814°, 0.61; 866°, 0.71; 922°, 0.78. Lanthanum chloride: 950°, 1.30; 1000°, 1.42; 1025°, 1.49; 1075°, 1.63; 1135°, 1.77. Praseodymium chloride: 824°, 0.82; 875°, 0.97; 965°, 1.26. Neodymium chloride: 775°, 0.63; 827°, 0.765; 900°, 0.945. Bismuth trichloride: 266°, 0.442; 315°, 0.506; 350°, 0.555. Tellurium dichloride: 206°, 0.042; 230°, 0.0668; 271°, 0.114; 305°, 0.151. Tellurium tetrachloride: 236°, 0.1145; 277°, 0.161; 316°, 0.203. Molybdenum pentachloride: 216°,  $1.8 \times 10^{-6}$ ; 258°,  $7.5 \times 10^{-6}$ . Tungsten hexachloride: 280°,  $1.98 \times 10^{-6}$ ; 305°,  $2.85 \times 10^{-6}$ ; 330°,  $6.94 \times 10^{-6}$ . Tungsten pentachloride: 250°,  $0.67 \times 10^{-6}$ ; 275°,  $1.35 \times 10^{-6}$ ; 300°,  $1.84 \times 10^{-6}$ . It is doubtful if the salt described as tellurium dichloride has any definite existence, as the two different specimens used for the conductivity measurements both contained about 2% more chlorine than is required by the formula  $\text{TeCl}_2$ . Lead tetrachloride, vanadium tetrachloride, phosphorus trichloride, phosphorus pentachloride, and selenium dichloride have electrolytic conduc-

tivities too small to be measured. The following values for the density of bismuth trichloride are abstracted:  $d^{250}$  3.87,  $d^{300}$  3.75,  $d^{350}$  3.64. W. H.-R.

**Dissociation Pressures of Hydrated Double Sulphates. II. Various Double Sulphates of the Type  $M''SO_4.M'SO_4.6H_2O$ .**

R. M. CAVEN and J. FERGUSON (*J. Chem. Soc.*, 1924, **125**, 1307—1312).—The vapour pressures,  $p$ , of the double sulphates of the type  $M''SO_4.M'SO_4.6H_2O$ , where  $M''$  is Mg, Zn, Cd, Mn,  $Fe''$ , Co, or Ni, and  $M'$  is K, Rb, or Cs, may be expressed by the relation:  $\log p = a + b/T - c/T^2$ . When  $M''$  is Cu, Cd, or Mn,  $p$  decreases in the order  $M' = K, Rb, Cs$ ; for the remaining metals the order is K, Cs, Rb. The values of  $p$  for the ammonium double salts are very near, but are lower than, the values for the corresponding rubidium compounds. All the double sulphates examined form dihydrates on losing water, except when  $M''$  is magnesium or ferrous iron, when tetrahydrates are formed (cf. A., 1917, ii, 534; T., 1922, **121**, 1406). S. K. T.

**Active Agents in Luminescent Zinc Sulphides, Willemites, and Kunzites.** T. TANAKA (*J. Opt. Soc. Amer.*, 1924, **8**, 659—667; cf. this vol., ii, 288).—The spectrum of the cathodoluminescence of 6 samples of zinc sulphide exhibited a series of bands attributed by the author (*loc. cit.*) to thallium, and also two series which had not been previously observed. It is concluded, from the wave-length intervals between the two series, and from other evidence, that these unknown bands are due to the presence of ytterbium. The luminescence of willemites and kunzites contained bands attributed to manganese, iron, thallium, and samarium, and also the two new series of bands. S. B.

**Hardness of Lead-Cadmium and Lead-Tin Alloys.** C. DI CAPUA and M. ARNONE (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 293—297).—If, as was indicated by thermal and conductivity measurements (A., 1922, ii, 576), lead and cadmium are completely immiscible in the solid state, the hardness diagram for their alloys should be rectilinear. This is, however, not the case, the hardness of lead being increased greatly by the presence of a very small proportion of cadmium and the curve changing its direction suddenly at about 1% of cadmium. Repetition of the thermal conductivity measurements shows a similar inflection at the same point, so that cadmium is soluble in lead in the solid state to the extent of about 1% at the ordinary temperature.

The alteration in the hardness curve produced by prolonged re-heating of the alloys is very small with lead-cadmium alloys, but with lead-tin alloys the character of the curve is entirely altered by such treatment. Tin dissolves 1—2% of lead and the latter about 10% of tin at the ordinary temperature. T. H. P.

**Internal Friction of Molten Metals and Alloys. I. Lead-Bismuth Alloys.** F. SAUERWALD (*Z. anorg. Chem.*, 1924, **135**, 255—264).—An apparatus is described in which the viscosity of molten metals and alloys may be measured at high temperatures

by a capillary method. Lead-bismuth alloys [%Pb=36.8, 43.5 (eutectic), 51.3] show a smaller viscosity than that calculated from the mixture rule; no maximum or minimum viscosity is observed for the eutectic alloy (cf. Plüss, A., 1916, ii, 294). S. K. T.

**Dissolution of Lead in Alkaline Liquids by Alternating Currents.** F. JIRSA and J. FABINGER (*Z. physikal. Chem.*, 1924, 109, 260—274).—In electrolysis by alternating currents, lead enters into solution as bivalent ions. The current required for dissolution is always greater than this statement would indicate owing to secondary reactions with hydroxyl ions, producing  $\text{HPbO}_2'$  and  $\text{PbO}_2''$  ions, which may then be reduced by the cathodic component of the current. This effect increases with the concentration of the solutions. Potential experiments support the view that the lead electrode is completely active, and shows no mechanical anodic passivity. S. B.

**Behaviour of Liquid Cuprous Sulphide, Ferrous Sulphide, Copper, and Iron.** G. TAMMANN and H. BOHNER (*Z. anorg. Chem.*, 1924, 135, 161—168).—The quaternary equilibrium diagram for the system:  $\text{Cu}_2\text{S} + \text{Fe} \rightleftharpoons \text{FeS} + 2\text{Cu}$  is discussed. Since at certain concentrations mixtures of liquid copper and cuprous sulphide and of iron and copper are immiscible, the diagram shows the existence of an area in which three layers are formed instead of two, one of sulphide and two metallic. The significance of this region is discussed, mainly on the basis of work by Baykoff (*Rev. Mét.*, 1909, 6, 536). When equivalent amounts of iron and cuprous sulphide are melted together, the copper and iron are practically equally divided between the two layers. This corresponds with the very small heat of the forward reaction in the above equation.

S. K. T.

**Supposed Existence of Copper Carbonyl.** E. MOND and C. HEBERLEIN (*J. Chem. Soc.*, 1924, 125, 1222—1223).—A repetition of Bertrand's experiments (this vol., ii, 47) does not support the existence of copper carbonyl. It is thought that the metallisation of insects can be explained by the adhesion and sintering of the copper oxide, which is shown to begin at 400°. S. K. T.

**Structure of Crystalline Mercury.** N. ALSÉN and G. AMINOFF (*Geol. Förening Stockholm Förhandl.*, 1922, 124—128; from *Chem. Zentr.*, 1924, i, 1754).—From X-ray analysis it is found that mercury has a hexagonal four-atom lattice with the following constants:  $a=3.84 \text{ \AA.}$ ;  $c=7.24 \text{ \AA.}$ ;  $1:c=1:1.88$ . The arrangement is similar to that found by Hull for zinc and cadmium.

G. W. R.

**Has Pure Aluminium a Transformation Point?** K. HONDA and I. IGARASI (*Sci. Rep. Tôhoku Imp. Univ.*, 1924, 12, 305—308).—When commercial aluminium is heated, an abnormal expansion occurs in the temperature range 300—450°. The abnormal expansion increases as the silicon content increases to 1%, but then rapidly decreases. The author concludes that specimens entirely



free from silicon would show a normal expansion, and that no evidence for a transformation point exists. The effect of adding iron to aluminium which already contains traces of silicon, is very slightly to diminish the abnormal expansion. W. H.-R.

**Colloid Chemical Characterisation of Technical Clays and Kaolins.** I. W. OSTWALD and F. PIEKENBROCK (*Koll. Chem. Beihefte*, 1924, **19**, 138—170).—The authors consider the possibility of characterising clays and kaolins by measurements of the viscosity of suspensions of various concentrations. A number of factors, such as the concentration of the original suspension, ageing, the diameter of the capillary, and the mechanical treatment of the suspension, need to be controlled. Suspensions of clays and kaolin differ markedly in their behaviour on mechanical treatment. The viscosity of clay suspensions increases slowly and steadily with repeated squirtings through a capillary, whilst the viscosity of kaolin suspensions increases rapidly to a maximum. It is suggested that in kaolin suspensions the viscosity is a function of the size-distribution of the particles, but that in clays the principal factor is a stronger power of hydration and swelling. [Cf. *B.*, 1924, 597.] E. M. C.

**Electro-deposition of Manganese.** I. A. J. ALLMAND and A. N. CAMPBELL (*Trans. Faraday Soc.*, 1924, **19**, 559—573).—The electro-deposition of manganese from solutions of the chloride and sulphate has been studied and the influence of composition of electrolyte, current density, and temperature determined. Pure manganese in coherent form can be prepared in small amounts by using a catholyte containing 300 g. of manganous sulphate tetrahydrate, 100 g. of ammonium sulphate, and 2.5 g. of sulphuric acid per litre, the acidity being maintained by suitable additions of acid. Using a rotating cathode, current efficiencies of 50—60% were obtained. S. S.

**Tervalent Manganese.** V. J. MEYER and J. MAREK (*Z. anorg. Chem.*, 1924, **133**, 325—340; cf. *A.*, 1923, i, 12).—Oxidation of manganous salts in the presence of phosphoric acid gives a violet solution which gradually deposits a greyish-green precipitate of manganic orthophosphate (Christensen, *A.*, 1884, ii, 397). The violet colour is due to the presence of diphosphatomanganic acid  $[\text{Mn}(\text{PO}_4)_2]\text{H}_3$ , which has been prepared by the interaction of anhydrous manganic acetate and concentrated orthophosphoric acid at 100°. The reddish-violet crystals are very unstable and readily absorb moisture with the formation of the greyish-green manganic orthophosphate. The solution in concentrated phosphoric acid is, however, more stable, and, when this solution is electrolysed, the manganese goes to the anode, indicating that it is present as a complex anion. The trihydrated mono-sodium, mono-lithium, mono-potassium, and mono-ammonium diphosphatomanganates have been prepared. A similar pentahydrated sodium salt has been prepared, and an anhydrous guanidine salt,  $[\text{Mn}(\text{PO}_4)_2]\text{H}_3 \cdot \text{CH}_5\text{N}_3$ . These salts are probably monoclinic, dark red or violet in colour

(guanidine salt, dark yellow). This difference between the colours of the hydrated and anhydrous salts indicates that the water of hydration is not contained in the complex anion, but is simply water of crystallisation. The potassium salt is deliquescent but the others are stable in air. They are decomposed by hot water, yielding manganic hydroxide, whilst their solution in dilute phosphoric acid gradually deposits the greyish-green manganic orthophosphate. The violet colour given by manganese to the sodium metaphosphate bead in dry tests is probably due to the presence of a salt of diphosphatomanganic acid. W. H. R.

**Pyrophoric Property of Metal Powders.** G. TAMMANN and N. NIKITIN (*Z. anorg. Chem.*, 1924, **135**, 201—204).—The iron obtained by reducing ferrous oxalate in hydrogen loses its pyrophoric property at 530—536°, if the oxalate is not stirred during reduction, and at 370—400° if it is stirred. The corresponding temperatures for nickel oxalate are 370—390° and 330—365° (with less than 0.05 g. salt). The smaller the amount of salt used, the more vigorously and the longer it is stirred, the more certain is the product to be non-pyrophoric. Stirring favours the formation of large grains, *i.e.*, a small total surface. The experiments indicate, therefore, that pyrophoric power depends on the sizes of the metal particles. S. K. T.

**High-temperature Density Measurements. V. Density and Expansion of Liquid and Solid Grey Pig-iron.** F. SAUERWALD, H. ALLENDORF, and P. LANDSCHÜTZ (*Z. anorg. Chem.*, 1924, **135**, 327—332).—The specific volume of solid pig-iron, measured in a slightly modified apparatus from that previously described (*Z. Metallk.*, 1922, **14**, 457), showed a maximum value of 0.1484 at about 840°, which is attributed to the formation of mixed crystals of cementite and  $\gamma$ -iron. At the melting point the specific volume decreased abnormally, probably due to the formation of cementite. The value of  $dv/dT$  for the liquid phase was  $0.32 \times 10^4$  over the range 1171—1315°. S. K. T.

**Structural Constitution of Iron-Carbon-Silicon Alloys.** K. HONDA and T. MURAKAMI (*Sci. Rep. Tôhoku Imp. Univ.*, 1924, **12**, 257—287).—Iron-carbon-silicon alloys, containing less than 30% of silicon and 4% of carbon, have been examined. In the primary crystallisation two types of crystals separate from the fused mass, namely, (1) a solid solution of iron, silicon, and carbon termed silico-austenite, and (2) a carbide or graphite. These form an eutectic if the carbon and silicon contents exceed a certain limit. As the silicon content increases from 0 to 21%, the eutectic temperature rises from 1130° to 1200°, and its carbon content falls from 4.3% to zero, *i.e.*, the solubility of carbon in molten iron decreases with rising silicon content. If the silicon content is less than 5.5%, the carbide mentioned above is pure cementite,  $\text{Fe}_3\text{C}$ , but with a greater silicon content its place is taken by a double compound or silico-carbide, of undetermined constitution, which is non-magnetic, readily decomposes with the formation of graphite,

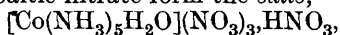
and forms no solid solution with cementite. On further cooling the solidified alloy, the silico-austenite deposits excess of silico-ferrite or of carbide, and at a certain temperature these form the eutectoid perlite. As the silicon content increases, the eutectoid temperature rises, and its carbon content decreases until, with more than 7% silicon, the change is no longer perceptible. If the silicon content exceeds 16%, the austenite on cooling deposits a compound,  $\text{Fe}_3\text{Si}_2$ , in addition to the double carbide. As the silicon content increases, the  $A_3$  and  $A_1$  points rise in temperature but the  $A_2$  point falls, so that the  $A_2$  point may occur at a lower temperature than the  $A_1$  point if the silicon content exceeds a certain amount. Graphite formation takes place very readily in these alloys owing to the instability of the double carbide, and to the fact that silicon lowers the solubility of carbon in the fused mass or in austenite. Graphitisation is favoured by increasing silicon content and also by slow cooling, so that rapidly cooled specimens which contain no graphite may produce graphite when annealed. The graphite in this system is usually not a primary product, but is produced by the decomposition of the double carbide. W. H.-R.

**Reversible Colloid of Iron.** A. F. G. CADENHEAD and W. H. VINING (*Can. Chem. Met.*, 1924, **8**, 65).—A substance resembling ferric hydroxide gel and hydrosol was isolated during the preparation of manganese acetate (cf. this vol., i, 826). CHEMICAL ABSTRACTS.

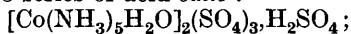
**Titration of Ferric Chloride with Sodium Hydroxide, using the Oxygen Electrode.** R. B. SMITH and P. M. GIESY (*J. Amer. Pharm. Assoc.*, 1923, **12**, 855—856).—Continuous curves were obtained, showing that ferric oxychloride does not exist.

CHEMICAL ABSTRACTS.

**Neutral and Acid Salts of Cobaltammines.** A. BENRATH and H. WÜRZBURGER (*Z. anorg. Chem.*, 1924, **135**, 226—232).—The formation of acid salts when neutral complex cobaltammines are treated with acid solutions of varying concentration is detected by analysis or by solubility curves. Aquopentamminecobaltic nitrate and hexamminecobaltic nitrate form the salts,



and  $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3, \text{HNO}_3$ , respectively. The corresponding sulphates form two series of acid salts:



$[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3, \text{H}_2\text{SO}_4$ , and  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{SO}_4)_3, 2\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$ ;  $[\text{Co}(\text{NH}_3)_6](\text{SO}_4)_3, 2\text{H}_2\text{SO}_4$ , respectively; the second of these salts has been previously described (A., 1898, ii, 592). The salt described by Klobb (A., 1902, ii, 143) does not appear to exist. The cobalt in these compounds has a co-ordination number of four. S. K. T.

**Evolution of the Molecule of Nickel Hydroxide in Contact with Water.** (MLLE.) S. VEIL (*Compt. rend.*, 1924, **178**, 842—844; cf. A., 1923, ii, 122, 373; this vol., ii, 183).—Nickel hydroxide was precipitated by the action of sodium hydroxide on a nickel salt. The precipitate was dissolved and reprecipitated several times, specimens of the oxide being prepared from each precipitate by

heating. The molecular coefficient of magnetisation of the hydroxide decreases with each successive precipitation; in the case of the oxides the value reaches a maximum and thence decreases.

H. J. E.

**Monocrystalline Tungsten.** A. E. VAN ARKEL (*Physica*, 1923, 3, 76—87; from *Chem. Zentr.*, 1924, i, 1651—1652).—The deposition of tungsten on a filament of monocrystalline tungsten in an atmosphere of dissociating tungsten hexachloride was studied. The effect of different conditions of experiment on the deposition of tungsten is discussed. The inclination of the crystal axis to the axis of the filament exerts an effect. Deposition takes place most readily on the 110 and 111 faces. The tendency to the formation of polycrystalline aggregates is greatest on the cube faces. The deposited tungsten is soft and pliable. After the filament has been subjected to mechanical treatment, the monocrystalline structure is lost and any further deposition takes place in the form of polycrystalline tungsten. X-Ray analysis shows that the filaments have a well-marked reticulate lamination perpendicular to the axis of the filament.

G. W. R.

**Crystal Structure of White Tin.** A. E. VAN ARKEL (*Proc. K. Akad. Wetensch.*, 1924, 27, 97—104).—In continuation of the work of Burger (*Physica*, 1922, 2, 56) on the properties of single crystal wires of tin, the author has taken röntgenograms to determine the orientation of the crystals in relation to the axis of the filament. The results are not in agreement with Bijl and Kolkmeijer's conclusions (A., 1919, ii, 108, 161), which do not explain the absence of a number of lines, exhibit divergencies in position and intensity for some of the lines, and do not explain satisfactorily the axial ratios given by Miller (*Ann. Phys. Chem.*, 1843, 58, 660). White tin is calculated to have eight atoms per structure element and a tetragonal diamond structure, in agreement with that derived by Mark and Póányi (A., 1923, ii, 768).

T. H. P.

**Arc Spectrum of Titanium.** C. C. KIESS and H. K. KIESS.—(See ii, 510.)

**Tervalent Vanadium.** I. J. MEYER and R. BACKA (*Z. anorg. Chem.*, 1924, 135, 177—193).—Anhydrous vanadium trichloride is prepared by passing carbon dioxide through vanadium tetrachloride at 140—150°. The latter chloride is obtained by passing chlorine over ferro-vanadium at dull red heat. Hydrogen chloride reacts at 300—400° with vanadium to give the trichloride, and with ferro-vanadium to give the dichloride. Anhydrous vanadium tribromide is best prepared by direct combination of the elements. The anhydrous tri-iodide could not be prepared.

*Hexaminevanadium trichloride*  $[V(NH_3)_6]Cl_3$ , and the corresponding bromide, are obtained by pouring liquid ammonia on to the appropriate halide; on moistening with concentrated nitric acid, both these compounds are converted to the nitrate,  $[V(NH_3)_6](NO_3)_3$ . All three compounds are decomposed by water:  $[V(NH_3)_6]Cl_3 + 3H_2O = V(OH)_3 + 3NH_3 + 3NH_4Cl$ ; they are unstable in air:  $[V(NH_3)_6]Cl_3 + O + 2H_2O = NH_4VO_3 + 3NH_4Cl + 2NH_3$ , and in moist

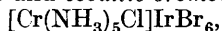
air they form the insoluble aquo-compound,  $[V(H_2O)_6]Cl_3$ . These compounds resemble the corresponding compounds of iron and aluminium rather than those of chromium and cobalt.

A *silicide*,  $VSi_2$ , is prepared by heating together vanadium pentoxide, silicon, and fluorspar. The action of chlorine compounds (e.g., carbonyl, thionyl, sulphuryl, and sulphur chlorides) at  $600^\circ$  on vanadium (which may be prepared in 93.5% purity by the Goldschmidt process) yields vanadium tetrachloride; carbon monoxide at  $500\text{--}800^\circ$  forms a carbide, the finely divided metal catalysing the reaction:  $2CO=CO_2+C$ . S. K. T.

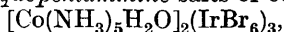
**Bivalent Bismuth.** E. NEUSSER (*Z. anorg. Chem.*, 1924, **135**, 313—326).—It is extremely improbable, theoretically, that bismuth can enter into combination as a bivalent element and the suboxide,  $BiO$ , is re-investigated from this point of view. The oxide, prepared by heating the basic oxalate or by reducing the hydroxide, is of variable composition, its bismuth content never reaching the theoretical value. This is not due to absorption of moisture, carbon dioxide, or oxygen; it is probably caused by the presence of hydroxide in the oxide. Metallic bismuth can be extracted from the substance by shaking with mercury. When heated for 16 to 18 hours in dry hydrogen sulphide, the suboxide behaves as a mixture of metal, trioxide, and hydroxide, each of which is attacked by the gas at a different rate. The presence of hydroxide explains the variable composition of the suboxide and also the low density ( $7.16$  at  $22^\circ$  when freshly prepared) compared with that calculated for a mixture of bismuth metal and trioxide. Tanatar's thermochemical results, supporting the existence of the suboxide, are criticised (A., 1901, ii, 553). S. K. T.

### **Bromoiridates of Complex Metal Bases and Chloro- and Bromo-iridates of Organic Bases of High Molecular Weight.**

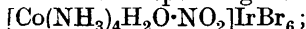
A. BENRATH [with W. BÜCHER, A. WOLBER, and J. ZEUTZIUS] (*Z. anorg. Chem.*, 1924, **135**, 233—254).—Fairly pure potassium bromoiridate is obtained in almost quantitative yield by warming together saturated solutions of potassium bromide and sodium chloroiridate, in presence of a little bromine, which is constantly renewed. The following new compounds are described: *hexammine-chromic nitrate bromoiridate*,  $[Cr(NH_3)_6]NO_3IrBr_6$ , and the *sulphate*, together with the corresponding *cobalt* compounds; *hexammine-chromic bromoiridate*,  $[Cr(NH_3)_6]_2[IrBr_6]_3$ , and the *cobalt* analogue; *chloropentamminechromic* and *cobaltic bromoiridates*,



etc.; the following *aquopentammine* salts of cobalt:



$[Co(NH_3)_5H_2O]Cl[IrBr_6]$  and the *sulphate*,  $[Co(NH_3)_5H_2O]_2Cl_4IrBr_6$  and the *sulphate*, and  $[Co(NH_3)_5H_2O]_4(SO_4)_3[IrBr_6]_3$ ; two *pentammine sulphates*,  $[Co(NH_3)_5SO_4]_2IrBr_6$ ,  $[Co(NH_3)_5SO_4]_4SO_4IrBr_6$ ; and the following *tetrammines*:  $[Co(NH_3)_4(NO_2)_2]_2IrBr_6$  (*cis*- and *trans*-modifications) and the corresponding *carbonate*;



$[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}(\text{OH})_2]\text{SO}_4\text{IrBr}_6$  and the *hydroxide*;

$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{SO}_4(\text{IrBr}_6)_2$ ,

and the corresponding *disulphate*. The number of ammine groups has no influence on the colour. The accumulation of acid residues in either sphere tends to deepen the colour, whilst their replacement by hydroxyl groups lightens it. The individual nature of the groups has a large influence.

The *chloro-* and *bromo-iridates* of the following complex bases are also prepared ( $x=1$  and  $2$ ;  $X=\text{Cl}$  and  $\text{Br}$ ): *quinine*,

$(\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2)_x\text{H}_2\text{IrX}_6$ ;

*cinchonine*,  $(\text{C}_{19}\text{H}_{22}\text{ON}_2)_x\text{H}_2\text{IrX}_6$ ; *cinchonidine*,

$(\text{C}_{19}\text{H}_{22}\text{ON}_2)_x\text{H}_2\text{IrX}_6$ ;

*strychnine*,  $(\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2)_2\text{H}_2\text{IrX}_6$ ; *brucine*,  $(\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2)_2\text{H}_2\text{IrX}_6$ ;

"*nitron*,"  $(\text{C}_{20}\text{H}_{16}\text{N}_4)_2\text{H}_2\text{IrBr}_6$ , the chloride having been previously prepared (A., 1922, ii, 515). These are nearly all obtained by mixing neutral or acid solutions of the base with a solution of sodium chloro- or bromo-iridate. The solubilities of most of the compounds described are measured by the conductivity method, since they are sparingly soluble. The chloroiridates are more soluble than the corresponding bromo-compounds, and the mono-alkaloidal salts are more soluble than the analogous dialkaloidal salts.

S. K. T.

## Mineralogical Chemistry.

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**Kämmererite in Chromite from Yugoslavia.** F. TUCAN (*Compt. rend.*, 1924, **178**, 1911—1913).—The Kämmererite found in the interstices of chromites from Yugoslavia has (*e.g.*) the composition,  $\text{SiO}_2$  33.03,  $\text{Al}_2\text{O}_3$  7.20,  $\text{Cr}_2\text{O}_3$  10.19,  $\text{FeO}$  0.96,  $\text{MgO}$  36.17,  $\text{H}_2\text{O}$  12.88. Specific gravity 2.59. The crystals were pale red and slightly dichroic. S. B.

**Benjaminite, a new Sulphosalt Mineral.** E. V. SHANNON (*Proc. U.S. Nat. Museum*, 1924, **65**, Art. 24, 1—9).—This occurs with muscovite, molybdenite, chalcopyrite, etc., in white vein-quartz near Round Mtn., Nye Co., Nevada. It is grey with metallic lustre and a fair cleavage in one direction. The streak is dull lead-grey;  $\text{H}=3\frac{1}{2}$ . It is soluble in hot strong nitric or hydrochloric acid. The best analysis gave I, and the mean of four, after deducting impurities, is given under II :

	Pb.	Cu.	Ag.	Fe.	Bi.	Mo.	S.	Quartz.	Total.
I.	21.70	6.65	2.78	0.58	41.45	1.30	15.53	8.86	98.85
II.	25.18	4.69	3.51	—	50.78	—	15.84	—	100.00

These results give the formula  $\text{Pb}_2(\text{Ag,Cu})_2\text{Bi}_4\text{S}_9$ , with the ratio  $\text{RS} + \text{R}_2\text{S} : \text{R}_2\text{S}_3 = 3 : 2$  as in the klaprotholite group. L. J. S.

**Crystalline Form of Becquerelite and Schoepite : their Composition and the Polymorphism of Uranium Hydroxide,  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ .** A. SCHOEP (*Bull. Soc. chim. Belg.*, 1924, **33**, 88—95).—Schoepite,  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ , contains traces of lead and iron. The

mineral crystallises in the orthorhombic system ( $a:b:c=0.426:1:0.875$ ). Becquerelite ( $a:b:c=0.5722:1:0.6173$ ) is of similar composition, but the higher percentage of lead indicates  $(\text{UO}_2, \text{Pb})\text{O} \cdot 2\text{H}_2\text{O}$  as a more consistent formula. Hydrated uranium trioxide prepared artificially (cf. Riban, A., 1882, 338; Aloy, A., 1900, ii, 484) is of two forms (a) orthorhombic tablets and (b) orthorhombic rectangular prisms, but some intermediate types are known.  
H. J. E.

**Silicates. II. Nontronite and Quartz Mixture from St. Andreasberg.** G. TAMMANN and C. F. GREVEMEYER (*Z. anorg. Chem.*, 1924, **135**, 197—200).—Nontronite,  $\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ , decomposes when heated into a mixture of iron oxide and silica (cf. A., 1923, ii, 758). Mica appears to form a sparingly soluble potassium aluminosilicate when heated at  $1000^\circ$ .  
S. K. T.

**Germanium in Smithsonite and Mine Waters.** J. H. MÜLLER (*Ind. Eng. Chem.*, 1924, **16**, 604—605).—Smithsonite from the Hudson mine near Salem, Kentucky, contains on an average 0.01% of germanium dioxide, which is also present in the mine-water (0.29% of the residues obtained on evaporation) and in the ore washings. The existence of germanium in a carbonate ore has not previously been observed.  
C. I.

**Relation of Composition, Colour, and Radiation to Luminescence in Calcites.** W. P. HEADDON (*Proc. Colo. Sci. Soc.*, 1923, **11**, 399—434; cf. *Amer. J. Sci.*, 1923, **5**, 31; **6**, 247).—The yellow colour and phosphorescence of calcites cannot be attributed to impurities (oxides of the cerium and yttrium groups, copper, manganese, iron, chromium, aluminium, nickel, and zinc), but may be connected with the atomic structure. CHEMICAL ABSTRACTS.

**Active Agents in Luminescent Zinc Sulphides, Willemite, and Kunzites.** T. TANAKA.—(See ii, 553.)

**Hafnium Content of Zirconium Minerals.** G. VON HEVESY and V. T. JANTZEN.—(See ii, 571.)

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### Analytical Chemistry.

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**Use of Porcelain Crucibles with Porous Bottoms in Analytical Chemistry.** G. F. HÜTTIG and K. SCHMITZ (*Z. anal. Chem.*, 1924, **64**, 224—226).—Porcelain crucibles with porous bottoms may be used in most analytical processes in place of Gooch or Munroe crucibles. The weight remains constant after use with practically all salt or acid solutions, but solutions of caustic alkalis must not be filtered through them. The crucibles are not hygroscopic, attain constant weight after heating for 20 mins. at 112°, and may be heated with the full flame of the Teclu burner without being damaged.

**Application of the Rigid Mercury Cathode in Electro-analysis.** I. H. PAWECK and E. WALTHER (*Z. anal. Chem.*, 1924, **64**, 89—96).—As a substitute for a platinum gauze cathode, a brass gauze on which mercury has been deposited by electrolysis for  $1\frac{1}{2}$  hours of a mercurous nitrate solution at a current density of 0.2 amp. per sq. dm. may be used with satisfactory results for the deposition of zinc from alkaline or acid solutions, bismuth and lead from nitrate solutions, and cadmium, iron, and nickel from sulphate solutions. After amalgamating the brass by electrolysis, the electrode is dipped into hot dilute hydrochloric acid until the mercury deposit becomes bright; the same treatment removes the deposited metal (except lead and bismuth which require nitric acid) and leaves the cathode in a suitable state for use again. [Cf. *B.*, 1924, 656.] A. R. P.

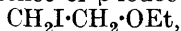
**Simple, Useful Forms of Hydrogen Electrode.** F. J. CONSIDINE (*Analyst*, 1924, **49**, 332—334).—An electrode using Barendrecht's suction device and Walpole's electrode for obtaining rapid readings by surface contact, and a modification suitable for "micro"-determinations are described. S. I. L.

**Detection of Chlorine, Bromine, and Iodine in Mixtures.** J. KUNFT (*Z. anal. Chem.*, 1924, **64**, 50—56).—Brief notes on various methods that have been proposed for the detection of chlorine, bromine, and iodine in mixtures are given. The most satisfactory method of detecting chlorine in the presence of the other halogens depends on the fact that silver chloride is decomposed by tribasic sodium arsenite whereas the other silver halides are unaffected. A. R. P.

**Alkalimetric Determination of Chlorine and Bromine Solutions, with Observations on Iodine Solutions.** E. RUPP (*Arch. Pharm.*, 1924, **262**, 3—7).—Chlorine or bromine are determined by adding the solution to a known excess of *N*- or 0.1*N*-sodium hydroxide containing hydrogen peroxide, and titrating the excess of alkali, using methyl red as indicator:  $\text{Cl}_2 + 2\text{NaOH} + \text{H}_2\text{O}_2 = 2\text{NaCl} + \text{O}_2 + 2\text{H}_2\text{O}$ . The acidity of the hydrogen peroxide must be determined by means of a blank titration.

With iodine solutions this method gives results about 2% low, owing to the fact that some iodate is at once produced and remains unreduced by the hydrogen peroxide. Sodium hypoiodite in presence of 10% sodium hydroxide solution is more than half converted to iodate and iodide when kept for 5 mins. in the cold, and the reaction is complete in a few hours.

Alcoholic solutions of iodine often cause irritation of the skin owing to the presence of free hydrogen iodide, produced by the reaction:  $\text{C}_2\text{H}_5\text{OH} + \text{I}_2 = \text{CH}_3\text{CHO} + 2\text{HI}$ . Serious headaches and giddiness sometimes caused to those working with such solutions are attributed to the presence of  $\beta$ -iodoethyl ethyl ether,



probably produced by way of ethylene iodide by reactions pre-

viously described (Aronstein and Kramps, A., 1880, 541; Baumstark, *J. Chem. Soc.*, 1875, 140). This compound could not actually be isolated from the alcoholic iodine solutions, owing to its great volatility. Its formation is probably catalysed by traces of chloride and cyanide which were found to be present. G. M. B.

**Accurate Evaluation of Potassium Chlorate by the Method of Bunsen.** E. C. WAGNER (*Ind. Eng. Chem.*, 1924, 16, 616—620).—By the use of an all-glass apparatus, and by exclusion of air, Bunsen's method for the determination of the chlorate content of potassium chlorate by distillation into potassium iodide gives accurate and concordant results. A wide-mouthed evolution flask, connected with a ground joint to an acid pipette with side tube, is charged with carbon dioxide, or a current of carbon dioxide is passed through it during the distillation. Hydrobromic acid is used in preference to hydrochloric acid and a blank test is always performed. The presence of appreciable quantities of bromate involves the application of a correction. The bromate is determined by titration of the iodine liberated from potassium iodide in acid solution. Under the conditions described, the chlorate does not react with the iodide. C. I.

**Iodide-Iodate Determinations.** S. HASSELSKOG (*Arch. Pharm.*, 1924, 262, 28—34).—The methods available for the determination of iodide in presence of an iodate are reviewed. The method of Müller and Wegelin (A., 1914, ii, 67) has been somewhat simplified. To 10 c.c. of the solution are added 1 c.c. of dilute phosphoric acid, 50 c.c. of water, and an excess of iodate solution. After 2 or 3 mins. a saturated solution of sodium phosphate is added until the reaction to litmus is neutral or alkaline, then 1 g. of pure sodium hydrogen carbonate and enough potassium iodide to dissolve all the liberated iodine. This is titrated with 0.1*N*-arsenious acid using starch as indicator. G. M. B.

**Determination of Ozone in the Presence of Hydrogen Peroxide.** M. BAMBERGER and K. TRAUTZL (*Z. anal. Chem.*, 1924, 64, 9—13).—The reaction between ozone and hydrogen peroxide proceeds only very slowly under ordinary conditions and not at all at the temperature of liquid ozone even if 90% hydrogen peroxide is dropped into the ozone. To separate hydrogen peroxide vapour from gases containing ozone the mixture is passed slowly through a spiral immersed in a mixture of ether and solid carbon dioxide which condenses the peroxide only. Separation and determination of the two substances in a mixture is effected by passing the gases through acidified 0.2*N*-permanganate, which destroys the peroxide, and absorbing the ozone in potassium iodide. Pure hydrogen peroxide decomposes explosively in contact with powdered bismuth; concentrated solutions, however, react more slowly with the evolution of ozonised oxygen. A. R. P.

**Contamination of Hydrogen by Sulphur, and a Sensitive Test for Very Small Quantities of Sulphur.** W. PRANDTL (*Z. anorg. Chem.*, 1924, 133, 361—371).—The substance to be tested

is mixed with pure calcium oxide and the mixture is heated in pure oxygen. The resulting mixture is heated to bright redness in a stream of moist hydrogen (which must be free from sulphur), and the issuing gas is passed through an alkaline lead solution, when a black precipitate or discoloration is produced if sulphur is present. The same method serves for the detection of traces of sulphur in hydrogen, and the oxides of magnesium or lanthanum may be used instead of calcium oxide. The preparation of these oxides absolutely free from sulphur is described. The method indicates that hydrogen prepared by the electrolysis of a solution of barium hydroxide is quite free from sulphur.

W. H.-R.

**Reaction of Alkali Hydrogen Sulphites with Mercuric Chloride.** A. GRAIRE (*Compt. rend.*, 1924, **178**, 1819—1822).—Mercuric chloride and sodium hydrogen sulphite solutions react in the cold, quantitatively if either be in excess, in accordance with the equation  $\text{HgCl}_2 + 2\text{NaHSO}_3 = 2\text{HCl} + \text{Na}_2\text{Hg}(\text{SO}_3)_2$ . The double sodium mercury sulphite decomposes on heating:  $\text{Na}_2\text{Hg}(\text{SO}_3)_2 = \text{Na}_2\text{SO}_4 + \text{Hg} + \text{SO}_2$ . The acid liberated in accordance with the first equation may be titrated, using methyl-orange as indicator. This reaction may be used in the analysis of mixtures of sulphite and hydrogen sulphite with or without excess of sulphur dioxide. The total  $\text{H}_2\text{SO}_3$  is found by iodometry and the hydrogen sulphite by adding a large excess of mercuric chloride and titrating in the cold, using methyl-orange or alizarin as indicator. Conversely, mercury may be determined in neutral solutions of the chloride, by adding a large excess of sodium hydrogen sulphite solution, neutral to methyl-orange, and titrating the liberated acid with sodium hydroxide.

G. M. B.

**Electrometric Determination of Soluble Sulphates.** E. MÜLLER and R. WERTHEIM (*Z. anorg. Chem.*, 1924, **133**, 411—416).—The aqueous solution containing the soluble sulphate is treated with alcohol, and a measured quantity of a standard solution of lead nitrate is added, in excess of that required completely to precipitate the sulphate. The lead sulphate is filtered off, washed with alcohol, and the amount of unchanged lead nitrate in the filtrate is determined by electrometric titration with standard ferrocyanide solution (cf. Niemz, *Diss.*, Dresden, 1920; Müller and Gäbler, A., 1923, ii, 90). If the lead sulphate is not removed, the method is not accurate owing to a slow reaction between the lead sulphate and ferrocyanide.

W. H.-R.

**Use of the Aldehyde-Bisulphite Reaction in Volumetric Analysis.** A. KURTENACKER (*Z. anal. Chem.*, 1924, **64**, 56—61).—The fact that the compound of formaldehyde and sodium hydrogen sulphite is not oxidised by iodine is made the basis of a method for determining thiosulphate in the presence of sulphite. The solution is rendered neutral to phenolphthalein, formaldehyde in excess is added, followed by an excess of 10% acetic acid above that required to decolorise the solution, and the mixture is titrated with iodine for thiosulphate.

A. R. P.

**Ageing of Volumetric Thiosulphate Solutions.** A. SKRABAL (*Z. anal. Chem.*, 1924, **64**, 107—112).—The stability of 0.1*N*-solutions of sodium thiosulphate having  $p_H$  between 5 and 12 has been investigated. After 5 months, the most acid solution had decreased 1.28% in strength, whereas solutions of  $p_H$  9—10 had not changed. Solutions of greater acidity than this did not obtain a constant titre at any time during the tests and, in the case of solutions of  $p_H$  5—6, sulphur separated during the first few weeks and then gradually redissolved. Both hydrogen sulphide and sulphur dioxide could be detected at different times in these solutions, so that they probably contained polythionic acids after prolonged storage. Addition of small quantities of copper sulphate lowered the titre even of the more alkaline solutions. A. R. P.

**Rôle of Adsorption in the Determination of Residual Nitrogen.** J. H. CASCÃO DE ANCIÃES (*Klin. Woch.*, 1924, **3**, 115; from *Chem. Zentr.*, 1924, i, 1839).—In the determination of residual nitrogen errors are possible owing to the adsorption by the protein precipitate of non-protein compounds of high molecular weight. G. W. R.

**Colour Reaction of Nitric Acid and Nitrous Acid.** L. DESVERGNES (*Ann. Chim. Analyt.*, 1924, [ii], **6**, 102—103).—An intense red coloration is obtained when a very small quantity of nitric or nitrous acid is treated with diphenyldiethylcarbamide in sulphuric acid solution; the sensitiveness of the reaction is 1 : 250,000. Other oxidising substances, such as chlorates and chromates, also give a red coloration with the reagent. W. P. S.

**Determination of Nitrites, Nitrates, and Selenium.** W. STRECKER and L. SCHATOW (*Z. anal. Chem.*, 1924, **64**, 218—224).—For the determination of nitrite the substance is heated with carbamide and hydrochloric acid in a flask through which a slow current of carbon dioxide is passed. The nitrogen evolved is collected over a 33% solution of potassium hydroxide and its volume measured. Nitrates may be determined in a similar apparatus by heating the substance with concentrated hydrochloric acid and ferrous chloride and measuring the evolved nitric oxide. By heating a neutral solution of a nitrite with a known weight of hydroxylamine sulphate or chloride, nitrous oxide is evolved; subsequent titration of the solution with 0.1*N*-alkali using phenolphthalein gives a measure of the hydroxylamine salt not consumed and from this the nitrite content of the original substance may be calculated. For the determination of selenium, the solution, which must contain the element in the form of its dioxide, is heated with hydrazine sulphate solution and the nitrogen evolved is collected and measured or the excess of hydrazine salt determined by titration with iodine or bromate. A. R. P.

**Colorimetric Determination of Nitrate Nitrogen.** F. M. SCALES and A. P. HARRISON (*Ind. Eng. Chem.*, 1924, **16**, 571—572).—An accurate and rapid method for the determination of the small amounts of nitrate in biological solutions is based on the

development of a rose colour on mixing with reduced strychnine and sulphuric acid in absence of light. Zinc, lead, or preferably mercury chloride enhance the colour, the depth of which increases with time but is destroyed by light. Nitrites interfere with the reaction and must be previously removed. C. I.

**Determination of Nitrates by Electrometric Titration.** J. B. ROBERTSON and A. J. PELLING (*J. S. Afr. Chem. Inst.*, 1924, 7, 9—13).—Ferrous sulphate may be oxidised by a nitrate in hydrochloric acid solution and the resulting ferric salt then titrated with titanium trichloride solution, the end-point of the titration being determined electrometrically. Or, a known volume of the nitrate solution may be added to a definite excess of ferrous sulphate solution and the excess then titrated with standard dichromate solution. W. P. S.

**Determination of Nitrates in Soil.** D. J. R. VAN WIJK (*Soil. Sci.*, 1924, 17, 163—178).—A number of standard methods for nitrate determination are compared critically. Laboratory details of a modified method are given, which consists essentially of extraction with water, reduction of the filtered extract at 20° with aluminium foil in the presence of sodium hydroxide solution, and subsequent distillation and nesslerisation. A. G. P.

**Determination of Total Phosphorus in Blood.** C. S. SMITH and A. L. BROWN (*J. Lab. Clin. Med.*, 1923, 9, 203—205).—The blood is evaporated with magnesium nitrate solution, ignited, the residue treated with hydrochloric and nitric acids, and the phosphoric acid determined volumetrically by the phosphomolybdate method. CHEMICAL ABSTRACTS.

**Simultaneous Determination of Minute Quantities of Sulphur and Phosphorus.** F. W. HEYL and B. FULLERTON (*J. Amer. Pharm. Assoc.*, 1923, 12, 617—620).—Using casein of known phosphorus content and pure potassium sulphate equivalent to 0.0015 g. of sulphur, a method of analysis was devised which is essentially the alkalimetric method for titrating ammonium phosphomolybdate and that for titrating benzidine sulphate. CHEMICAL ABSTRACTS.

**Determination of Hypophosphorous and Phosphorous Acids with Iodic Acid.** A. BRUKL and M. BEHR (*Z. anal. Chem.*, 1924, 64, 23—28).—The solution, which must not contain nitrates or chlorides, is acidified with dilute sulphuric acid and boiled with an excess of iodic acid until all iodine has been expelled. After cooling and diluting, the excess of iodic acid is determined by adding potassium iodide and titrating the liberated iodine with thiosulphate. If salts of both hypophosphorous and phosphorous acids are present in the same solution the liquid is evaporated to dryness with a slight excess of an alcoholic solution of potassium hydroxide, and the residue is digested cold with 96% alcohol for 2 hours; potassium hypophosphite dissolves and after expulsion of the alcohol by boiling is determined as above, whilst the residue is analysed in a similar way for phosphite. A. R. P.

**Titration of Arsenious Acid with Permanganate.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1924, 61, 738—742).—The titration must be carried out under such conditions as to prevent the formation of manganic salts, indicated by a brownish- or yellowish-green colour, as these are only very slowly reduced. In sulphuric acid solution the titration must be carried out slowly, at the b. p. With dilute solutions of the arsenious oxide in hydrochloric acid at 100°, very accurate results are quickly obtainable. S. I. L.

**Oxidation of Acetic Acid by Various Metallic Chromates Compared with Oxidation by Silver Dichromate in the Determination of Carbon by the Silver Sulphochromic Method.** L. J. SIMON (*Compt. rend.*, 1924, 178, 1816—1819; cf. A., 1922, ii, 593, 867).—Comparative experiments were made on the oxidation of acetic acid by a mixture of concentrated sulphuric acid with equivalent weights of the chromates of silver, cobalt, nickel, mercury, copper, iron, zinc, and magnesium, the carbon dioxide produced after 30 minutes' heating being determined both gravimetrically and volumetrically. The action was complete with silver chromate, less than half so with the cobalt salt and the efficiency of the process diminished in the other cases in the above order. The process is not to be confused with the ordinary wet oxidation method, where mercuric chromate is an efficient catalyst. G. M. B.

**Micro Determination of Carbon and Nitrogen in Organic Compounds by the Wet Method.** H. DIETERLE (*Arch. Pharm.*, 1924, 262, 35—40).—Details are given of the micro determination of carbon based on the method of Fritsch (A., 1897, ii, 124) the substance being decomposed by potassium dichromate and concentrated sulphuric acid in a stream of oxygen, and the products passed through a short combustion tube containing 8—9 cms. of a mixture of copper oxide and lead chromate. The nitrogen is determined by the Kjeldahl method, the distillation being carried out in a current of steam and the ammonia titrated by means of 0.05N-acid and borax solutions with methyl-red as indicator. G. M. B.

**Reagent for Carbon Monoxide.** A. DAMIENS (*Compt. rend.*, 1924, 178, 849—852).—The compound of cuprous sulphate and ethylene (Damiens, A., 1922, i, 1105) is stable when in suspension in sulphuric acid and in this condition it readily absorbs carbon monoxide. It is recommended as a reagent for the determination of this gas in gaseous mixtures, and details are given of the method of use and of the results obtained. The compound formed by carbon monoxide, precipitated as a white powder of the composition  $\text{Cu}_2\text{SO}_4 \cdot 2\text{CO}$ , has, under the conditions specified, practically no dissociation pressure. As the reagent also absorbs oxygen, ethylene, and acetylene, these gases must be removed from mixtures by the appropriate methods before determining carbon monoxide.

H. J. E.

**Determination of Carbonic Acid Present as Carbonate in Soils.** P. B. SANYOL.—(See i, 820.)

**Analysis of Sodium Peroxide.** E. BOSSHARD and E. FURRER (*Helv. Chim. Acta*, 1924, **7**, 486—489).—Grossmann's method (A., 1905, ii, 284), consisting in measuring the volume of oxygen evolved on treating sodium peroxide with acid in presence of cobalt nitrate, gives more accurate results if the solution is boiled for a short time. Methods based on titrating with potassium permanganate the hydrogen peroxide formed on dissolving sodium peroxide in water or dilute acid, give low results, through loss of peroxide due to the heat of hydration of sodium peroxide. This loss can be overcome by triturating the sodium peroxide (0.2 to 0.4 g.) with orthoboric acid (3 to 5 g.), adding 100 c.c. of water and 10 c.c. of dilute (1 : 5) sulphuric acid, and titrating the free hydrogen peroxide with 0.1*N*-permanganate. The results obtained by this method agree with those given by the gasometric method. E. H. R.

**Rapid Electro-analytical Separation of Silver, Copper, and Bismuth by means of Graduated Potentials.** A. LASSIEUR (*Compt. rend.*, 1924, **178**, 847—849).—Using the apparatus previously described (this vol., ii, 15), the separate deposition of silver and copper may be effected without difficulty from most solutions; certain special cases are mentioned. The separation of silver from bismuth is similar. In the case of copper and bismuth, Sand's method (T., 1907, **91**, 373) yields a copper deposit which contains bismuth. The author recommends working in ammoniacal solution; the bismuth is thus precipitated during deposition of the copper and, on acidifying, it may then be determined. Careful regulation of the auxiliary potential is necessary. H. J. E.

**Electrometric Determination of Barium in Presence and Absence of Calcium.** E. MÜLLER and R. WERTHEIM (*Z. anorg. Chem.*, 1924, **135**, 269—272).—Freshly-precipitated lead sulphate, when shaken for 24 hours with barium chloride solution, is converted into barium sulphate to the extent of about 98%. The amount of the conversion is determined by titrating the lead in the solution electrometrically with potassium ferrocyanide. This process may be used to determine barium; the presence of calcium does not influence the determination. S. K. T.

**Electrolytic Precipitation of Zinc from Alkaline Solution and its Application to Rapid Separations from Other Metals.** K. BREISCH (*Z. anal. Chem.*, 1924, **64**, 13—23).—Zinc is quantitatively deposited from potassium hydroxide solutions on a revolving silver gauze cathode at a current density of 3 amp. per sq. dm. If much nitrate is present it must be destroyed by boiling with hydrochloric acid solution and paraformaldehyde. In the presence of nickel or aluminium the acid zinc solution is poured into an excess of potassium hydroxide solution containing hydrogen peroxide and the liquid is electrolysed without filtration. In the presence of iron, sodium sulphide is added to the acid liquid followed by potassium hydroxide and potassium cyanide until everything has



dissolved. An excess of sodium sulphide is added to the solution before electrolysis to prevent anodic oxidation of the ferrocyanide and subsequent partial deposition of iron on the cathode.

A. R. P.

#### **Separation of Mercury and Cadmium by Means of Pyridine.**

G. ROTTER (*Z. anal. Chem.*, 1924, **64**, 102—106).—The neutral chloride solution of the two metals is treated with an excess of ammonium thiocyanate, then with a slight excess of dilute pyridine solution. After 1 hour the precipitate is collected, washed, dissolved in dilute hydrochloric acid, and reprecipitated by the addition of ammonia, ammonium thiocyanate, and pyridine. The precipitate of  $\text{Cd}(\text{C}_5\text{H}_5\text{N})_2(\text{CNS})_2$  is evaporated to dryness with nitric acid and the residue heated to destroy organic matter, then converted to cadmium sulphate for weighing. The combined filtrates are treated with hydrogen sulphide for mercury.

A. R. P.

#### **Solubility of Lead Sulphate in Dilute Sulphuric Acid Solutions and its Bearing on the Quantitative Separation of Lead as Sulphate.**

A. E. DAWKINS and P. R. WELDON (*Proc. Soc. Chem. Ind. Victoria*, 1922, **22**, 940—948).—The solubility of lead sulphate at 30° in sulphuric acid solutions containing 0.1 to 20% of free acid varies irregularly between 0.71 and 1.05 mg. per 100 c.c. of solution and is therefore sufficiently high to render inaccurate the determination of small quantities of lead by precipitation as sulphate unless the volume of solution is kept very small.

A. R. P.

**Nascent Hydrogen Sulphide as a Reagent for the Determination of Platinum and Copper.** R. DOHT (*Z. anal. Chem.*, 1924, **64**, 37—40).—The solution, containing copper or platinum and free from nitric acid, is heated to boiling with hydrochloric acid and a large excess of hypophosphorous acid and a 3—4% solution of sulphur dioxide is gradually added until the precipitate of platinum or copper sulphide and free sulphur coagulates and settles, and the solution becomes colourless. The precipitate is free from iron and, in the case of platinum, may be converted into (and weighed as) metal by direct ignition.

A. R. P.

#### **Poisoning by Mercuric Chloride and the Limiting Amount of Mercuric Chloride Detectable by Post-mortem Tests.**

A. SARTORI (*Chem.-Ztg.*, 1924, **48**, 141—142).—In testing for mercury in the organs, the organic matter is destroyed by heating with hydrochloric acid and potassium chlorate on the water-bath and the solution treated with hydrogen sulphide. The precipitate is purified, and redissolved in hydrochloric acid with potassium chlorate and the solution, after evaporation at 50—60°, tested for mercury by the copper strip test. Synthetic tests showed that 0.05 mg. of mercuric chloride could be detected in a weakly acid aqueous solution if the strip after immersion was treated with iodine vapour and examined for the characteristic mercuric iodide under the microscope. On the other hand, less than 2 mg. of mercuric chloride could not be detected in a broth containing 200 g. of

cooked potatoes and 10 g. of sugar after treatment by the above process.

A. R. P.

**Local Microchemical Detection of Alumina.** H. HERMANN (*Z. anal. Chem.*, 1924, **64**, 48—50).—In order to obtain an idea of the distribution of alumina in a rock section or similar mixture, the specimen is heated in a platinum crucible in an atmosphere of ammonium fluoride vapour for 30 minutes at 100—150° whereby a film of aluminium fluoride, varying in thickness according to the distribution of the oxide through the mass, is obtained. This film is rendered visible by immersing the washed specimen for  $\frac{1}{2}$  an hour in a 1% solution of sodium phosphate coloured deep-red with alizarin. After drying on filter-paper the specimen is examined under the microscope; the intensity of the colour adsorbed depends on the amount of aluminium fluoride present, variations of 5% in the alumina content of different parts of the specimen being readily discernible. [Cf. *B.*, 1924, 633.]

A. R. P.

**Determination of Manganese by the Silver Nitrate-Persulphate Process.** K. SWOBODA (*Z. anal. Chem.*, 1924, **64**, 156—164).—The determination of manganese in steels and alloys by oxidation to permanganate with persulphate in the presence of silver nitrate followed by titration with sodium arsenite gives good results only when carried out under exactly specified conditions using as a standard a material similar to that being analysed and of known manganese content. Addition of potassium fluoride or of hydrofluoric acid to the liquid immediately before titration gives results which closely approximate to the theoretical, assuming that the arsenite then reduces the permanganate only as far as the tervalent state.

A. R. P.

**Determination of Manganese. II. Manganous Oxalate as a Primary Standard.** R. W. COLTMAN (*Ind. Eng. Chem.*, 1924, **16**, 606—609).—Manganous oxalate is well suited for use as a standard for control determinations of manganese. The trihydrate (pink, prismatic needles) passes into the dihydrate (white, rhombohedral plates from hot solutions) on warming with water at 80°. The dihydrate, which is preferred, is prepared by the interaction of oxalic acid and potassium permanganate. The salt is stable in contact with either dry or moist air at the ordinary temperature.

C. I.

**Modification of Vogel's Reaction for Cobalt.** F. J. ALLEN and A. R. MIDDLETON (*Proc. Indiana Acad. Sci.*, 1922, 147—152).—In *N*-hydrochloric or sulphuric acid-*N*-potassium, sodium, or ammonium thiocyanate solution, using 0.2 vol. of ethyl alcohol, and just sufficient ether to give a separate layer, 0.001 mg. of cobalt in 8 c.c. can be detected.

CHEMICAL ABSTRACTS.

**Qualitative Analysis of the Tin Group.** R. W. HUFFERD (*Proc. Indiana Acad. Sci.*, 1922, 137—138).—The arsenic, antimony, and tin are separated first with ammonium sulphide, and then with

ammonia; the antimony and tin sulphides are dissolved in hydrochloric acid, and aluminium is used for the reduction.

CHEMICAL ABSTRACTS.

**Detection of Tin and Mercury by Means of a Spot Test.**

N. A. TANANAEV (*Z. anorg. Chem.*, 1924, **133**, 372—374).—A black stain is produced if a mercuric chloride test paper is treated with 1 drop of a solution containing stannous tin, and then with 1 drop of aniline. The stannous ion is the only cation in the five analytical groups that will reduce mercuric chloride to metallic mercury in the presence of aniline, and the test can therefore be used in the presence of any of the ordinary metals. If the tin is present in the stannic condition, it is first reduced to the stannous form by means of magnesium and hydrochloric acid. By using a test paper soaked in a solution of stannous chloride, the same reaction serves for the detection of mercury.

W. H.-R.

**Hafnium Content of Zirconium Minerals.**

G. VON HEVESY and V. T. JANTZEN (*Z. anorg. chem.*, 1924, **133**, 113—118).—The hafnium content of minerals is determined by mixing a known quantity of tantalum with the mineral and comparing the intensity of the X-ray spectra, which is proportional to the existing mixture of the two elements. Minerals containing no zirconium are also free from hafnium. In general, zirconium oxides, rich in zirconium, are poor in hafnium, and decomposed zircons (e.g., silicates), poor in zirconium and containing a large quantity of rare earths, are rich in hafnium. The latter always contain thorium and uranium and hence the simple and rapid radioactive method can be employed in the search for zirconium minerals rich in hafnium. The average hafnium content of zirconium minerals being 3%, it is estimated that the hafnium content of the earth's crust is about 0.00045%.

J. W. B.

**Reagent for the Determination of Antimony.**

F. FEIGL (*Z. anal. Chem.*, 1924, **64**, 41—47).—Faintly acid solutions of trivalent antimony compounds give white, silky precipitates with pyrogallol. The precipitation is incomplete in neutral, alkaline, or acetic acid solutions. The test will detect 0.025 mg. of antimony in 5 c.c. For the quantitative separation of antimony from lead, tin, or trivalent arsenic, the faintly acid chloride solution is treated with sufficient sodium potassium tartrate to replace the free mineral acid, then with five times the theoretical quantity of pyrogallol. After 2 hours, the precipitate is collected in a Gooch crucible, washed with cold water, dried at 110°, and weighed as  $C_6H_4O_3 \cdot SbOH$ .

A. R. P.

**Determination of Tantalum and Niobium.**

C. WENZEL (*Anal. Asoc. Quím. Argentina*, 1923, ii, 297—303).—The most satisfactory method for the determination of tantalum and niobium in minerals consists in fusion with sodium hydrogen sulphate and separation of niobium and tantalum by means of the potassium double fluorides.

G. W. R.

**Determination of Glycerol by Oxidation with Potassium Iodate and Sulphuric Acid.** R. STREIBINGER and J. STREIT (*Z. anal. Chem.*, 1924, **64**, 136—143).—The fat is saponified by boiling with a solution of sodium hydroxide in methyl alcohol, the alcohol is evaporated off, and the solution acidified with sulphuric acid, filtered, evaporated to half its volume, and again filtered. The filtrate is treated with an excess of potassium iodate and sulphuric acid and the liquid is evaporated until the acid evolves copious fumes and vapours of iodine are no longer seen in the flask. After cooling and diluting with water the excess of iodate is determined iodometrically as usual. The results obtained by this method are somewhat lower than those calculated from the saponification value of the fat but agree well with figures obtained by the permanganate method. [Cf. *B.*, 1924, 640.] A. R. P.

**Phenylhydrazine Test for Formaldehyde.** A. B. LYONS (*J. Amer. Pharm. Assoc.*, 1924, **13**, 7—9).—Gettler's test for formaldehyde (A., 1920, ii, 562) is the most satisfactory single test; substitution of ferric chloride and hydrochloric acid for sodium nitroprusside gives erratic results, but if potassium ferricyanide or ammonium persulphate is used instead of ferric chloride the reaction is trustworthy, and sensitive because the colouring matter in great dilutions may be extracted with light petroleum. Evaporation of the solvent yields an orange-yellow residue, which becomes violet-red when dry if acid is present; vapours of nitric acid change the colour to violet. CHEMICAL ABSTRACTS.

**Resorcinol and Phloroglucinol as Colour Reagents.** E. V. LYNN and F. A. LEE (*J. Amer. Pharm. Assoc.*, 1923, **12**, 418—419).—Colour reactions given by a 1% solution of resorcinol or phloroglucinol in 36% hydrochloric acid (using a saturated aqueous solution of the less soluble, or a 1% solution of the more soluble aldehydes) are tabulated for cinnamaldehyde, furfuraldehyde, formaldehyde, paraformaldehyde, acetaldehyde, citronella oil, geranium oil, benzaldehyde, butyraldehyde, piperonaldehyde, eugenol, vanillin, and *p*-tolualdehyde. CHEMICAL ABSTRACTS.

**Determination of Sugar in Urine.** G. W. PUCHER (*J. Lab. Clin. Med.*, 1924, **9**, 268—270).—Mixtures of 10%, 20%, and 40% of urine in 3% sulphuric acid are separately shaken with Lloyd's reagent and filtered through a dry filter; the sugar is determined in a portion of the filtrate by heating with picric acid and sodium carbonate, and comparison with a standard by the Myer-Benedict colorimetric method. Tests with creatinine showed that Lloyd's reagent is effective for its removal. CHEMICAL ABSTRACTS.

**Determination of Fumaric and Maleic Acid by Halogenometric Methods.** B. M. MARGOSCHES and W. HINER (*Z. anal. Chem.*, 1924, **64**, 61—72).—Fumaric and maleic acids are only slightly attacked by any of the usual brominating solutions, but in faintly alkaline solutions they absorb bromine quantitatively

from solutions in potassium bromide, and, in very slightly acid solutions, from mixtures of bromide and bromate. The excess of bromine in each case is determined by addition of hydrochloric acid and potassium iodide followed by titration with thiosulphate.

A. R. P.

**Titration of Oxalic Acid with Permanganate.** I. M. KOLTHOFF (*Z. anal. Chem.*, 1924, 64, 185—211).—The most satisfactory results are obtained if the oxalic acid solution contains 30 c.c. of 4*N*-sulphuric or hydrochloric acid in 100—200 c.c., and if the titration is carried out at 75—85° by adding the permanganate very slowly at first, then increasing the rate of addition towards the end. If manganese sulphate is added to the solution the titration may be carried out at 40°; at 100°, however, the presence of manganous or chromic salts leads to low results. Under ordinary conditions, a certain amount of hydrogen peroxide is formed during the titration, but only in the presence of oxygen from the air and principally during, and just after, the induction period of the reaction. The reverse operation of adding oxalic acid to permanganate and titrating the excess of oxalic acid with a standard solution of permanganate results in the consumption of about 0.5% too much permanganate.

A. R. P.

**Oxalic Acid as a Titration Standard.** W. D. TREADWELL and H. JOHNER (*Helv. Chim. Acta*, 1924, 7, 528—534).—The vapour pressure of crystallised oxalic acid was measured at temperatures between 18° and 82° by a dew-point method. The vapour-pressure curve can be expressed by the equation  $\log p = -3304/T + 11,364$ . The vapour-pressure curve of water can be expressed by a similar equation,  $\log p = -2295/T + 9,074$ . The molecular heat of hydration at 18° of oxalic acid by liquid water is calculated to be 3045 cal., in good agreement with other determinations. On account of the low value of the vapour pressure of hydrated oxalic acid, 1.2 mm. at 18°, it adsorbs water when air-dried, and hence gives results about 0.7% too high when used for standardising permanganate. Correct results are obtained using the hydrated acid dried by a current of air which has been previously passed over a mixture of hydrated and anhydrous oxalic acid; or using sublimed anhydrous oxalic acid or dried sodium oxalate.

E. H. R.

**Detection and Determination of Oxalic Acid [in Urine].** J. DADLEZ and W. JANKOWSKA (*Compt. rend. Soc. Biol.*, 1924, 90, 310—311; from *Chem. Zentr.*, 1924, i, 1839).—The concentrated urine is treated with hydrochloric acid, and extracted four times with ether containing 10% of ethyl alcohol. The oxalic acid is precipitated from the ethereal, concentrated, filtered extract as the calcium salt.

G. W. R.

**Detection and Determination of Tartaric Acid.** A. KLING and A. LASSIEUR (*Ann. Chim. Analyt.*, 1924, [ii], 6, 103—104).—A reply to François and Lormand (this vol., ii, 129) maintaining the accuracy of the calcium racemate method.

W. P. S.

**Application of Fluorescence Phenomena to the Identification of Medicaments.** E. BAYLE and R. FABRE (*J. Pharm. Chim.*, 1924, [vii], 29, 535—543; cf. this vol., ii, 220).—A number of compounds exhibit fluorescence when placed on a piece of porous porcelain at the focus of a convex lens and subjected to ultra-violet light of 3650 Å. from a Georges mercury lamp. The phenomenon affords a means of separating crystalline mixtures of fluorescent and non-fluorescent compounds (e.g., novocaine and stovaine) and of detecting the presence of impurities (e.g., salicylic acid in milk). Sodium salicylate exhibits a pronounced violet fluorescence which is still perceptible in a 1 : 25,000 solution and is a maximum in a 1 : 10 solution. The dominant wave-length of the fluorescence is determined by direct comparison with the spectrum from an incandescence lamp, and the relative intensity estimated by comparing a number of compounds, arranged side by side in pastille form, taking the intensity of the fluorescence of sodium salicylate as 20. The fluorescence induced as above in pyrocatechol, quinol, derivatives of benzoic and hydroxybenzoic acids, and other compounds (e.g., coumarin, "saccharin," sulphanilic acid, novocaine, etc.) is described. W. T. K. B.

**Detection of Ethyl Phthalate.** H. WEWERS (*Pharm. Ztg.*, 1924, 69, 346).—In a test proposed by the German Customs for the detection of ethyl phthalate in brandy, the dilute sample is extracted with light petroleum, the extract heated with sulphuric acid, and treated with a small quantity of pyrogallol; a violet-red coloration indicates the presence of ethyl phthalate. The author finds that this test is untrustworthy, since the coloration is obtained with the reagents alone. W. P. S.

**Detection of Ethyl Phthalate in Alcohol and Alcoholic Preparations.** F. UTZ (*Pharm. Zentralk.*, 1924, 65, 201—206).—For the detection of ethyl phthalate in denatured alcohol, or in tinctures and extracts prepared with the same, a mixture of 1 c.c. of the alcohol and 1 c.c. of concentrated sulphuric acid is heated to fuming; the red solution is cooled, a small quantity of resorcinol is added, and the mixture again heated until the colour changes to brownish-red. After cooling, excess of ammonia is added and a small quantity of the mixture is poured into a large volume of water. If the alcohol contained ethyl phthalate an intense yellowish-green fluorescence is obtained. In the case of tinctures etc., a preliminary treatment with lead acetate is necessary followed by extraction with light petroleum. W. P. S.

**Osmium Tetroxide as a Reagent for the Gold-beater's Skin Test for Tannins.** P. H. PRICE (*Analyst*, 1924, 49, 336).—The reagent proposed by Mitchell (this vol., ii, 356) is less delicate than the ferrous salts employed by the author (this vol., ii, 209). S. I. L.

**Nelson's Method of Determining Ascaridole.** T. KARIYONE and Y. KIMURA (*J. Pharm. Soc. Japan*, 1924, No. 504, 86—89).—Nelson's method (*J. Amer. Pharm. Assoc.*, 1921, 11, 836) for deter-

mining ascaridole in chenopodium oil is improved by the use of 70 wt.-% acetic acid instead of 60 vol.-% acid. The error is within about 5%.

K. K.

**Reactivity of Iodine towards Fats. II. Behaviour of Aqueous Iodine Solutions.** B. M. MARGOSCHES and W. HINNER (*Z. angew. Chem.*, 1924, **37**, 202—205; cf. this vol., i, 487).—Solutions of iodine in aqueous potassium iodide react with fats, in the absence of a solvent for the latter, in a manner similar to that previously observed with alcoholic solutions (cf. *Z. deuts. Oel-u. Fettind.*, 1924, **44**, 97), i.e., the iodine used approximates to the Hübl iodine value. Increasing the concentration of the potassium iodide considerably lowers the quantity of iodine absorbed by the fat. In the presence of a fat solvent (e.g., carbon tetrachloride), only a fraction of the iodine theoretically required is actually used. The ratio of the concentration of potassium iodide to iodine influences the iodine absorption in the same way as before, but even more strongly. This is explained by the observed fact that increasing the concentration of potassium iodide lessens the amount of iodine dissolving in the carbon tetrachloride, until, when the ratio of potassium iodide to iodine is 18 to 1, practically all the iodine is retained in the aqueous solution. The experiments without a fat solvent were accompanied by considerable acid formation, which was not observed in the second series of experiments. W. T. K. B.

**Determination of Urea in Blood.** C. PAGEL (*Bull. Soc. Chim. biol.*, 1924, **6**, 190).—Urea determinations carried out on volumes of blood consecutively collected in one operation in a series of different vessels do not give concordant results.

J. P.

**Determination of Dulcin [*p*-Phenetylcarbamide] by means of Xanthydrol.** G. REIF (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 238—248).—*p*-Phenetyl-xanthylcarbamide, fine needles, m. p. 246°, is obtained by treating dulcin dissolved in 50 vol.-% acetic acid with methyl-alcoholic xanthydrol at ordinary temperatures. The majority of substances usually present in foodstuffs are without any disturbing effect on this reaction. Substances such as carbamides, amides, and allantoin which form insoluble compounds with xanthydrol, are removed during the process of determining dulcin in foodstuffs which is given in detail and includes a purification with neutral lead acetate, treatment with sodium hydroxide, and extraction of the dulcin with ethyl acetate. "Saccharin" also forms an insoluble compound with xanthydrol, but not in quantitative yield under the conditions described. It must therefore be removed by the extraction of the alkaline solution with ethyl acetate, in which the saccharin compound is insoluble.

H. C. R.

**Determination of the Tyrosine Content of Proteins. II.** O. FÜRTH (*Biochem. Z.*, 1924, **146**, 259—274).—The diazo-reaction (Lautenschläger, A., 1918, ii, 466), the addition of bromine (cf. Fürth and Fleischmann, A., 1922, ii, 406) the colour reactions with

phosphomolybdic acid (Folin and Looney, A., 1922, ii, 539) and with Millon's reagent, and the gravimetric method do not yield trustworthy indications of the tyrosine content of proteins, although satisfactory results are obtained with pure tyrosine solutions. These methods serve, however, to prove that gelatin contains no tyrosine, whilst 10—11% of the amino-acid is present in silk-fibroin. J. P.

**Analysis of Proteins. III. Determination of Histidine and Tyrosine by Bromination.** R. H. A. PLIMMER and H. PHILLIPS (*Biochem. J.*, 1924, **18**, 312—321).—Histidine can be determined in the phosphotungstic acid precipitate of the hexone bases by bromination with bromate and bromide since arginine and lysine do not take up bromine and the cystine content of this fraction which also reacts with bromine is usually not very significant. The presence of large amounts of cystine in protein may, however, cause erroneous results. The products of decomposition of tryptophan also absorb bromine but they can be removed from the hydrolysed protein in the humin by precipitation with lime.

S. S. Z.

**Determination of Tryptophan in Proteins.** O. FÜRTH and Z. DISCHE (*Biochem. Z.*, 1924, **146**, 275—296).—The hydrolysis of a protein by trypsin or by the long-continued action of alkali, but not by pepsin or by alkali acting for a short period, leads to a diminution in the Voisenet colour reaction for tryptophan (Fürth and Nobel, A., 1920, i, 74; Fürth and Lieben, *ibid.*, ii, 71). This is not due to destruction of the tryptophan, but is explained by the fact that the intensity of the colour reaction in a solution of free tryptophan is dependent on the concentration of hydrochloric acid used, whilst in an unhydrolysed protein it is independent of the acid concentration. This error in determining tryptophan may be avoided by using as standard a pure protein of known tryptophan content. This method is preferred to that of Folin and Looney (A., 1922, ii, 539).

J. P.

**Error due to Impure Picric Acid in Creatinine Determinations.** C. NEWCOMB (*Biochem. J.*, 1924, **18**, 291—293).—A correction is made for the impurity in picric acid, which produces a red colour with alkali, by reading two solutions of known creatinine concentration against one another, utilising the same picric acid in both cases.

S. S. Z.

**Analysis of Proteins. IV. Some Analyses of Gelatin.** R. H. A. PLIMMER and T. SHIMAMURA (*Biochem. J.*, 1924, **18**, 322—328).—Erratic results have been obtained in analysing gelatin by Van Slyke's method. Known quantities of histidine added to hydrolysed gelatin have not been accurately determined. The colorimetric method of determining histidine has also not given trustworthy results. This is supposed to be connected with the phosphotungstic precipitation. Tyrosine can be determined by the colorimetric method in solutions of hydrolysed proteins either after removing humin, or in the monoamino-fraction. The results are lower than by the direct method.

S. S. Z.



## General and Physical Chemistry.

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**Atomism in Modern Physics.** R. A. MILLIKAN (*J. Chem. Soc.*, 1924, **125**, 1405—1417).—Faraday Lecture, delivered before the Chemical Society on June 12th, 1924.

**Extension to Line Spectra of a Property already Recognised for Band Spectra.** DESLANDRES (*Compt. rend.*, 1924, **179**, 5—11).—The conclusion that in band spectra the frequency of the head of the most intense band is approximately a whole number multiple of a fundamental frequency, 1062.5 (cf. A., 1919, ii, 486; 1920, ii, 69), is extended, and shown to apply to the most intense lines in the line spectra of various elements. The intense  $D_1$  and  $D_2$  lines of sodium, and the  $D_3$  helium line have frequencies which differ very little from a whole number multiple (16) of the fundamental frequency, and, for the 54 examples of line spectra given, the mean deviation from the rule is only 42 Å. In the case of hydrogen, only the principal line in the infra red (18756.17 Å., Paschen's series) shows agreement. The fundamental frequency probably varies slightly with the atomic number of the element, or is constant only for elements in the same period of the natural classification. When an electron from the outer shell is displaced and radiation is emitted, the nucleus and inner ring of electrons are also excited and emit certain characteristic radiations, multiples of the fundamental frequency, which are the most intense lines of the spectra. J. W. B.

**Theory of Helium Spectrum.** W. HEISENBERG (*Z. Physik*, 1924, **25**, 175—176).—A criticism of Wisniewski's model of the helium atom (this vol., ii, 361), which was designed to give the terms of the neutral helium spectrum. It is stated that Wisniewski has only partly allowed for the mutual effect of the two electrons in the atom. S. B.

**Interferometer Measurements of Longer Waves in the Iron Arc Spectrum.** W. F. MEGGERS and C. C. KIESS (*U.S. Bur. Standards, Sci. Paper* 479; 1924, **19**, 273—280).—New secondary wave-length standards have been established in the iron spectrum between 5534 Å. and 8824 Å. The previous measurements in this region are also tabulated. A diagram is given of the dispersion of the phase change at reflection in interferometer films of silver and copper. The dispersion curves of the two metals are very different. S. B.

**New Spectra of the Neutral Lithium Atom.** M. MORAND (*Compt. rend.*, 1924, **178**, 1897—1899; cf. this vol., ii, 509).—A new group of spectral series, attributed to neutral lithium, has been found in the light emitted by lithium positive rays. The lines are very weak. 3713 is given as the first member of the

principal series, 4814, 4053, and 3756 as the first members of the sharp series, and 5488, 4244, 3841, and 3653 as the first lines of the diffuse series. These wave-lengths correspond with an ionising potential of 7.1 volts (normal value for lithium, 5.36 volts). The author suggests the existence of two forms of ionised lithium, the neutralisation of each producing a different spectrum. An analogy is drawn with the two spectra of neutral helium. S. B.

**Series Spectra in Oxygen in the Region 900—1400 Å.** J. J. HOPFIELD (*Astrophys. J.*, 1924, 59, 114—124; cf. A., 1923, ii, 708; this vol., ii, 2).—New series of triplets, of constant frequency difference, have been observed in the extreme ultra-violet; a wide space separates the longest wave-length of the new series from the shortest possible wave-length of any previously observed for oxygen, and no oxygen lines of the arc type appear in this gap. If, as is supposed, the new triple level  $OP_{123}$  is the valency level, the existence of three forms of atomic oxygen, two being metastable, is suggested. The ionising potential of the stable form is then calculated to be 13.56 volts, and the resonance potential 9.106 volts.

A. A. E.

**Spectrum of Fluorine.** H. G. GALE and G. S. MONK (*Astrophys. J.*, 1924, 59, 125—132; cf. A., 1923, ii, 803).—Fluorine was obtained by the electrolysis of fused potassium hydrogen fluoride at 245° in a copper vessel (as cathode), employing a hard graphite rod as anode, and passing the gas through (a) fused sodium fluoride, (b) a trap at -100°. The line spectrum of fluorine, observed from 7800 Å. to 3400 Å. at atmospheric pressure and by the use of vacuum tubes, is recorded, as also are the positions of the heads of ten bands between 7000 Å. and 5100 Å.

A. A. E.

**Vacuum Spark Spectrum of Calcium.** J. A. ANDERSON (*Astrophys. J.*, 1924, 59, 76—96).—The vacuum spark spectrum of calcium (of which the chief impurities were magnesium, strontium, oxygen, and nitrogen) from 2094.5 Å. to 6162.2 Å. is tabulated; 850 lines were observed, many possibly being due to  $Ca^{++}$ . The intensities are given on a logarithmic scale to the base 2.

A. A. E.

**Structure of the Iron Spectrum.** H. GIESELER and W. GROTRIAN (*Z. Physik*, 1924, 25, 165—172).—The recognition of a new multiplet in the iron spectrum has made it possible to calculate the absolute values of the  $d$ -terms of the quintet system. The results indicate an ionisation potential of 8.15 volts for the iron atom. Laporte's assignment of orbits in this spectrum (this vol., ii, 364) is criticised. S. B.

**Production of Radiations between the Ultra-violet and X-Rays.** G. REBOUL and BODIN (*Compt. rend.*, 1924, 179, 37—39; cf. *ibid.*, 1922, 174, 1452).—Radiations of wave-length between that of the ultra-violet and X-rays, and capable of ionising gases, are produced when cells composed of pastilles of metallic compounds, previously powdered, are traversed by an electric

current. The radiation is due to the variation in speed of the electrons in traversing a sharp potential gradient: it depends on the chemical composition and state of aggregation of the material employed, and, for a given compound, the intensity of the radiation depends on the potential employed, small increases in potential sometimes causing enormous changes in the intensity of the radiation. For a given substance, the intensity of the radiation is also increased when the current is increased, but, in general, cells with the smallest resistance, and therefore carrying the largest currents, emit least radiation. The coefficients of absorption of the rays by air vary from 9 to 15  $\text{cm}^{-1}$  and diminish as the distance of the grid electrode from the cell is increased. The radiation is therefore probably complex and can be separated by passage through gaseous layers of varying thicknesses. J. W. B.

**Analysis of Hafnium by X-Ray Spectra.** G. VON HEVESY and V. T. JANTZEN.—(See ii, 571.)

**Band Spectrum of Hydrogen.** H. S. ALLEN (*Proc. Roy. Soc.*, 1924, A, 106, 69—82).—The wave numbers of the lines forming the first and second bands of Fulcher in the secondary spectrum of hydrogen are mathematically discussed. It is argued that the lines of the various series  $S_1$ — $S_7$  in the first band are all derived from the same molecular system. The value of the constants in the quantum formula depends on the value assigned to  $m$  for the various lines. On one assumption, the calculated moment of inertia is in close agreement with Sommerfeld's estimate,  $I = 1.85 \times 10^{-41}$  g.  $\text{cm}^2$ . If, however, the first three be taken as "half-quantum" series, the remainder being whole quantum series, the values for the moment of inertia are found to be practically the same for all series,  $1.76 \times 10^{-41}$  g.  $\text{cm}^2$ . The constants calculated for the second band correspond with smaller values of the moment of inertia, and it is concluded that there is insufficient evidence to support Kiutti's view that the two bands are due to the same molecular system. Certain series associated with Fulcher's bands are discussed and some new series recorded. L. J. H.

**Origin of Iodine Band Spectra.** O. OLDENBERG (*Z. Physik*, 1924, 25, 136—159).—Extensive observations have been made on the fluorescence spectra of iodine. Additions of foreign gases cause changes of intensity distribution in the ultra-violet bands, which are described. The band at 3460 Å. obtained by Gerlach and Gromann (A., 1923, ii, 803) in the electrical excitation spectrum appears in fluorescence only in the presence of foreign gases. It is not continuous, but can be resolved into a series of bands. The author concludes that this spectrum is due to the recombination of positive and negative iodine ions, and is not, as has been suggested, the "electron affinity" spectrum. A new continuous spectrum at about 5100 Å. appears only in the fluorescence from mixtures of iodine and nitrogen, and is attributed to an iodine-nitrogen molecule. An attempt to obtain the line series absorption of iodine was unsuccessful. S. B.

**Spectroscopy of Explosions.** P. LAFFITTE (*Compt. rend.*, 1924, **178**, 2176—2178).—In the case of a gaseous explosion ( $\text{CS}_2 + 3\text{O}_2$ ) the light from either the zone of combustion or the explosion wave gave a continuous spectrum and a number of the spectral lines of sodium and calcium due to the glass of the containing vessel. With a solid explosive (dynamite) the spectrum was continuous without any metallic lines, but the lines due to the material of the enclosing walls were very apparent in the spectrum of the detonation wave. G. M. B.

**Absorption of Lithium Vapour.** A. L. NARAYAN and D. GUNNAIYA (*Proc. Roy. Soc.*, 1924, **A**, **106**, 51—54).—The absorption spectrum of lithium was studied at various vapour densities corresponding with temperatures up to  $1200^\circ$ . Channelled absorption spectra were found on both sides of the first line of the principal series and also there is a fine line absorption spectrum on either side of it. The gradual development of the channelled spectrum with increasing density shows that it is as complicated as that of sodium, and each of the bands on greater resolution would probably be found to consist of a large number of fine lines. It is possible that the complexity of these spectra for the alkali metals increases on passing to those of low atomic weight. Among the bands reported in the red are those at 7281, 7080.4, 6948, 6777.1—6702.0 (lithium red line absorption region), 6645, and many others up to 6186, and in the blue-green 5137.0, 5045, 4952, and others up to 4618.3. L. J. H.

**Tautomerism of Ethyl Acetoacetate and Acetylacetone. Absorption Spectra of These and Related Compounds.** P. GROSSMANN.—(See i, 834.)

**Studies in Chemical Reactivity. II. The Anthracene  $\rightleftharpoons$  Dianthracene Reactions, Photochemical and Thermal.** H. A. TAYLOR and W. C. McC. LEWIS (*J. Amer. Chem. Soc.*, 1924, **46**, 1606—1614).—Solutions of anthracene in phenetole show two narrow absorption bands at 4750 and 4450 Å., which are within the region of fluorescence. The corresponding energy change is 61,300 cal. per mol. of the fluorescing substance, and it is concluded that the fluorescence in the anthracene-dianthracene system is due to the return of an activated molecule of anthracene to the normal state, and is not due to the dianthracene molecule. Anthracene in solution in phenetole shows only one absorption band in the infra-red, viz., at  $1.8\ \mu$ , but, since polymerisation does not occur as a thermal phenomenon in the dark, it is concluded that the bands in the visible are the photochemically effective ones. The photopolymerisation is regarded as consisting in the activation of a single molecule of anthracene which then reacts with an unactivated molecule to form the polymer. Thermal data for the depolymerisation of dianthracene indicate that the critical increment of the dianthracene molecule is 40,000 cal., and that the dianthracene molecule should absorb at 7070 Å. Such absorption has not yet been observed, but it has been possible to bring about the photo-

depolymerisation of dianthracene by radiation of this wave-length, a very much smaller effect being produced by radiation of 6000 and 8000 Å. Dianthracene shows no absorption in the region 4750—4450 Å., or in the infra-red region 0.8  $\mu$  to 3.0  $\mu$ .

W. H.-R.

**Purification of Organic Solvents: Alcohol, Ether, and Hexane.** A. CASTILLE and V. HENRI (*Bull. Soc. Chim. biol.*, 1924, 6, 299).—Precise details are given of methods by which these solvents can be obtained optically pure as tested by a study of the ultra-violet absorption spectra. Hexane is considered to be the best of all organic solvents. [Cf. *B.*, 1924, 576.] C. T. G.

**K and L Absorption and Emission Spectra of Tungsten.** C. B. CROFUTT (*Physical Rev.*, 1924, 24, 9—15).—Careful measurements of six lines and comparison of the others therewith give the following values for the absorption wave-lengths of tungsten:— $LA_1$ , 1.2122 Å.;  $LA_2$ , 1.0716 Å.;  $LA_3$ , 1.0217 Å.; in the *K* series, comparison with four lines gave  $KA$  0.17802 Å. Four new emission lines were observed in the *L* series:— $\beta_{15}$  1.2432 Å.;  $\beta_{16}$  1.2166;  $\gamma_{12}$  1.0748;  $n$  1.0699. Two of the *L* lines, and all the *K* lines, agree with the selection principle. Four lines in the *L* series are not in agreement, but quantitatively correspond with transitions between energy levels. Also there are two lines in this series not in agreement with the accepted energy levels. A. A. E.

**X-Ray Absorption Spectra.** D. COSTER (*Z. Physik*, 1924, 25, 83—98).—The fine structure of the *K* series of titanium, vanadium, chromium, and manganese, and of the *L* series of tin, antimony, tellurium, and iodine has been examined in absorption. Solid compounds of the elements were used as the absorbing material. It was found that the position of satellites on both sides of the main absorption lines depended on the state of chemical combination of the atom. An absorption line on the long wave-length side of the absorption-edge was met with only when the element was in one of the higher states of oxidation. The authors suggest in explanation that changes in the outer, or valency, rings of the atom can affect the energy of the inner electrons, responsible for *X*-ray spectra.

S. B.

**Röntgenographic-Chemical Investigations.** H. M. SIEGBAHN (*Z. physikal. Chem.*, 1924, 109, 431—434).—Polemical against Stintzing (cf. this vol., ii, 83, 216). It is maintained that the difficulties of which Stintzing complains are due mainly to the use of insufficiently high vacua.

L. J. H.

**Compton Effect.** M. DE BROGLIE and A. DAUVILLIER (*Compt. rend.*, 1924, 179, 11—14).—A continuation of previous work (*ibid.*, 1924, 178, 908, 2076). When a radiator of fused silica is used it was found that the intensities of the two diffuse components for a quartz crystal (cut parallel to its optical axis) were almost identical, but that the Compton effect is more intense than with an aluminium radiator. For rock salt, the Compton effect is very feeble. The

"tertiary radiation" obtained by Clark and Duane (this vol., ii, 368, 369) was particularly sought for, using the  $K$ -radiation of silver, and a calcium radiator, but no radiation, linear or diffuse, appeared in the region calculated for this tertiary radiation. That observed by Clark and Duane, using the  $K$ -radiation of molybdenum and radiators of carbon, oxygen, aluminium, sulphur, sodium, and chlorine is quite different from the effects obtained using the  $K$ -radiation of silver and radiators of beryllium, boron, carbon, oxygen, aluminium, silicon, sodium, and chlorine, when only the Compton effect without any "tertiary radiation" is observed. Clark and Duane's contention that the shift of the maximum of the  $K$ -rays (the Compton effect) is due to filtration is not supported by the authors' results.

J. W. B.

**Absorption and Scattering of  $\gamma$ -Rays.** N. AHMAD and E. C. STONER (*Proc. Roy. Soc.*, 1924, A, 106, 8—19).—The results of previous work (this vol., ii, 440) on the absorption of penetrating  $\gamma$ -rays from radium- $B$  and - $C$  by numerous elements are discussed mathematically with special reference to apparent absorption due to scattering. It is found that the total absorption may be represented by  $0.29 \sigma_0 Z + 2.29 \times 10^{-2} \lambda^3 Z^4$ , where  $\sigma_0$  is the scattering per electron calculated on classical theory,  $Z$  is the atomic number, and  $\lambda$  is the mean effective wave-length, taken as  $0.019 \text{ \AA.}$  as an upper limit. The scattering per electron is approximately constant and between  $20^\circ$  and  $80^\circ$  is equal to  $0.14\sigma_0$ . It is therefore independent of the position and binding of the electron. This supports the view that the first term in the above expression corresponds with scattering absorption and the second with true absorption. The results are in qualitative agreement with Compton's distribution formula (A., 1923, ii, 280), but this leads to lower values for the total scattering absorption and to much lower values for the relative scattering than those observed.

L. J. H.

**Secondary Radiation from  $\gamma$ -Rays.** D. SKOBELZYN (*Z. Physik*, 1924, 24, 393—399).—The author has observed that the passage of  $\gamma$ -rays through gases in a Wilson cloud chamber gives rise to a number of electrons with velocities corresponding with paths of about 1 cm. These velocities are much less than those which electrons would attain by the absorption of a complete quantum of  $\gamma$ -radiation. The directions of motion of the electrons do not, in general, coincide with the path of the exciting  $\gamma$ -rays. The observation is in favour of the Debye-Compton theory of scattering; on the basis of this, it can be explained as a recoil effect, the scattered radiation not being in the form of a spherical wave.

S. B.

**Isotropic Increase of the Index of Refraction of Liquids in an Electric Field.** PAUTHENIER (*Compt. rend.*, 1924, 178, 1899—1902).—Benzene and carbon tetrachloride have been examined for changes of refractive index in electric fields of about 50,000 volts per cm. An increase in refractive index was observed, independent of the birefringence simultaneously produced. The

order of the effect was that predicted by a formula of Helmholtz for electrostriction. The changes were observed by an interferometer. S. B.

**Spectrophotometric Definition of the Colour of Fluorescence.** H. GEORGE and E. BAYLE (*Compt. rend.*, 1924, 178, 1895—1897).—A method is described for the quantitative comparison of the fluorescence of a series of substances. The material under examination is illuminated by ultra-violet light filtered through nickel oxide, and the distribution of intensity with wavelength in the fluorescent light is compared with the distribution in sunlight by a spectrophotometer. S. B.

**Polarisation of Fluorescent Light from Dye Solutions.** F. WEIGERT and G. KÄPPLER (*Z. Physik*, 1924, 25, 99—117).—The degree of polarisation of the fluorescence from aqueous solutions of fluorescein increases from nearly zero at extreme dilution to about 19% for 3% solutions. With glycerin as a solvent, however, the phenomena are reversed; the light from dilute solutions is 30% polarised, but that from more concentrated solutions is almost unpolarised. The viscosity of the solutions has only a secondary influence on the polarisation. S. B.

**Phosphorescence of American Iceland Spar after Radium Radiation.** S. C. LIND.—(See ii, 621.)

**Absorption Edges of Phosphors.** F. SCHMIDT (*Ann. Physik*, 1924, 74, 362).—A study of the long-duration phosphorescence of CaS-Cu and CaS-Mn phosphors. A variation of previously used experimental methods is employed in order to increase the accuracy. The phosphor, made by adding small quantities of manganese to a calcium sulphide containing large copper impurity, is spread on a surface and illuminated by the continuous spectrum from an ultra-violet light source. The positions of the absorption edges (*d*-maxima) are measured by a micrometer in terms of the wavelengths of the exciting radiation. By a suitable choice of the phosphor (*e.g.*, Cu-Mn), it is possible to observe the effects of the two metals separately, as the manganese effect is of much shorter duration than that of the copper. After the light is cut off, the first effect observed is due to the yellow band of Mn $\alpha$ , which after a few minutes gives place to the effect of the Cu $\alpha$  green band. In this way, it is possible to obtain the absolute wave-lengths (wave-lengths divided by the square root of the dielectric constant) for both the copper and manganese series without the possibility of errors due to the determinations of the dielectric constants. It is shown that the absolute wave-lengths of the *d*-maxima occur at the same points for Mn $\alpha$  and Cu $\alpha$ , for a range of dielectric constants from 5.45 to 6.80. The positions of the Mn $\alpha$  and Cu $\alpha$  bands which give rise to these maxima are independent of the dielectric constant. A new *d*-maximum is observed at 1740 Å. This had not been previously observed on account of the higher values of the dielectric constants used by other workers. With such high values the appearance of such a line would have been inconsistent with Stokes'

law. The  $d$ -maxima for the  $\text{Cu}\beta$  and  $\gamma$  bands are also determined. A summary of all the results so far obtained for such phosphors is given, and it is shown that the bands  $\text{Cu}\alpha$ ,  $\text{Mn}\alpha$ ,  $\text{Zn}\alpha$ ,  $\text{Pb}\beta$ ,  $\text{Ag}\beta$ ,  $\text{Bi}\beta$  give rise to a series consistent with Lenard's law,  $\nu_{\text{abs}} = K/n^2$ , where  $\nu$  is the frequency,  $K$  a constant, and  $n$  an integer. The observed maxima correspond with values of  $n$  from 8 to 12. A new notation is suggested. G. S.

**Photo-electric Effect and Temperature [Phosphorescence].** M. CURIE (*Compt. rend.*, 1924, **179**, 105—108).—In continuation of earlier work (cf. this vol., ii, 514), the effect of temperature, at atmospheric pressure, on the photo-electric effect of various substances containing impurities which produce phosphorescence, is studied. The conclusions previously drawn are confirmed; with calcium sulphide containing bismuth as an impurity, there is a rapid decrease in the photo-electric effect as the temperature is increased from  $18^\circ$  to  $100^\circ$ , due, probably, to loss of moisture and the consequent decrease in conductivity of the sulphide. At  $200^\circ$ , the photo-electric effect practically disappears. At higher temperatures, up to  $400^\circ$ , the photo-electric effect reappears to a smaller degree, probably due to the increase in conductivity of the sulphide. The surface of the sulphide is altered superficially on heating or on prolonged exposure to air, the photo-electric effect being then much smaller. Fluorescence decreases rapidly with increase of temperature, but disappears while there is still a pronounced photo-electric effect, thus confirming the absence of relation between these two phenomena. The photo-electric effect of white fluorspar (Durham) increases rapidly to a maximum at  $100^\circ$ . Sulphides of zinc and cadmium containing copper as an impurity show no photo-electric effect in air. J. W. B.

**Spectra of Cathodoluminescence of Zinc Sulphides, Willemites, and Kunzites.** T. TANAKA.—(See ii, 553.)

**Luminous Spectra of Solid Nitrogen and their Application to the Aurora Borealis and the Diffuse Light of the Evening Sky.** L. VEGARD (*Compt. rend.*, 1924, **179**, 35—37).—A further record (cf. this vol., ii, 436) of spectra obtained by bombarding solid nitrogen with cathode rays. Using a spectrometer with greater dispersion, it is shown that the band  $N_1$  possesses 3 maxima (1 intense and 2 feeble) whilst the band  $N_2$  appears as a single diffuse line (5229.4). When a film of solid argon containing traces of nitrogen is employed, the bands  $N_1$  and  $N_2$  are very intense. The wavelength of the principal maximum in  $N_1$  varies between 5555 and 5604 Å. for different concentrations of nitrogen. The bands diminish in size, independently of temperature, as the particles of nitrogen become smaller. The line of the aurora borealis (5577) is the limiting form of the band  $N_1$  when the crystals of nitrogen in space are reduced to molecular dimensions. The spectrum of the aurora borealis is probably produced mainly by cathode rays, since solid nitrogen bombarded with slow cathode rays yields bands in the ultra-violet and red corresponding with those of the aurora borealis,



whilst penetrating cathode rays and canal rays both produce similar effects, viz., intense  $N_1$  and  $N_2$  bands, and a series of diffuse bands in the blue and violet, quite different from the observed spectrum of the aurora borealis. These diffuse bands probably constitute a stage in the evolution of the bands observed by Rayleigh in diffuse nocturnal light.

J. W. B.

**Luminous Discharge in Chlorine. Electron Affinity of Halogen Molecules.** W. A. NOYES, jun. (*J. Amer. Chem. Soc.*, 1924, **46**, 1598—1606).—The luminous discharge in chlorine at low temperatures usually disappears at a potential which is some multiple of 8.2 volts plus a small correction. The potentials necessary to maintain luminosity in iodine, bromine, and chlorine are of the same order, and the point at 8.2 volts in the case of chlorine may correspond with the formation of a molecular ion. Other points were found at some multiple of the ionisation potential plus 4.0 volts, and it is suggested that this may correspond with a resonance potential of chlorine. Halogen molecules may take up electrons according to the reaction  $X_2 + 2e = 2X^-$ . The free energy change of this reaction is large and negative, which indicates that the free electrons must attain ionising speed in a shorter distance than the mean free path.

W. H.-R.

**Different Types of Ions in Hydrogen.** H. D. SMYTH (*Nature*, 1924, **114**, 124).—A previous conclusion, that the primary product of ionisation of hydrogen at about 17 volts is molecular ions, is confirmed; however, as the pressure is increased, atomic ions do not necessarily become dominant. Peaks have been observed corresponding with apparent values of  $m/e = \frac{1}{2}$  and  $\frac{1}{3}$ .

A. A. E.

**Dissociation of Hydrogen and Nitrogen by Excited Mercury Atoms.** O. S. DUFFENDACK and K. T. COMPTON (*Physical Rev.*, 1924, **23**, 583—592).—The dissociation of hydrogen in low-voltage arcs, as measured by pressure changes resulting from reduction of copper oxide, was not observed below a minimum voltage (13), but above 16 volts the rate was rapid, decreasing to 65 volts. Dissociation from contact with the hot filament was always superimposed on the electrical dissociation. With mercury arcs, the dissociation was several times more rapid, the hydrogen molecules presumably being activated by excited mercury atoms in the  $2p_2$  state. The effect was observed, but not so markedly, with nitrogen, owing possibly to the small number of mercury atoms with electrons displaced to the  $2P$  orbit. Above 70 volts, a very active form of nitrogen appears, the conductivity of the arc increasing enormously, and a "flare" is produced.

A. A. E.

**New Photo-electric and Ionisation Effect.** U. A. OSCHWALD and A. G. FARROW (*Proc. Physical Soc.*, 1924, **36**, 214—252).—The initial voltage necessary to light a neon lamp can be considerably lowered by exposure to light, X-rays, or the influence of radioactive substances. The effect varies greatly among different lamps and sometimes is non-existent. In one case, the necessary initial voltage in the dark was about 180, and this was continually

lowered, at first rapidly and then more slowly, with increasing intensity of illumination, until at 1 foot-candle the voltage was almost independent of the intensity of the light (about 165 v.). On allowing a narrow beam to impinge on different parts of the lamp, it was found that the electrodes were equally sensitive, but if these were missed and the beam passed through the gas only little effect was observed. With dispersed light, the orange region of the spectrum was found most effective. Even very soft X-rays were effective, as was the presence of any radioactive material. In the discussion, it was suggested that the phenomena were probably associated with an almost invisible film (not understood) which forms on the electrodes during one stage in the process of manufacture, if hydrogen or water-vapour be present in the gas. L. J. H.

**New Photo-electric Cell.** J. TYKOCINSKI-TYKOCINER and J. KUNZ (*Science*, 1924, **59**, 320—321).—The cell consists of a glass tube with terminal bulbs; inside each bulb is a hemispherical deposit of potassium and a platinum electrode connected with the sensitive layer. When the bulb with its electrode connected to the negative pole of a battery is illuminated, it shows the usual photo-electric effect; if the connecting tube (containing no visible deposit) is also illuminated, an increased deflection of the galvanometer is observed, a linear relation existing between the extent of illumination of the tube and the current produced. A. A. E.

**Ionisation Gauge. II. Relation between Ionisation Current at Constant Pressure and Number of Electrons per Molecule.** C. G. FOUND and S. DUSHMAN (*Physical Rev.*, 1924, **23**, 734—743).—The ionisation gauge previously described and calibrated with argon (*ibid.*, 1921, **17**, 7) has been calibrated with mercury and iodine, using the published values for vapour pressures. For hydrogen, helium, neon, nitrogen, and carbon monoxide readings were compared with those of a McLeod gauge. Except with hydrogen and helium, where the value is approximately half as great, all the above gases yield nearly constant values for  $K \times N$  (where  $K$  is a constant in the expression: pressure =  $K \times$  positive ionisation, and  $N$  is the total number of electrons per mol.). With the exception of the hydrogen anomaly, these results are analogous to those obtained with another method by Kleeman (*A.*, 1907, ii, 423). The vapour pressure of naphthalene between  $-11^\circ$  and  $18^\circ$  is recorded. A. A. E.

**Piezo-electricity and Molecular Asymmetry.** R. LUCAS (*Compt. rend.*, 1924, **178**, 1890—1892).—The author concludes, from an examination of many camphor derivatives, alkaloids, and complex salts, that all optically active crystals also have piezo-electric properties. It is suggested that piezo-electricity may be of use in determining the symmetry of crystals which do not show hemihedral faces, and to which the etching method is inapplicable. S. B.

**Paramagnetism Independent of Temperature.** P. WEISS and (Mlle.) P. COLLET (*Compt. rend.*, 1924, **178**, 2146—2149).—The paramagnetism of potassium dichromate in solution is constant

between  $14^{\circ}$  and  $50^{\circ}$ , the atomic permeability for chromium calculated therefrom being  $63.3 \times 10^{-6}$ . This and previously recorded values for the elements potassium, calcium, titanium, vanadium, manganese, and iron, when plotted against the atomic numbers, fall on a curve which is very similar to that of Cabrera (A., 1923, ii, 123) relating the moments of ions (as deduced from the variable paramagnetism) with the number of electrons in the ions (atomic number-valency). The parallelism between these two curves is accounted for by the hypothesis that substances of constant paramagnetism have the same atomic moments as ions with the same number of electrons, and that the permeabilities are proportional to the moments.

Atoms of substances showing this constant paramagnetism possess an internal magnetic field of the order  $3 \times 10^8$  gauss.

G. M. B.

**Magnetostriction of a Magnetite Crystal.** C. W. HEAPS (*Physical Rev.*, 1924, 24, 60—67).—The magnetostriction of an octagonal magnetite crystal has been measured along three axes in fields up to 5000 gauss. To explain the results, a model of the magnetic element in magnetite is suggested, similar to Ewing's recent model. The experiments favour the view that the rotating magnetic element is a group of non-parallel electron orbits inside the atom.

W. E. G.

**Radioactivity of some Indian Minerals.** N. A. YAJNIK and S. J. KOHLI.—(See ii, 620.)

**Anomalous Emission of  $\alpha$ -Particles from Polonium.** R. W. LAWSON (*Nature*, 1924, 114, 121—122).—A criticism of the conclusions of Kutzner (this vol., ii, 226); additional evidence of the importance of the phenomenon of aggregate recoil is adduced, and it is shown that effects identical with those observed by Kutzner would be expected on this basis.

A. A. E.

**Number of  $\alpha$ -Particles Emitted by Radium.** V. F. HESS and R. W. LAWSON (*Z. Physik*, 1924, 24, 402—410).—The authors state that the accuracy of Geiger and Werner's observations on the  $\alpha$ -particle emission of radium (this vol., ii, 227) is misleading, owing to the absorption of emanation by platinum used in the apparatus, and for other reasons. They consider their earlier estimate (*Wien. Ber.*, 1918, 127, 405) of  $3.72 \times 10^{10}$   $\alpha$ -particles per gram of radium per second to be nearer the true value.

S. B.

**Emanation Method for Radium.** F. E. E. GERMANN (*Science*, 1924, 59, 340—341).—A simple device for unsealing the flask when connected with the gas burette is described.

A. A. E.

**Evolution and Disintegration of Matter.** F. W. CLARKE (*U.S. Geological Survey, Prof. Paper*, 132D, 1924, 51—86).—The possible course of the evolution and disintegration of the elements is discussed, and a *résumé* is given of physical and astrophysical knowledge bearing on this subject.

S. B.

**Structure of Silicon.** H. COLLINS (*Chem. News*, 1924, **129**, 47—49).—Speculative. A. A. E.

**Structure of Calcium.** H. COLLINS (*Chem. News*, 1924, **129**, 95—97).—Speculative. A. A. E.

**Growth of Crystals.** H. TERTSCH (*Z. anorg. Chem.*, 1924, **136**, 203—215).—Niggli's conclusions regarding the method of development of crystal faces and the relative frequency with which they occur are criticised (cf. A., 1920, ii, 295). The question is discussed with relation to sodium chloride and zinc blende, and it is shown that the probability of the formation of any definite crystal face does not depend wholly on the thickness of the partly crystalline layer as postulated by Niggli, but is also influenced by the free atomic valencies of the surface layer and by the number of ions on the surface of the crystal which are acting in the same direction.

A. R. P.

**Baeyer's "Strain-theory" and the Structure of Diamond.** E. MOHR (*J. pr. Chem.*, 1924, [ii], **107**, 391—392).—The author finds that in some of his conclusions (A., 1919, ii, 229) he was anticipated by Nold (*Z. Krist. Min.*, 1910, **48**, 321).

W. A. S.

**Crystal Structure of Argon.** F. SIMON and C. VON SIMSON (*Z. Physik*, 1924, **25**, 160—164).—Solid argon has the close-packed, face-centred cubic lattice structure, and the Bragg "atomic radius" is 1.92 Å. The density of the solid is  $1.65 \pm 0.02$ . Since the mean atomic radius of  $K^+$  and  $Cl^-$ , with the same electronic arrangement as iodine, is 1.56 Å., it is concluded that the atomic radius is dependent on the forces between the atoms. Combining these results with previous data, the authors have calculated that the force of attraction between atoms of argon falls off with the 9th power, and the repulsive force with the 15th power, of the distance separating them.

S. B.

**Arrangement of Atoms in Calomel Crystals.** C. MAUGUIN (*Compt. rend.*, 1924, **178**, 1913—1916).—The interatomic distances in calomel crystals have been studied by the X-ray method. The author concludes that a natural grouping,  $ClHgHgCl$ , is indicated by his results, in support of the chemical evidence for the double molecule.

S. B.

**Structure of Crystalline Mercury.** N. ALSÉN and G. AMINOFF.—(See ii, 554.)

**Crystal Structure of White Tin.** A. E. VAN ARKEL.—(See ii, 558.)

**Crystal Structure of Uranyl Nitrate Hexahydrate.** L. PAULING and R. D. DICKINSON.—(See ii, 619.)

**Structure of Mixed Crystals.** A. E. VAN ARKEL.—(See ii, 618.)

**X-Ray Spectrum of Cellulose.** H. W. GONNELL (*Z. Physik*, 1924, **25**, 118—120).—It is concluded from the structure of the

individual points in the X-ray diffraction patterns of various samples of cellulose that this substance must contain more than one crystalline constituent. S. B.

**Fluidity of Crystallised Salts.** A. BENRATH and W. STANDOP.—(See ii, 607.)

**Absolute Entropy and Chemical Constants of Polyatomic Gases.** J. K. SYRKIN (*Z. Physik*, 1924, **24**, 355—365).—General expressions are obtained for the absolute entropy of gases, and for their chemical constants. The mass and dimensions of the molecule are factors in the expressions. Moderately good agreement is obtained with the experimental values for chemical constants. S. B.

**Relationship between Specific Heat,  $C_v$ , of the Internal Energy  $U$  and the Equation of State of Bodies on the Basis of the Second Law of Thermodynamics.** W. JAZYNA (*Z. Physik*, 1924, **25**, 133—134).

**Measurement of the Specific Heats,  $C_v$ , of Gases by the Differential Method. II.** M. TRAUTZ and K. HEBBEL (*Ann. Physik*, 1924, **74**, 285).—The specific heat,  $C_v$ , of hydrogen, nitrogen, and carbon dioxide has been accurately determined by a differential method; two vessels—a measuring flask and a gas flask—are connected by a sensitive manometer. The volume of the measuring flask can be altered by removing oil from it. Heat is supplied to the gas in each vessel by a hot filament; a small cloud of hot gas is formed which slowly makes its way towards the walls of the vessel. Before it reaches the walls, the filament has given up all its heat to the gas. Although the apparatus is designed to measure specific heats over a wide range of temperature, the results are confined to a temperature range of 14—24°. The measurements are made to about 0.001 cal., an accuracy some ten times greater than that of previous determinations. The temperature coefficients of  $C_v$  for air and nitrogen are very small; those for hydrogen and carbon dioxide are greater than the values previously accepted. G. S.

**Specific Heat and Thermal Diffusivity of certain Explosives.** III. A. M. PRENTISS.—(See i, 844.)

**Specific Heats of Trinitrotoluene, "Tetryl," Picric Acid, and their Molecular Complexes.** C. A. TAYLOR and W. H. RINKENBACH.—(See i, 843.)

**Irregularities in the Specific Heats of certain Organic Liquids.** J. W. WILLIAMS and F. DANIELS (*J. Amer. Chem. Soc.*, 1924, **46**, 1569—1577).—The irregularities previously noted by the authors (this vol., ii, 450) in the specific heat-temperature curves of benzene, ethylbenzene, and carbon tetrachloride have been investigated in detail, and are genuine effects not due to experimental errors. They indicate molecular changes in the liquids, for which differential specific heat measurements offer a very delicate

test, as no irregularities are shown by density or vapour-pressure measurements. The curves obtained for benzene and ethylbenzene saturated with water are much more regular than those for the pure substances, indicating that water catalyses the change from one molecular species to another.

W. H.-R.

**Compressibility of Liquids and the Velocity of Sound in Liquids.** D. BUNGETZIANU (*Bul. Soc. Romane Stiin.*, 1922, **25**, 69—125).—The compressibility of, and velocity of sound in water, certain aqueous solutions, and other liquids is determined by a resonance method.

A. A. E.

**[Relation between] Internal Friction (Viscosity) and Free Space [of Liquids].** W. HERZ (*Z. anorg. Chem.*, 1924, **136**, 325—328).—The "free space,"  $\Delta$ , of a liquid is defined as the difference between the molecular volume,  $M$ , of a liquid and the actual volume of its particles, and is given by the equation  $\Delta = M/d - M/d_0$ , where  $d$  and  $d_0$  are the densities at any temperature,  $t^\circ$ , and at absolute zero, respectively. If  $\epsilon$  is the absolute viscosity at  $t^\circ$ , then the product  $\Delta \cdot \epsilon$  decreases with rise of temperature, rapidly at first and then more slowly, and appears to reach a minimum constant value at temperatures approaching the boiling point of the liquid. The values of  $\epsilon$ ,  $d$ ,  $\Delta$ , and  $\Delta \cdot \epsilon$  have been found for the methyl esters of the fatty acids from formic to butyric inclusive, for the paraffins from pentane to octane inclusive, and for methyl, ethyl, and propyl alcohols. In all the series, the change in the value of  $\Delta \cdot \epsilon$  for each member between the same temperatures increases with the molecular weight, i.e., it is greater the farther the comparison temperature is from the critical temperature of the liquid.

A. R. P.

**Freezing Point of Organic Substances. VIII. Melting Points of Esters containing a  $C_5$  Group.** G. LIEVENS (*Bull. Soc. chim. Belg.*, 1924, **33**, 122—131).—The variation of boiling point with pressure, of density and refractive index with temperature have been determined for a series of esters of which either the alcoholic or acidic group contains five carbon atoms. From the available data it appears that esters which are derived from a given acid show in their freezing points a tendency to pass from normal alternation in the lower members to inverse alternation in the higher, whilst the reverse tendency is exhibited when the esters compared are those which contain the same alcohol.

H. J. E.

**Methylal as a Solvent.** A. BOURGOM (*Bull. Soc. chim. Belg.*, 1924, **33**, 101—115).—A list of inorganic salts classified according to their solubility in methylal is given. The solubility curve for mercuric iodide shows a break at  $125^\circ$ , the transition temperature of the red to the yellow form. The critical temperatures of vaporisation for various mixtures of mercuric iodide and methylal have been determined. The densities, refractive indices, freezing and boiling points of homogeneous mixtures of methylal and water and the composition of the conjugate liquids have also been measured. The two liquids are completely miscible above  $160.3^\circ$ , and the

critical composition corresponds with 57.34% of methylal. Certain mixtures rich in water which are homogeneous at the ordinary temperature separate into two layers on heating, the solubility curve reaching a minimum at 82°. It is stated that methylal may advantageously be substituted for ether in the preparation of certain organo-magnesium compounds. H. J. E.

**Fractional Distillation of Small Quantities.** L. CRISMER (*Bull. Soc. chim. Belg.*, 1924, **33**, 255—256).—A claim for priority against Widmer (this vol., ii, 234). J. W. B.

**Osmotic Pressure of Salvarsan and Neosalvarsan Solutions.** J. M. JOHNSON (*U.S. Pub. Health Service, Hyg. Lab. Bull.*, 1924, No. **135**, 33—37).—Variations in the osmotic pressure of salvarsan and neosalvarsan bear no relation to the content of arsenic, but are probably entirely due to variations in the content of inorganic salt. Heating causes very little change in the osmotic pressure of solutions of neosalvarsan, or of solutions of salvarsan after treatment with alkali. CHEMICAL ABSTRACTS.

**Determination of Molecular Weights of Amino-acids in Aqueous Salt Solutions.** P. PFEIFFER and (MISS) O. ÄNGERN (*Z. physiol. Chem.*, 1924, **135**, 16—28; cf. A., 1916, i, 125).—The combination of amino-acids with neutral salts in aqueous solution has been studied by measurement of freezing-point depression. Whereas potassium iodide and sodium and ammonium acetate produce the same depression in salt solutions as in pure water, amino-acids give appreciably smaller depressions, indicating a combination of the amino-acids with the salt molecules or ions. The combination increases in the order *dl*-alanine, sarcosine, glycine, glycylglycine, diglycylglycine. This order is independent of the nature of the salt, but the actual amount of combination varies considerably, being greater for the alkaline-earth metals than for the alkali metals, and increasing in the order chloride, bromide, iodide, thiocyanate, nitrate. The combination of the amino-acids with sodium salts of organic acids is less than with sodium chloride and bears no relation to the ionisation constant of the acid. The combination increases with increasing salt concentration, and for a given salt concentration is proportional to the concentration of the amino-acid. E. M. C.

**Molecular Conductivity of Potassium Iodide in Organic Solvents.** N. A. YAJNIK and B. R. SOBTI (*J. Proc. Asiatic Soc. Bengal*, 1922, **18**, 72—73).—The molecular conductivity of potassium iodide in methyl alcohol, acetone, pyridine, epichlorohydrin, furfuraldehyde, benzaldehyde, and nitrobenzene increases with decrease in concentration. The ionising power of the solvent runs parallel with the dielectric constant; reported viscosity relationships were not observed. CHEMICAL ABSTRACTS.

**Buffer Mechanism for the Calcium-ion Concentration and Determination of Calcium Ion Buffer Values.** I. N. KUGELMASS (*J. Biol. Chem.*, 1924, **60**, 237—256).—The calcium-ion concentration of a solution may be regulated by the use of mixtures of an

acid HA and the soluble salt BA, where HA is an acid such as carbonic or phosphoric acid, which forms an insoluble normal calcium salt and a soluble acid calcium salt. The equation representing the calcium-ion concentration, expressed in the usual logarithmic notation, is  $p_{Ca} = p_K + n \log[BA]^2/[HA]$ , where  $p_K$  is a constant,  $[HA]$  the concentration of the buffer acid,  $[BA]$  that of the buffer salt, and  $n$  is the ratio of the valency of calcium to the basicity of the buffer acid. The author develops this equation mathematically after the method of Van Slyke (A., 1922, i, 893), and obtains an expression for the calcium buffer value of a solution defined by the equation  $\rho = d[BA]/dp_{Ca}$ . This buffer value for the carbonates of normal blood-serum at  $p_H$  7.35 is  $3.5 \times 10^{-3}$  and for the serum phosphates is  $0.5 \times 10^{-3}$ . Since the buffer value for a mixture is the sum of the separate values, it follows that the true buffer value of the carbonates and phosphates in blood-serum is  $4.0 \times 10^{-3}$ .

C. R. H.

**Electrometric Study of the Hydrolysis of Salts.** P. JOB (*Compt. rend.*, 1924, 179, 49—52).—The measurement of hydrogen-ion concentration has been applied to the study of the hydrolysis of salts of weak acids and bases. In the action of hydrochloric acid on 0.001*N*-sodium pyrophosphate solution three stages may be distinguished: (1) the addition of 1 mol. of acid to 1 mol. of salt,  $H^+ + P_2O_7^{4-} \rightarrow HP_2O_7^{3-}$  ( $k = 3 \times 10^{-9}$ ); (2) the reaction  $HP_2O_7^{3-} + H^+ \rightarrow H_2P_2O_7^{2-}$  ( $k = 10^{-6}$ ); (3) when all the pyrophosphate is converted into the disodium salt it behaves as a neutral salt. The curve obtained for borax shows that the ion  $B_4O_7$  only exists in very small quantity in solution, and is transformed into boric acid and the metaborate ion,  $H_2BO_3$ , the observed hydrolysis being that of a mixture of these two. The hydrolysis of ammonium salts and alkali acetates is shown to conform with the ionic theory for solutions from 0.001*N* to 0.03*N*, and for hydrogen-ion concentrations of  $10^{-7}$  to  $10^{-3}$  for acetates and of  $10^{-7}$  to  $3 \times 10^{-12}$  for ammonium salts.

J. W. B.

**Acid-Base Equilibria of Salvosan Solutions.** E. ELVOVE and W. M. CLARK (*U.S. Pub. Health Service, Hyg. Lab. Bull.* 135, 1924, 2—11).—The hydrogen-electrode method is preferred to the indicator method of measuring the  $p_H$  values of salvosan. Large variations of  $p_H$  were found in solutions to which 1.125—2 equivalents of alkali had been added.

CHEMICAL ABSTRACTS.

**Dissolution of Gelatin.** F. FAIRBROTHER (*Biochem. J.*, 1924, 18, 647—650).—Gelatin dissolves on standing in contact with water, dilute acid, or dilute alkali at the ordinary temperature primarily in an unaltered condition. Some hydrolysis probably occurs later. It is suggested that the framework of a gelatin gel consists, not only of isoelectric gelatin, but also of gelatin cations.

S. S. Z.

**Titration Curve of Gelatin.** W. R. ATKIN and G. W. DOUGLAS (*J. Soc. Leather Trades Chem.*, 1924, 8, 359—370).—The  $p_H$  curves obtained when gelatin is titrated with hydrochloric acid and with



sodium hydroxide have been determined. The curve appears to consist of four portions,  $p_H$  1.7—4.7,  $p_H$  4.7—7.7,  $p_H$  7.7,  $p_H$  7.7—12.6, and the authors recognise two sigmoid branches. From the portion of the curve between  $p_H$  4.7 and  $p_H$  7.7 it is inferred that the calculated equivalent weight of gelatin is 3290. The curve from  $p_H$  7.7 to  $p_H$  12.6 corresponds with a combining weight of 2060. The latter branch of the curve is supposed to be due to a keto-enol transformation. The second isoelectric point recorded by Wilson at  $p_H$  7.7 is a point of inflection in the above curve, and appears to represent the commencement of the introduction of alkali into the  $-CO\cdot NH-$  group in which keto-enol transformation has taken place.

D. W.

**Dimensions and Weight of the Molecules of the Serum Proteins.** P. L. DU NOÛY (*Compt. rend.*, 1924, **178**, 1904—1906).—The dimensions of the molecules of the serum proteins have been deduced from the position of minima in the surface tension-concentration curves of protein solutions, combined with assumptions regarding the orientation of the molecules in the surface layers. The length of the albumin molecule is given as  $4.41 \times 10^{-7}$  cm., and the thickness as  $3.25 \times 10^{-7}$  cm. The corresponding molecular weight is 36,600.

S. B.

**Jellies, as Contrasted with Gels and Curds. Soaps in Dry Alcohol.** M. E. LAING and J. W. MCBAIN (*Kolloid-Z.*, 1924, **35**, 19—21).—The authors direct attention to errors that have arisen from the confusion of soap jellies with curds. The term "jelly" should be applied only to completely transparent elastic masses, such as gelatin jelly; flocculent and gelatinous precipitates or crystals should be termed gels. Jellies, as distinguished from gels, can be formed without marked interference with the equilibria in the solution. There is no proof that soap solutions or jellies possess emulsoid character. The speed of the process is not the determining factor in the formation of jellies or crystals. Potassium and sodium soap solutions in dry alcohol crystallise in flakes on cooling; jellies are formed only when sufficient water is present to bring the necessary colloid into solution.

E. M. C.

**Experiments in Support of Tammann's Theory of the Glassy State.** D. BALAREV (*Z. anorg. Chem.*, 1924, **136**, 221—222).—When zinc or cadmium pyrophosphate is heated on a platinum loop in the Bunsen flame until almost all is molten, the bead crystallises completely during cooling provided that a crystalline nucleus is present. A bead that is entirely liquid solidifies to a glassy mass on cooling quickly, but crystallises when slowly cooled, and a glassy bead on reheating always crystallises before it melts. A fused mixture of equal parts of the two pyrophosphates yields a glass on cooling, and this, on reheating slowly, commences to crystallise from the surface inwards; this action ceases on cooling again, showing that a supercooled liquid will crystallise completely in the presence of nuclei only under conditions that ensure a certain definite rate of crystallisation.

A. R. P.

**Electrical Double Layer and its Relation to Ionic Migration.** J. W. McBAIN (*J. Physical Chem.*, 1924, **28**, 706—714).—A modified view of the double layer is proposed in which only a very few, sparsely distributed ions are mobile. This conception is developed and is shown to harmonise with the migration data previously determined for soap sols (cf. T., 1923, **123**, 2417). The new theory invalidates the fundamental assumptions of all previous mathematical treatment. Experimental results should be recorded in the form in which they are observed and not in terms of contact potential. S. K. T.

**Extension of the Application of the Law of Gases to Surface Solutions.** A. MARCELIN (*Compt. rend.*, 1924, **179**, 33—35).—The product of the area occupied by a given quantity of oleic acid on the surface of water and the surface pressure of the film has been found to be constant over the range extending from the saturated surface to that represented by a surface 28 times as large (cf. this vol., ii, 390). The speed of displacement of the edge of the film at each instant is proportional to the surface pressure, and this affords a rapid means of measurement when direct measurements become impossible. J. W. B.

**Adsorption. I. Adsorption and Heterogeneous Chemical Equilibrium.** P. N. PAVLOV (*Kolloid-Z.*, 1924, **35**, 3—11).—The equilibrium states resulting from the interaction of soluble and insoluble salts such as potassium sulphate and barium carbonate are considered in reference to the phenomenon of adsorption. So-called adsorption curves of various types are indicated by the experimental data for the equilibria which have been examined. For reactions yielding a new solid phase of lower solubility product than that of the adsorbent, as in the case of barium carbonate and potassium sulphate, the initial portion of the curve is concave to the axis representing the concentration of the soluble salt. When the new solid phase has a higher solubility product than the adsorbent, as in the case of barium sulphate and potassium carbonate, the curve is of the sigmoid type and is convex in its initial portion. The curve for potassium chromate-lead carbonate exhibits a maximum; the smaller adsorption found in the more concentrated solutions in this case is probably the result of a series of separate reactions. The curve for potassium oxalate-calcium carbonate also shows a maximum adsorption of oxalate, which is actually greater than that equivalent to the total amount of calcium carbonate. It is suggested that this anomaly may be due to the existence of labile double salts. E. M. C.

**Adsorption by Zirconium Oxide Gels. III. Hydrogen Peroxide, Hydrochloric Acid, and Perchloric Acid.** E. WEDEKIND and H. WILKE (*Kolloid-Z.*, 1924, **35**, 23—34; cf. this vol., ii, 238).—Zirconium oxide gel rapidly catalyses the decomposition of hydrogen peroxide, especially in concentrated solutions. The removal of hydrogen peroxide by zirconium oxide gel during very short periods of contact with dilute solutions can be represented

by the usual adsorption equation. After prolonged contact the hydrogen peroxide in solution is almost completely decomposed, but large amounts remain in the substrate. It is suggested that the reaction consists of an initial adsorption followed by a fairly rapid chemical combination to form a complex peroxide. Hydrochloric acid and perchloric acid are rapidly and reversibly adsorbed by zirconium oxide gel. The tendency of the adsorption complexes formed by zirconium oxide gels with acids to be converted into salts does not appear to be determined by the strengths of the acids. The characteristics of solid solution, adsorption, and chemical combination are discussed.

E. M. C.

**Swelling and Viscosity of Japanese Konyaku.** S. DOKAN (*Kolloid-Z.*, 1924, **35**, 11—18).—Konyaku powder is a Japanese foodstuff derived from a tuber similar to the potato. Although a polysaccharide, it differs markedly from agar in its colloidal properties. Salts have little action in dilute solution, but in normal concentration they give rise to increased swelling and peptisation and reduce the viscosity. Bi- and ter-valent cations have the most marked effects, whilst acids have but little influence. Potassium hydroxide is clearly distinguished from other electrolytes in its action, in that the viscosity is diminished very appreciably by this electrolyte even at low concentrations.

E. M. C.

**Production of Liesegang Lines in a Capillary Space.** J. BRODERSEN (*Kolloid-Z.*, 1924, **35**, 21—23).—Sodium chloride from a 2% solution was allowed to diffuse into a silver nitrate solution (10%) contained in a capillary space formed between microscope cover-slips. With a chamber of 0.04 mm. thickness, the precipitate formed a large number of approximately parallel lines; with thicker or thinner chambers, the lines were less clearly defined. The formation of these Liesegang lines was followed under the microscope and was considered to be the result of a simple diffusion process.

E. M. C.

**Protective Effect on Suspensions of the Addition of Quantities of Electrolytes too small to cause Flocculation.** A. BOUTARIC and (MLLE.) G. PENEAU (*Compt. rend.*, 1924, **179**, 46—49).—The addition of electrolytes to colloidal solutions of gamboge and mastic in quantities too small to produce flocculation has a protective effect on the suspension. For a given volume containing definite quantities of colloid and electrolyte, the speed of flocculation diminishes with decrease in the concentration of the added electrolyte (cf. Boutaric and Vuillaume, A., 1921, ii, 537). Colloidal solutions of mastic and gamboge to which have been added quantities of an electrolyte insufficient to cause flocculation are found to flocculate more slowly on the addition of a further equal quantity of the same electrolyte than the colloidal solution which has not been so treated. No such protective action is generally observed in the case of arsenic sulphide sols. The addition of a different electrolyte from that used as a protective agent sometimes accelerates and sometimes retards flocculation. Thus the addition of potassium

chloride to a gamboge suspension protects it from flocculation by barium chloride and sodium chloride solutions, but with sulphuric and hydrochloric acids flocculation is accelerated. J. W. B.

**Effect of Alterations in Hydrogen-ion Concentration on the Precipitation of Positive and Negative Iron Hydroxide Sols.** P. RONA and F. LIPMANN (*Biochem. Z.*, 1924, **147**, 163—173).—With diminishing hydrogen-ion concentration, positively charged ferric hydroxide sols become more sensitive to the flocculating action of anions. These follow a series similar to that of Hofmeister; the sequence is not affected by alterations in hydrogen-ion concentration, the order being  $[\text{Br}, \text{NO}_3, \text{Cl}] < \text{CNS} < \text{F} < \text{SO}_4 < \text{citrate}$  (cf. Loeb, *J. Gen. Physiol.*, 1922, **5**, 665, 693). Importance is attached to the degree of hydration of the sol and to salt hydrolysis in these observations. The negative charge of ferric hydroxide sols in the presence of citrate is closely related to the degree of acidity. J. P.

**Removal of Polonium from a Sodium Hydroxide Solution by Different (Adsorbing) Substances.** J. ESCHER-DESRIVIÈRES (*Compt. rend.*, 1924, **178**, 1713—1715).—The removal of polonium from a sodium hydroxide solution, by the precipitation of an insoluble hydroxide, such as bismuth or ferric hydroxide, or its adsorption from the same solution by animal charcoal, depends, for a given weight of the adsorbing agent, upon the concentration of the alkali. With ferric hydroxide, the action may be represented quantitatively by the equation  $X = (a/m^k)e^{\alpha n}$ , where  $X$  is the ratio of dissolved to precipitated polonium,  $m$  the weight of ferric chloride to be precipitated,  $n$  the amount of sodium hydroxide,  $k$  a constant, and  $\alpha$  a constant depending on the units employed. The exponent  $\alpha$  depends on the nature of the precipitating or adsorbing agent, changing abruptly to a different value when a certain concentration of alkali is reached. If this discontinuity be real, it may correspond with a change in the nature of the ion or complex with which the polonium is associated.

In feebly alkaline solutions ( $N/10$  sodium hydroxide), the polonium is rapidly removed by traces of solid matter, or is deposited on the walls of the containing vessel. M. S. B.

**Oxidation and Reduction Potentials of Organic Compounds.** E. BILLMANN (*Trans. Faraday Soc.*, 1924, **19**, 676—691).—A review of recent work on reduction potentials with special reference to the quinhydrone electrode and its modifications, and to the reduction potentials of substituted quinones, alloxantins, and azo compounds. S. S.

**Determination of the Affinity Constants of Bases by the Hydrogen and Quinhydrone Electrodes.** J. N. PRING (*Trans. Faraday Soc.*, 1924, **19**, 705—717).—The hydrolysis and affinity constants for twelve amino-bases dissolved in water, and in mixtures of water and acetone, have been determined electrometrically by means of the hydrogen and quinhydrone electrodes. In most cases, the results were checked by a colorimetric determination of

$p_H$ . The values found for  $k_h = [H']\{[X_3N] + [X_3NHOH]\} / [X_3NH']$  and for  $k_b = [X_3NH']\{[OH']\} / \{[X_3N] + [X_3NHOH]\}$  in aqueous solutions in the neighbourhood of  $20^\circ$  are:—Diethylaniline,  $k_h = 2.3 \times 10^{-7}$ ,  $k_b = 4.5 \times 10^{-8}$ ; *p*-phenylenediamine,  $k_h = 8.0 \times 10^{-7}$ ,  $k_b = 1.0 \times 10^{-8}$ ; dimethyl-*p*-toluidine,  $k_h = 2.5 \times 10^{-6}$ ,  $k_b = 3.0 \times 10^{-9}$ ; benzidine,  $k_h = 6.6 \times 10^{-6}$ ,  $k_b = 1.6 \times 10^{-9}$ ; dimethylaniline,  $k_h = 7.6 \times 10^{-6}$ ,  $k_b = 1.0 \times 10^{-9}$ ; ethylaniline,  $k_h = 7.0 \times 10^{-6}$ ,  $k_b = 1.0 \times 10^{-9}$ ; *p*-toluidine,  $k_h = 7.6 \times 10^{-6}$ ,  $k_b = 1.0 \times 10^{-9}$ ; methylaniline,  $k_h = 2 \times 10^{-5}$ ,  $k_b = 5.0 \times 10^{-10}$ ; aniline,  $k_h = 2.5 \times 10^{-5}$ ,  $k_b = 3.0 \times 10^{-10}$ ; *p*-nitrosodimethylaniline,  $k_h = 5 \times 10^{-5}$ ,  $k_b = 1.0 \times 10^{-10}$ ; glycine,  $k_h = 3.5 \times 10^{-3}$ ,  $k_b = 3.0 \times 10^{-12}$ ; *p*-aminobenzoic acid,  $k_h = 5.6 \times 10^{-3}$ ,  $k_b = 1.5 \times 10^{-12}$ . Similar measurements made with solvents containing 50 and 90 volume per cent. acetone show that the apparent basicity decreases rapidly with increasing acetone content, but with a few exceptions the order of the basicities is unchanged. The following values were obtained for  $[H']\{[OH']\} / [H_2O]$ :— $2.10 \times 10^{-16}$  in pure water at  $20^\circ$ ,  $1.09 \times 10^{-17}$  in 50% acetone at  $20^\circ$ , and  $3.6 \times 10^{-21}$  in 90% acetone at  $15^\circ$ . S. S.

#### Oxidation-Reduction. V. Electrode Potentials of Simple Indophenols Each in Equilibrium with its Reduction Product.

B. COHEN, H. D. GIBBS, and W. M. CLARK (*U.S. Pub. Health Repts.*, 1924, **39**, 381—414).—The equation applicable in all cases at  $30^\circ$  is  $E_h = E_o - 0.03006[\log(S_r/S_o) - \log(K_r K_2 + K_r [H^+]^2) - \log(H^+) + \log(K_o + [H^+])]$ , where  $E_h$  is the electrode potential difference referred to the normal hydrogen electrode,  $E_o$  is a constant for a given system,  $S_r$  and  $S_o$  are the concentrations of reducing and oxidising substances, respectively, and  $K_o$ ,  $K_r$ , and  $K_2$  are acid ionisation constants. The essential feature of dye reduction is the transfer of electron pairs. CHEMICAL ABSTRACTS.

**Concentration Cells and the Electrolysis of Sodium Ethoxide Solutions.** M. SHIKATA (*Trans. Faraday Soc.*, 1924, **19**, 721—728).—The mercury dropping electrode has been used in the investigation of the electrolysis of alcoholic sodium ethoxide solutions, and it is shown that the deposition of sodium ions at such an electrode is reversible. With the aid of a standard sodium amalgam electrode the *E.M.F.* of a series of concentration cells has been measured, and it is found that the activity of the sodium ion increases rapidly in more concentrated ethoxide solutions. Conductivity and vapour pressure measurements indicate that this effect is probably due to a decrease in solvation. S. S.

**Electrode Potentials in Non-aqueous Solvents.** E. BAUR (*Trans. Faraday Soc.*, 1924, **12**, 718—720).—Electrode potentials in non-aqueous solvents may be measured by using a chain such as metal | metallic salt in phenol | KCl in phenol | KCl in water | X, where X is a calomel electrode. Of the potentials concerned,  $\pi_1$  is known,  $\pi_3$  is zero when the potassium chloride is in equilibrium between phenol and water, and  $\pi_4$  can be made negligibly small or measured by diffusion cells in the usual manner. Hence  $\pi_2$  can be calculated from the *E.M.F.* of the combination. S. S.

**Measurement of certain "Inaccessible" Potentials with a Controlled Oxygen Electrode.** A. K. GOARD and E. K. RIDEAL (*Trans. Faraday Soc.*, 1924, **19**, 740—747).—When a platinum electrode is immersed in alkaline arsenite-arsenate solutions, a steady potential is not obtained. If, however, the oxygen content of the electrode is "controlled" by previous immersion in  $N/100$  permanganate solution the potential rapidly attains a maximum and then falls off. This maximum is accurately reproducible and may be used to study the reduction potential of such systems, if the reaction between the reducing agent and the oxygen in the electrode is not too rapid. S. S.

**Heterogeneous Equilibria. II. Kinetic Interpretation of the Nernst Theory of Electromotive Force.** J. A. V. BUTLER (*Trans. Faraday Soc.*, 1924, **19**, 729—733).—A kinetic interpretation of the Nernst equation  $E = E_0 + (RT/nF)\log C$  is developed from the considerations previously advanced (this vol., ii, 530). It is found that  $E_0$ , the normal potential, is a composite term and is given by  $U/nF + (RT/nF)\log_e(AN_0/1000A'N_1)$ , where  $U$  is the heat absorbed when 1 gram ion passes into solution,  $N_0$  is Avogadro's number,  $N_1$  the number of atoms per sq. cm. of metal surface,  $A = \sqrt{R/2\pi M}$ , where  $M$  = mol. wt., and  $A' = \nu\sqrt{R/W_1'}\pi$ , where  $\nu$  is the vibration frequency of the atoms in the metal and  $W_1'$  is the work done by 1 gram ion against the non-electric attractive forces of metal and solution. Taking  $\nu$  as the "reststrahlen" frequency and  $W_1'$  as the latent heat of fusion, it is found for five metals that values of  $E_0 - U/nF$  of the right order of magnitude are obtained. S. S.

**Heterogeneous Equilibria. III. Kinetic Theory of Reversible Oxidation Potentials at Inert Electrodes.** J. A. V. BUTLER (*Trans. Faraday Soc.*, 1924, **19**, 734—739).—The statistical methods previously developed (this vol., ii, 530, and preceding abstract) are applied to the discussion of reversible oxidation potentials, and a general expression is obtained which is in agreement with the thermodynamic equation  $E = E_0 + (RT/nF)\log_e(c_1/c_2)$ . The normal potential,  $E_0$ , is shown to be a complex quantity depending on (1) the ionisation potential corresponding to the loss of an electron by the reduced molecule, (2) the difference in the energies of hydration of the two substances concerned, (3) the thermionic work function of the metal, and (4) certain statistical constants of unknown magnitude. S. S.

**Processes at the Mercury Dropping Cathode. I. Deposition of Metals.** J. HEYROVSKÝ (*Trans. Faraday Soc.*, 1924, **19**, 692—702).—A dropping mercury cathode is described which enables the deposition of metals to be studied under conditions closely approaching reversibility. The deposition potential on a mercury drop,  $\pi_N$ , differs from the electrolytic potential  $E.P.$  of the pure metal. For zinc  $\pi_N = -0.865$ ,  $E.P. = -1.043$  volts, for cadmium  $\pi_N = -0.348$ ,  $E.P. = -0.683$ , and for lead  $\pi_N = -0.264$ ,  $E.P. = -0.415$ . These three metals readily form amalgams, and the difference between  $\pi_N$  and  $E.P.$  measures the affinity of the

metal for mercury. For iron,  $\pi_N = -1.115$ ,  $E.P. = -0.714$ , the increased negative potential being due to the insolubility of iron in mercury. Arsenic gives similar results. The dropping electrode is also used to determine the solubility product of lead and zinc hydroxides. The presence of very small amounts of impurities produces "waves" in the current-*E.M.F.* curve, and these can be identified by their position on the *E.M.F.* scale. Examples of this electrochemical method of analysis are quoted. S. S.

**Processes at the Mercury Dropping Cathode. II. Hydrogen Overpotential.** J. HEYROVSKÝ (*Trans. Faraday Soc.*, 1924, 19, 785—788).—The current-*E.M.F.* curves obtained with the mercury dropping electrode in acid, neutral, and alkaline solutions show that a high overvoltage for hydrogen is obtained at the mercury surface, although this behaves normally for the reversible deposition of cations. No indication of the existence of a surface layer of hydride or of a gas film is obtained. It is considered that the discharged hydrogen atoms behave like the atoms of a reactive metal of solution tension  $-1.9$  volts which has no affinity for mercury. The rapidity with which these atoms disappear from the surface by diffusion affords little opportunity for their combination to form molecules. S. S.

**Electromotive Equilibrium and Polarisation.** A. SMITS (*Trans. Faraday Soc.*, 1924, 19, 772—784).—Polarisation and passivity phenomena are considered to be due to the slow establishment of equilibrium in the metal itself rather than in the layer of solution adjacent to it. The rate at which internal equilibrium is attained is profoundly affected by catalysts. Experiments on the potential of aluminium-mercury electrodes in a saturated solution of aluminium acetylacetonate in acetylacetonate indicate that the purest aluminium contains retarding catalysts (probably oxides) and that the addition of mercury activates the metal by catalysing the establishment of inner equilibrium. S. S.

**Irreversible Electrode Phenomena.** H. J. T. ELLINGHAM and A. J. ALLMAND (*Trans. Faraday Soc.*, 1924, 19, 748—771).—A review and bibliography of work on overvoltage and allied phenomena. S. S.

**Influence of Obstructive Films on Anodic Processes.** U. R. EVANS (*Trans. Faraday Soc.*, 1924, 19, 789—799).—The anodic attack of a metal is markedly affected by adherent films produced by electrolysis, which, if non-conducting, may produce valve action. Passivity is regarded as the result of a layer of attached oxygen atoms and there is not necessarily an abrupt change between the active and passive states. The influence of partial passivity on the determination of the normal potentials of certain metals is discussed. S. S.

**Overvoltage and Physical Properties.** J. R. PARTINGTON (*Chem. News*, 1924, 129, 77).—The relation between the over-

voltage and m. p. of metals (Weeks, this vol., ii, 527) fails to obtain when more nearly correct values for the m. p. are employed.

A. A. E.

**Gas Film Theory of Overvoltage.** N. V. S. KNIBBS (*Trans. Faraday Soc.*, 1924, **19**, 800—807).—The phenomena of hydrogen overvoltage are considered to be best explained in terms of Haber's theory of an adsorbed gas layer which varies in thickness with the current density.

S. S.

**Measurement and Cause of Overvoltage.** S. GLASSTONE (*Trans. Faraday Soc.*, 1924, **19**, 808—816).—At a given current density the overvoltage of lead, copper, and mercury electrodes measured by the direct method varies with the size of the electrode, large electrodes giving higher values. Measurements by the commutator method, using a special commutator (T., 1923, **123**, 1745), by means of which instantaneous values of the potential of the test electrode were measured at intervals of 0.002, 0.004, 0.006, 0.012 second after the polarising current was cut off, afford values which decrease with time, and by extrapolation to zero time an overvoltage value is obtained which is independent of the size of the electrode and for small current densities is identical with the value found by the direct method. At higher current densities, the direct method gives higher results, the difference increasing with the current density and with the size of the electrode. This difference is ascribed to the "surface resistance" of a metal-gas-electrolyte system, which is, however, less than 4 ohms for an electrode of 1 sq. cm. area. Hydrogen overvoltage is considered to be due to the presence of monatomic hydrogen in the neighbourhood of the electrode; the voltage observed is determined by the current density and by the speed of compensating processes such as diffusion, the reaction  $2\text{H} \rightarrow \text{H}_2$ , and bubble formation.

S. S.

**Thermal Method for the Study of Gaseous Systems.** G. PICCARDI (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 395—397).—The method previously described (this vol., ii, 536) gives results for hydrogen, nitrogen, oxygen, carbon dioxide and monoxide, and air which are in good agreement with those required by theory.

T. H. P.

**Atomic Dissociation of Hydrogen and Chlorine. II. Dissociation of Hydrogen.** K. WOHL (*Z. Elektrochem.*, 1924, **30**, 49—62).—By exploding a mixture of hydrogen and chlorine in presence of hydrogen chloride or an excess of hydrogen, the mean molecular heat of undissociated hydrogen chloride gas is found to be represented by the expression  $C_v = 4.963 + (E_T - E_{291})/(T - 291)$  for values of  $T$  between 1950° and 2580° Abs. In this,  $E$  is the vibrational energy of the hydrogen chloride molecule. Up to 2200°, the molecular heat is given equally well by the linear relation  $C_v = 4.98 + 0.00048t$ . The molecular heat of hydrogen between 1000° and 2500° Abs. is given by  $C_v = 4.75 + 0.00038t$ . Contrary to Piers' data, the temperature coefficients for hydrogen and hydrogen chloride are unquestionably different. The dissociation of hydrogen



chloride is given by  $\log K = -[(43900 + F_{H_2} + F_{Cl_2} - 2F_{HCl})/4.571T] - 0.96$ , where  $F$  is the free energy of the atomic vibrations. For the dissociation of hydrogen at constant volume, the author gives the formula  $\log K_h = -95000/4.571T + 1.5 \log T - F_{H_2}/4.571T + 0.55$ , from which the following values are obtained for  $\log K_h$  and the percentage dissociation: 1700°, -5.00, 0.16; 2000°, -3.56, 0.83; 2300°, -2.46, 3.0. If use is made of the theoretical chemical constant for monatomic hydrogen, it follows that the heat of dissociation of hydrogen is given approximately by  $U_{H_2} = 95000 + 0.993T - F_{H_2} \pm 2000$  cal. H. T.

**Ratio of Equilibrium Constants [for Reactions] in Gaseous and Liquid Phases.** W. SWIENTOSLAWSKI (*Bull. Soc. chim.*, 1924, [iv], **35**, 690—695).—Nernst's expression for the ratio between the equilibrium constants for a reaction which takes place when the substances concerned are (1) in the gaseous state, (2) in solution is modified by the introduction of the author's  $z$  function (*A.*, 1923, ii, 546). S. K. T.

**Equilibrium in the Double Decomposition of Salts in Aqueous Solution.** LEMARCHAND (*Compt. rend.*, 1924, **179**, 41—43).—The equilibrium in the reaction between magnesium oxalate and ammonium chloride in aqueous solution has been investigated thermochemically. The corrected data are said to indicate that the position of equilibrium in aqueous solution corresponds with 66.5% production of ammonium oxalate. This result does not agree with the conclusion of Malaguti (*Ann. Chim. Phys.*, 1853, [3], **37**, 198). J. W. B.

**Isothermal Reaction Velocity in Homo-heterogeneous Systems in Absence of Solvent.** K. HÖJENDAHL (*J. Physical Chem.*, 1924, **28**, 758—768).—It is shown theoretically that, in the absence of catalysts, reactions in homo-heterogeneous systems are of the first order. The theory is confirmed for the maleic acid-fumaric acid system, in which both the main reactions are unimolecular (maleic acid  $\rightarrow$  fumaric acid; maleic acid  $\rightarrow$  malic acid + maleic anhydride). The calculated position of the infrared absorption band for the former reaction agrees with that observed; the observed velocity coefficient for the same reaction is closer to that deduced from Dushman's equation than that obtained from Lewis' quantum relation. S. K. T.

**In-, Uni-, and Multi-variant Equilibria.** XXVI. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amst.*, 1924, **27**, 279—290).—A theoretical discussion of the influence of temperature and pressure on phase equilibria. G. M. B.

**Temperature Coefficients of some Reactions.** R. C. BANERJI (*J. Proc. Asiatic Soc. Bengal*, 1922, **18**, 66).—Temperature coefficients for the unimolecular reactions (a) interaction of oxalic and iodic acids, (b) production of chloroform from trichloroacetic acid are 3.27 at 29—59° (2.96 at 59—69°) and 4.3 at 80—90°, respectively. CHEMICAL ABSTRACTS.

**Oxidations and Reductions during Passage through a Septum. Hypothesis of Catalytic Activation by a Boundary.** P. GIRARD (*Compt. rend.*, 1924, **178**, 1847—1849; cf. Girard and Plataud, this vol., ii, 396, 397).—The hypothesis put forward to account for the observed phenomena is based on the assumption that the septum behaves as a catalytic agent in bringing about electrostatic instability in the solution. As a result, there occurs an inter-ionic transfer of electrons. The septum may be charged positively or negatively by adsorption of hydrogen or of hydroxyl ions, thus leaving in the solution an excess of ions of opposite sign to that of the charge. This lack of electrostatic equilibrium is balanced by migration of electrons from some negative to positive ions or molecules, which by this means become activated. Such activated molecules when in the vicinity of hydrogen ions adsorbed on the septum would part with their electrons and undergo reduction by the nascent hydrogen thus formed; in the case of hydroxyl adsorption, the ions from which an electron had been transferred would undergo oxidation by an analogous process. H. J. E.

**Autoxidation and Anti-oxygenic Action. Catalytic Properties of Sulphur and its Compounds.** C. MOUREU and C. DUFRAISSE (*Compt. rend.*, 1924, **178**, 1861—1864).—In continuation of the authors' work on autoxidation (A., 1923, ii, 308; this vol., i, 635), observations have been made on the catalytic activity of sulphur compounds. Sulphur itself retards the autoxidation of benzaldehyde as vigorously as does quinol. Previous observations on the catalytic behaviour of sulphur compounds are tabulated.

S. B.

**Formation of Photo-electrically Active Films of Cuprous Oxide.** J. PIONCHON and (MLLE.) F. DÉMORA (*Compt. rend.*, 1924, **178**, 1885—1887).—A plate of copper cleaned by nitric acid and immersed in *N*/2000 to *N*/10 solutions of copper sulphate, becomes covered, under the influence of air and sunlight, with a lilac-coloured film of a compound which is probably cuprous oxide. These films are photo-electrically active, and two copper plates so prepared and immersed in dilute copper sulphate solution form a photo-electric cell. An electric arc consuming 7 amps. produced an *E.M.F.* of 60 millivolts when placed at a distance of 40 cm. from such a cell.

S. B.

**[Formation of Photo-electrically Active Films of Cuprous Oxide.]** A. COTTON (*Compt. rend.*, 1924, **178**, 1887).—The observations of Pionchon and Démora (see preceding abstract) resemble those of G. Athanasiu (*ibid.*, 1924, **178**, 386).

S. B.

**New Electric Oven.** A. TIAN (*Bull. Soc. chim.*, 1924, [iv], **35**, 804—808).—The oven consists of a copper vessel lined with glass. Uniform temperature is ensured by a preliminary heating of the circulating air. The apparatus may also be used as a vacuum desiccator, or for heating substances in a vacuum.

S. K. T.

**High-vacuum Pumps.** A. CLAASSEN (*Chem. Weekblad*, 1924, 21, 368—371).—An account of the various pumps constructed during recent years by Gaede, Holweck, Langmuir, Volmer, Stintzing, and others. S. I. L.

**Preparation of Ozone by means of Flames as a Lecture Experiment.** K. A. HOFMANN and P. KRONENBERG (*Ber.*, 1924, 57, [B], 1200—1203).—The combustion of hydrogen, coal gas, or acetylene in a large excess of oxygen can be regulated so that ozone is produced in such quantity that its most important reactions can be demonstrated readily and its odour is perceptible throughout a large room. The gas is supplied to the interior, the oxygen to the exterior of a small blowpipe burner, the flame being about 2 mm. high and 1 mm. in diameter. It is allowed to impinge on a quartz tube cooled by circulating water; the tube is mounted in a glass cylinder which must also be cooled and through which the flame gases escape. The yield of ozone is very much greater than that calculated from Nernst's theorem. H. W.

**Metastability of the Elements and Chemical Compounds in Consequence of Enantiotropy or Monotropy.** VII. E. COHEN (*Proc. K. Akad. Wetensch. Amst.*, 1924, 27, 226—227; cf. A., 1916, ii, 183).—Attention is directed to observations of Ruys and of Deville on slow changes in the density of sulphur after solidifying from the molten state. It would seem to have been known more than 75 years ago that liquid sulphur yields a metastable mixture of several modifications on solidification. G. M. B.

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## Inorganic Chemistry.

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**Physico-chemical Calculations Relative to the Degree of Dissociation of Substances dissolved in Mineral Waters. II.** C. PORLEZZA (*Annali Chim. Appl.*, 1924, **14**, 155—206; cf. this vol., ii, 469).—The author discusses the methods of calculating, firstly, the proportions of the dissociated and undissociated parts of the salts dissolved in a mineral water and, secondly, the physico-chemical constants of the water. T. H. P.

**Concentration of Merck's "Perhydrol" [Hydrogen Peroxide].** A. H. ERDENBRECHER (*Z. angew. Chem.*, 1924, **37**, 507—508).—Concentrated (85%) hydrogen peroxide is a fairly harmless liquid which can be kept, without appreciable decomposition, in ordinary steamed glass vessels. Hydrogen peroxide containing 13·17% of available oxygen is distilled at 15 mm. pressure in a glass apparatus, provided with ground-glass connexions, which has been previously steamed. Filtered air is drawn through the liquid (in a water-bath at 35—48°) and the distillate is collected in an ice-cooled receiver. A yield of 80·4% of hydrogen

peroxide containing 36.1% of available oxygen is left in the distilling flask, the loss through decomposition being 1.68% of the original available oxygen. W. T. K. B.

**Volatility of Bromine in Solutions of Different Electrolytes and its Bearing on Bromometric Analysis.** G. JANDER and H. FEIT (*Z. anorg. Chem.*, 1924, **136**, 305—312).—The volatility of bromine from aqueous solutions increases on the addition of calcium chloride, but decreases with increasing concentration of sodium chloride, hydrogen chloride, or potassium bromide, and is smallest in *N*-hydrochloric acid solution containing 15% of potassium bromide. Such a solution of bromine (0.1*N*) may be used to replace the more expensive iodine solution in volumetric analysis, using as indicator indigo-carmin added just before reaching the end-point, or preferably quinoline-yellow, which may be added at the commencement of a titration. Potassium bromide may be used in place of the iodide in distillation processes such as the determination of chromic acid; the liberated bromine is distilled into sodium arsenite solution and the excess of the latter titrated with 0.1*N*-bromine, using quinoline-yellow as indicator. A. R. P.

**Tellurium.** W. BILTZ and H. FRIEDRICH (*Z. anorg. Chem.*, 1924, **136**, 416—420).—Tellurium tetrachloride and silver chloride when melted together in a sealed tube give a liquid which separates into two layers when more than 20 mol.-% of silver chloride is present. The lower layer consists of almost pure silver chloride and freezes at 440—455°; the upper layer contains the silver chloride-tellurium tetrachloride eutectic together with excess of silver chloride. The eutectic melts at 210° and contains about 9 mol.-% of silver chloride, whilst pure tellurium tetrachloride melts at 224°. Metallic silver decomposes tellurium tetrachloride, forming in all cases silver telluride and chloride, excess of tellurium tetrachloride having no further action on the silver telluride. In its halogen compounds, therefore, tellurium behaves like a noble metal. A. R. P.

**Tellurium Dichloride.** K. LINDNER and L. APOLANT (*Z. anorg. Chem.*, 1924, **136**, 381—386).—When powdered tellurium is heated in a stream of carbonyl chloride, brown vapours of tellurium dichloride are evolved. These condense into a velvety-black, crystalline mass which is decomposed by water with the separation of elementary tellurium and the formation of tellurium oxychloride,  $\text{TeOCl}_2$ . Repeated sublimation of the dichloride with a deficiency of ammonium chloride yields ammonium chlorotellurite,  $(\text{NH}_4)_2\text{TeCl}_4$ , as a greenish-black, compact mass which is not hygroscopic and remains unaltered in the air. A. R. P.

**Catalytic Oxidation of Ammonia to Nitrous Gases and Nitric Acid.** G. KASSNER (*Z. angew. Chem.*, 1924, **37**, 373—382).—Ammonia is directly oxidised by air to nitric acid by a catalyst, "nitroxan," which consists of an equimolecular mixture, or a compound, of barium metaplumbate and barium manganate. At low temperatures (<450°), the nitric acid is retained as barium nitrate, which is adsorbed as such by the catalyst. It may be

removed by lixiviation, the catalyst being replenished with barium hydroxide. The catalyst improves with continuous use. At higher temperatures ( $>500^{\circ}$ ), the gaseous products contain a greater proportion of nitrogen dioxide, which, in the presence of the oxygen and the water which is formed, is rapidly condensed to liquid nitric acid. These methods will give a 100% conversion of ammonia into nitrate. The theory of the reaction is discussed in detail. [Cf. *B.*, 1924, 744.] S. K. T.

**Reduction of Free Nitric Acid by Ferrous, Stannous, or Titanous Salts.** L. H. MILLIGAN and G. R. GILLETTE (*J. Physical Chem.*, 1924, 28, 744—757).—The reduction of 15% nitric acid by ferrous sulphate at  $20^{\circ}$  is accompanied by a period of induction, after which the nitric oxide-ferrous salt complex forms and decomposes into nitric oxide and nitrogen dioxide. The former oxide is the sole product when small quantities of acid are used with a boiling solution. Stannous chloride reduces cold 10—50% nitric acid to hydroxylamine salts, which, under appropriate conditions, react with excess of acid to give nitrous oxide and traces of nitrogen and other oxides. Ammonium salts are only formed, together with hydroxylamine salts, when small quantities of the acid are used. Nitric acid is reduced by titanous chloride mainly to nitric and nitrous oxides, irrespective of the concentrations of the reagents. Catalysis evidently plays an important rôle, because the more highly reduced compound (hydroxylamine) is produced by the weaker reducing agent (stannous chloride); the titanous salt probably decomposes nitrohydroxylamic acid, catalytically, into nitric oxide. A mechanism is outlined for the reduction of free nitric acid. S. K. T.

**Non-luminous Oxidation of Phosphorus in an Oxygen Atmosphere.** LORD RAYLEIGH (*Proc. Roy. Soc.*, 1924, A, 106, 1—8).—In continuation of previous work (A., 1921, ii, 546; 1923, ii, 755), it is shown that oxidation of phosphorus by moist oxygen at atmospheric pressure occurs slowly and without luminosity below  $15^{\circ}$ . The change from the dark to luminous oxidation is quite sharp and definite. Stringent photographic tests show that no light is emitted in the former case. By suitable manipulation, it is possible to obtain the oxidation either with or without luminosity at the same temperature and pressure. In the former case, the reaction is more than 140 times as rapid. It is further shown that the effect is a volume reaction occurring in the vapour phase. L. J. H.

**Transitions of the Polymetaphosphates.** P. PASCAL (*Compt. rend.*, 1924, 178, 1906—1908).—When sodium trimetaphosphate is heated between  $607^{\circ}$  and  $640^{\circ}$  (m. p.) a tetrametaphosphate is produced. Above  $640^{\circ}$ , the hexametaphosphate is formed. The changes are reversible, and owing to its narrow range of stability the tetrametaphosphate must be obtained by sudden chilling. A diagram is given illustrating the transition temperatures of the various metaphosphates of sodium and potassium. S. B.

**Solid Hydride of Arsenic.** E. J. WEEKS and J. G. F. DRUCE (*Chem. News*, 1924, 129, 31—32).—Solid arsenic hydride,  $\text{As}_2\text{H}_2$ , is obtained by the reduction of a solution of arsenic trichloride in aqueous hydrochloric acid with an ethereal solution of stannous chloride:  $2\text{AsCl}_3 + 4\text{SnCl}_2 + 2\text{HCl} = \text{As}_2\text{H}_2 + 4\text{SnCl}_4$ . A. A. E.

**Cause of the Colour produced in Glasses of Anhydrous Borax and Sodium Metaphosphate by Fusion with Metallic Oxides.** T. COHN (*Chem. News*, 1924, 129, 32—35).—The colours obtained with oxides of cobalt, nickel, or copper are due to the formation of metaborates and pyrophosphates, respectively; no colour changes due to colloid phenomena were observed.

A. A. E.

**Adsorption of Dyes by Diamond, Charcoal, and Artificial Silk.** F. PANETH and A. RADU (*Ber.*, 1924, 57, [B], 1221—1225).—The investigations of Paneth and Thimann (this vol., ii, 612) have opened up the possibility of measuring the specific surfaces of materials to which the microscopic and radioactive methods are not applicable, by determining the adsorption of suitable dyes. Examination of the behaviour of methylene-blue towards diamond powder proves that the dye is only absorbed in a unimolecular layer. Methylene-blue is more extensively absorbed by technical animal, beech, bone, or activated sugar charcoal than is methyl-green or ponceau-2R, and since only a unimolecular layer is considered to be formed, the values of the specific surface obtained with this dye must be regarded as approaching most nearly the true values. With lead nitrate the same orders of magnitude are observed, but with acetone the results are considerably higher than with methylene-blue, probably owing to the presence of such minute fissures in the carbon as are penetrable to the small acetone molecules, but impenetrable to the larger methylene-blue molecules. Measurement of the specific surface of acetate silk by the microscopic and absorption methods gives concordant results, but this is not the case with copper and nitro silks. The microscopic method appears in these instances to be inapplicable, since it fails to take into account the internal surface. Microscopic investigation shows the fibres of nitro and copper silks to be stained throughout, even when the adsorption has not attained its maximum, whereas the fibres of acetate silk are only stained externally.

H. W.

**Absorption of Carbon Monoxide by Cuprous Sulphate in presence of Sulphuric Acid. Application to the Production of Hydrogen from Water-gas.** A. DAMIENS (*Compt. rend.*, 1924, 178, 2178—2181; cf. this vol., ii, 567).—Measurements have been made of the pressures of carbon monoxide in equilibrium with solutions of cuprous sulphate in sulphuric acid. At temperatures below  $80^\circ$ , and with acid of not less than 84% concentration, no dissociation tension could be observed until more than 1 mol. proportion of carbon monoxide had been absorbed, relative to the cuprous sulphate. The observed tension then rose to a maximum

of 270 mm. at the limit of absorption with a mol. ratio of 2. When a more dilute acid was used as solvent, a dissociation tension appeared at a much lower value of the molecular ratio, and increased when the temperature was raised. The absorption of the gas becomes more rapid as the temperature is raised to 60°. G. M. B.

**Density of Carbon Dioxide from Natural Limestones.** A. P. LIDOV (*Ore Messenger, Moscow*, 1916, **1**, 123—125).—Determinations of the density of carbon dioxide obtained from various natural sources give results lower than the theoretical.

CHEMICAL ABSTRACTS.

**Apparatus for the Extraction and Purification of Radium Emanation.** W. MUND (*Bull. Soc. chim. Belg.*, 1924, **33**, 256—260).—An apparatus for purifying and collecting the emanation from a solution of radium bromide is so constructed that the emanation never comes into contact with a stopcock or greased joint. The greater part of the electrolytic gas, also produced, is destroyed by explosion, the water formed being absorbed by phosphorus pentoxide. Carbon dioxide is absorbed by potassium hydroxide, and the remaining traces of oxygen and hydrogen are removed by means of heated copper and copper oxide. Finally, the emanation is condensed in liquid air and the apparatus repeatedly evacuated. The emanation is allowed to vaporise and collect in the required vessel, which is then sealed off. In 3 hours it is thus possible to obtain 100 millicuries of the emanation in a volume of several c.mm., gaseous impurities present exerting a partial pressure of less than 50 mm. of mercury. J. W. B.

**Potassium Ammonioaluminate, Potassium Ammonomanganite, and Manganous Amide.** F. W. BERGSTROM (*J. Amer. Chem. Soc.*, 1924, **46**, 1545—1558).—Potassium ammonioaluminate,  $\text{Al}(\text{NH}_2)_3 \cdot \text{KNH}_2$ , has been prepared by the action of amalgamated aluminium on solutions of potassium or potassamide in liquid ammonia. It crystallises in colourless needles and generally resembles the corresponding sodium compound (A., 1923, ii, 31; this vol., ii, 106). When heated at 50° in a vacuum, it yields the substance  $\text{Al}(\text{NH}_2)_2 \cdot \text{NHK}$ , which is white and non-crystalline.

Potassium ammonomanganite,  $\text{Mn}(\text{NHK})_2 \cdot 2\text{NH}_3$ , is formed by the very slow action of metallic manganese on a solution of potassium or potassamide in liquid ammonia, or more readily by pouring a solution of manganous thiocyanate in liquid ammonia into an excess of a solution of potassamide. It is a compound of bivalent manganese and forms cream-coloured crystals which absorb oxygen from the air and are vigorously hydrolysed by water.

Impure manganous amide,  $\text{Mn}(\text{NH}_2)_2$ , is formed by the action of potassamide on excess of a solution of manganous thiocyanate in liquid ammonia. When heated in a vacuum it gives off ammonia, forming products of indefinite composition. W. H.-R.

**Fluidity of Crystallised Salts.** A. BENRATH and W. STANDOP (*Z. anorg. Chem.*, 1924, **136**, 367—380).—The fluidity of sodium and potassium nitrates has been determined at various temperatures



by measuring the time required to squeeze a certain amount of the salt through a small orifice under a constant high pressure. In both cases, the fluidity,  $f$ , may be expressed by the equations  $\log f = a + bt$  for constant pressure,  $p$ , and  $\log f = \alpha + \beta p$ , for constant temperature,  $t$ , where  $a$ ,  $b$ ,  $\alpha$ , and  $\beta$  are constants for each salt. If both temperature and pressure vary, then  $\log f = a + bt + cp$ . Addition of sodium nitrate to potassium nitrate increases the viscosity very considerably. Rubidium nitrate is more plastic than potassium nitrate, and the latter is more plastic than sodium nitrate; ammonium nitrate under the high pressures required in the test decomposes, often with explosive violence. The thread of salt which is squeezed out in the press remains flexible for many hours at the temperature at which it is formed; it has the appearance of a slightly turbid, thin glass rod and shows no sign of crystallisation. On cooling, however, crystallisation takes place within a few hours, showing that the original thread consists of supercooled liquid.

A. R. P.

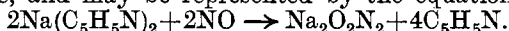
**Some Fundamental Atomic Weights.** E. ZINTL and A. MEUWSEN (*Z. anorg. Chem.*, 1924, **136**, 223—237).—The atomic weights of sodium, chlorine, and silver have been redetermined by converting sodium nitrate into sodium chloride by heating in a stream of hydrogen chloride and using the figures of Richards and Wells for the ratios  $\text{AgCl}/\text{Ag}$  and  $\text{NaCl}/\text{Ag}$ . The mean of ten very concordant results gave the ratio  $\text{NaNO}_3/\text{NaCl} = 1.45422 \pm 0.0000077$ , from which the atomic weights of sodium, silver, and chlorine are 22.9985, 107.880, and 35.457, respectively, if that of nitrogen is taken as 14.008.

A. R. P.

**Decomposition of Sodium Hydrogen Sulphite in Aqueous Solution.** T. SABALITSCHKA and G. KUBISCH (*Arch. Pharm.*, 1924, **262**, 105—106).—Sodium hydrogen sulphite solutions decompose on long standing and the end-product is sodium sulphate formed presumably by gradual oxidation of the sodium sulphite first produced in accordance with the results of other investigators (cf. Foerster and others, *A.*, 1923, ii, 853).

W. A. S.

**Preparation of Sodium Hyponitrite.** E. WEITZ and W. VOLLMEYER (*Ber.*, 1924, **57**, [B], 1015—1018).—In the preparation of sodium hyponitrite by Joannis' method (*A.*, 1894, ii, 280; 1906, ii, 161) the tedious preparation of the solution of the metal in liquid ammonia may be avoided by substituting for it the solution in pyridine described by Emmert (*A.*, 1915, i, 454), which is intermediate in its properties between the "sodium-ammonium" solution and the quaternary pyridinium radicals of Weitz and König (*A.*, 1922, i, 1186). The reaction takes place at the ordinary temperature, and may be represented by the equation



A yellow, crystalline sodium salt,  $\text{Na}_2\text{O}_2\text{N}_2 \cdot 9\text{H}_2\text{O}$  (cf. Divers and Haga, *T.*, 1889, **75**, 99), was also prepared by the methods of Joannis and Kirschner (*A.*, 1898, ii, 373); when heated it yields nitrous oxide and sodium monoxide. The silver salt is yellow and not

explosive (cf. A., 1897, ii, 25). The crude sodium hyponitrite from the pyridine solution explodes when heated. R. B.

**Conversion of Sodium Hydrogen Carbonate into Sodium Carbonate in Aqueous Solution at Various Temperatures.**

T. SABALITSCHKA and G. KUBISCH (*Arch. Pharm.*, 1924, **262**, 106—111).—Sodium hydrogen carbonate decomposes slowly in 2% aqueous solution at the ordinary temperature; even in a stoppered bottle, about 4% has undergone decomposition in about 4 weeks; when the bottle is frequently opened more change takes place, whilst when the solution is exposed to the air up to 13% decomposes in the same time. When the solution is heated for a short time, or made up with hot water, comparatively little decomposition takes place, and 5 hours' boiling is needed to effect a 94.8% conversion. The theoretical interpretation of these results is discussed (cf. McCoy, A., 1903, ii, 413; Kunz-Krause and Richter, A., 1919, ii, 423). W. A. S.

**Compounds of Silver Salts with Carbon Monoxide.** W. MANCHOT [with J. KÖNIG and H. GALL] (*Ber.*, 1924, **57**, [B], 1157—1158).—Carbon monoxide is freely and rapidly soluble in a solution of silver sulphate in concentrated sulphuric acid. The rapidity of absorption increases with increasing concentration of the acid, and is very marked with the 95% acid containing phosphoric oxide and particularly so with the fuming acid. The reaction is reversible and the absorbed carbon monoxide is liberated in a vacuum. It also depends greatly on the temperature. H. W.

**Decomposition of Calcium Fluoride with Concentrated Sulphuric Acid.** W. TRAUBE and W. LANGE (*Ber.*, 1924, **57**, [B], 1038—1045; cf. A., 1913, ii, 947; 1921, ii, 539).—The unsatisfactory yields of hydrogen fluoride and the lengthy period of distillation required in the interaction of calcium fluoride and sulphuric acid have already been attributed by Ruff and Braun (A., 1914, ii, 263) to the formation of calcium fluorosulphonate, and an exhaustive study of the reaction has been made by means of methods previously described (A., 1921, ii, 539). In equimolecular mixtures of calcium fluoride and concentrated sulphuric acid, liberation of hydrogen fluoride first takes place, the extent of this reaction depending, within limits, on the physical condition of the calcium fluoride and the thoroughness with which the compounds are mixed. The hydrofluoric acid reacts with unchanged sulphuric acid, giving rise to fluorosulphonic acid up to an equilibrium mixture the composition of which is determined by the temperature and concentration of the sulphuric acid. Low temperatures and a low content of water in the sulphuric acid favour the formation of fluorosulphonic acid. The reaction is thereby retarded and brought to equilibrium before all the calcium fluoride is attacked and this equilibrium is gradually destroyed by heating the mixture at 100°, whereby the fluorosulphonic acid is hydrolysed to hydrogen fluoride and sulphuric acid, the latter then decomposing the residual calcium fluoride. Excess of sulphuric acid promotes formation of fluoro-

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sulphonic acid, giving lower yields of hydrogen fluoride, whilst with excess of calcium fluoride the formation of fluorosulphonic acid practically ceases, and the formation of hydrogen fluoride is accelerated.

R. B.

**Heat Effects which accompany the Setting of Plaster of Paris.** L. CHASSEVENT (*Compt. rend.*, 1924, **179**, 44—46).—The evolution of heat caused by the hydration of plaster of Paris under different conditions is investigated (cf. Cloez, A., 1903, ii, 292). Curves showing the relation between the heat evolved when anhydrous calcium sulphate, prepared at 200°, is hydrated, the weight of material used, and time; also the heat evolved by the hydration of anhydrous calcium sulphate prepared at different temperatures, and of the hemihydrate, are given. Heat is evolved in two stages, first due to the hydration of the anhydrous calcium sulphate to form the hemihydrate and the formation of a saturated solution of this, then due to the crystallisation of the dihydrate and further solution of the hemihydrate which, in presence of the dihydrate, immediately crystallises in this form. Between 300° and 500°, the evolution of heat is slower the higher is the temperature of dehydration. The hydration of the hemihydrate can only be effected by means of atmospheric water vapour (otherwise it is impossible to exclude seeds of the dihydrate) and the form of the curve is practically the same as for the anhydrous salt. J. W. B.

**Action of Phosphoryl Chloride on Metallic Hydroxides.** M. GARINO and M. RAFFAGHELLO (*Gazzetta*, 1924, **54**, 351—362).—Like metallic oxides (cf. Bassett and Taylor, T., 1911, **99**, 1402), hydroxides of bivalent metals react with phosphoryl chloride, forming additive products of the general formula,  $R(OH)_2 \cdot 2POCl_3$ . The compounds obtained with calcium and magnesium hydroxides are both crystalline and dissolve in water forming acid solutions. With nickelous hydroxide an analogous compound is apparently formed but it was not obtained pure. With aniline and with ether, the calcium hydroxide compound forms crystalline *additive compounds* of the compositions,  $Ca(OH)_2 \cdot 2POCl_3 \cdot 2NH_2Ph$  and  $Ca(OH)_2 \cdot P_2O_3Cl_4 \cdot 2Et_2O$ , respectively.

T. H. P.

**Alkaline-earth Sub-salts.** A. GUNTZ and F. BENOIT (*Bull. Soc. chim.*, 1924, [iv], **35**, 709—728).—The subhalides, suboxides, and subsulphides of barium and strontium are prepared, in an impure state, by fusing the respective normal salts with the appropriate metal; the yield of subhalide increases with the atomic weights of the metal and the halogen. The formation of subbromides and subiodides is retarded by copper and silver, whereas the formation of subchlorides is accelerated. That the substances are true compounds is proved by the amount of heat evolved during their formation, by their reaction towards liquid ammonia at  $-30^\circ$ :  $2BaCl + 14NH_3 = Ba_3N_2 + BaCl_2 + 8NH_3$ , and by their behaviour towards nitrogen and hydrogen at  $400^\circ$ :  $2BaCl + H_2 = BaH_2 + BaCl_2$ ;  $6BaCl + N_2 = Ba_3N_2 + 3BaCl_2$ . Barium subsulphide

yields hydrogen and hydrogen sulphide with hydrochloric acid; the subchloride liberates hydrogen from water and potassium from potassium chloride at  $850^{\circ}$ . Barium could not be prepared by electrolysis of the fused chloride; strontium was obtained in this way only with great difficulty. Electrolysis of solid barium and strontium chlorides at  $600^{\circ}$  yields the subchlorides. S. K. T.

**Rôle of Water in Reactions in the Solid State. II.** D. BALAREV (*Z. anorg. Chem.*, 1924, **136**, 216—220; cf. this vol., ii, 483).—Barium oxide combines vigorously with lead dioxide, manganese dioxide, and uranium oxide,  $U_3O_8$ , at temperatures below  $360^{\circ}$  with the evolution of much heat. The temperature at which the reaction begins depends on the water content of the mixture and on the pressure to which the mixture has been subjected; an increase of either causes a lowering of the reaction temperature. A mixture of barium oxide and tin oxide, whether compressed or not, does not react below  $360^{\circ}$ , the melting point of barium hydroxide, and little heat is evolved in the reaction. In all these reactions, the presence of a small quantity of barium hydroxide acts as a catalyst in accelerating the combination of the two oxides, and it may reasonably be assumed that this is due to the formation of a film of liquid or nearly liquid hydroxide on the particles of barium oxide. When the two oxides are pressed strongly together the heat generated by a slight local action is sufficient to melt the hydroxide and the reaction then sets in with increasing vigour to completion. In support of this theory is the fact that barium oxide containing a trace of water reacts with manganese dioxide at  $240^{\circ}$ , whilst calcium oxide does not do so below  $930^{\circ}$ . A. R. P.

**Crystalline Lattices of Magnesium Hydroxide and Carbonate.** G. R. LEVI and A. FERRARI (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 397—401).—The fundamental element of the space lattice of magnesium hydroxide is a parallelepiped with rhombic base of side  $3.114 \text{ \AA}$ . and acute angle  $60^{\circ}$  and with height  $4.735 \text{ \AA}$ . The volume is thus  $39.80 \times 10^{-24} \text{ c.c.}$  and the calculated density 2.40, which agrees well with the values 2.35—2.46 and 2.36 found for the natural and artificial products. T. H. P.

**Mechanism of the Reduction of Zinc Oxide [by Carbon].** A. D'HOOGE (*Bull. Acad. Roy. Belg.*, 1923, **9**, 323—336).—The reduction of zinc oxide by carbon takes place through the intermediate action of carbon monoxide and is accelerated by the presence of a small quantity of oxygen. In the absence of oxygen, a temperature well above  $1000^{\circ}$  is required to bring about any change in a mixture of zinc oxide and carbon. The reaction between zinc oxide and carbon monoxide commences at about  $420^{\circ}$  and its velocity increases rapidly with the temperature; below  $700^{\circ}$ , a certain amount of free carbon is deposited and the quantity of carbon dioxide present is in excess of that produced by the reduction of zinc oxide owing to decomposition of carbon monoxide. [Cf. *B.*, 1924, 260.] A. R. P.

**Variation of Molecular Weights of certain Metals with Temperature.** A. JOUNIAUX (*Bull. Soc. chim.*, 1924, [iv], 35, 696—705).—Consideration of previously published data shows that, over the temperature range m. p. to b. p., zinc, cadmium, and thallium are monatomic, whilst lead has an atomic weight of 280, and bismuth, 245. In the latter case, the molecular weight increases rapidly as the temperature falls below the m. p. or rises above the b. p. (cf. this vol., ii, 452). S. K. T.

**Lead. VII. Equilibrium in the System Lead Oxide-Phosphoric Anhydride-Water at 25°.** L. T. FAIRHALL (*J. Amer. Chem. Soc.*, 1924, 46, 1593—1598).—At ordinary temperature the primary product of the reaction between solutions of lead salts and of disodium phosphate, is the salt  $Pb_3(PO_4)_2$ . On keeping, this is slowly transformed into the secondary lead salt,  $PbHPO_4$ , which is the equilibrium product. The isotherm at 25° of the system lead oxide-phosphoric anhydride-water has been determined by Schreinemaker's residue method. At equilibrium at 25°, tertiary lead phosphate cannot exist in the presence of even a small amount of acid, but the secondary salt exists over a considerable range of concentration of phosphoric acid, whilst primary lead orthophosphate,  $PbH_4(PO_4)_2$ , also exists within certain limits. On the other hand, when suspended in boiling water, secondary lead phosphate is slowly changed into tertiary lead phosphate. W. H.-R.

**Adsorption of Dyes by Crystals.** F. PANETH and W. THIMANN (*Ber.*, 1924, 57, [B], 1215—1220).—Comparative measurements of the surfaces of crystals of lead sulphate, lead chromate, lead chloride, lead sulphide, barium sulphate, strontium sulphate, and calcium sulphate by the microscopic and radioactive methods (cf. A., 1922, ii, 618, 619) give results which are generally in agreement with one another, thus establishing the correctness of the assumptions on which the radioactive method depends. In the cases of the sulphates of the alkaline-earths, the relationship,  $\text{Isotope surface} / \text{Isotope solution} = \text{Element surface} / \text{Element solution}$ , is not immediately applicable, since the elements have no radioactive isotopes. In these instances, the formula with isomorphous, but not isotopic, substances must be modified by the introduction of a "solubility factor"  $k$ , which expresses the relationship of the solubilities in the particular solvent. In the cases of certain natural crystals, the radioactive method gives distinctly lower results than the microscopic process, and can only be employed when it has been demonstrated that kinetic exchange takes place over the whole surface.

The adsorption of ponceau 2R, methylene-blue, naphthol-yellow, and methyl-green in addition to sodium brucinesulphonate and acetone by lead sulphate, lead sulphide, bismuth sulphide, bismuth phosphate, and barium sulphate has been measured. In every case, the maximum of absorption is reached before 100% of the surface is covered with a unimolecular layer. H. W.

**Thallothallic Chlorides and Bromides.** A. BENRATH [with W. LAMBERZ and O. KRÜGER] (*Z. anorg. Chem.*, 1924, 136, 358—366).—Solubility determinations in the system thallic chloride-

thallic chloride show that the only compounds capable of existence in the solid state are  $Tl_3[TlCl_6]$ , yellow, and  $Tl[TlCl_4]$ , white. Similarly, the corresponding bromides  $Tl_3[TlBr_6]$ , red, and  $Tl[TlBr_4]$ , yellow, are the only possible intermediate bromides. A. R. P.

**Action of Oxygen and the Halogens on Metallic Mixed Crystals, Metals, and Binary Compounds.** G. TAMMANN and H. BREDEMEIER (*Z. anorg. Chem.*, 1924, **136**, 337—357).—Observations of the rate of thickening of the colour films produced on heating alloys of copper with gold, nickel, and manganese show that the rate of internal diffusion of copper in mixed-crystal alloys falls proportionally with an increase in the amount of added metal. If, as a measure of this rate of diffusion, the time required at  $275^\circ$  to produce an oxide layer of any definite thickness is compared for each alloy, then the rate decreases with an increase in the m. p. of the added metal when the amount added is between 0.3 and 0.4 mol. per mol. of copper; in all cases, the rate is an exponential function of the temperature. Aluminium-copper alloys behave somewhat differently; for the formation of oxide layers equivalent to an air-layer of 300  $\mu\mu$  or less, the rate of thickening decreases rapidly with an increase of the aluminium content, but for thicker layers it is independent of the aluminium content and increases considerably. The time-thickness curves in both stages follow the logarithmic law and are both straight lines at all temperatures up to  $315^\circ$ . When a stream of air containing iodine vapour is passed over silver covered with a thin coating of silver bromide or iodide, this coating increases in thickness at a rate which decreases parabolically with the time, and the amount of iodine that diffuses through the chloride or bromide layer is inversely proportional to the thickness of the layer. In a damp atmosphere containing chlorine the thickness of the reaction layer on copper that has previously been coloured by heating in the air, increases proportionally to the logarithm of the time of exposure until the cuprous oxide in the original oxide film is converted into an oxychloride; the layer then increases logarithmically at a greater rate. The colouring of copper and of silver by sodium sulphide solutions and of silver by hydrogen sulphide in air follows a similar course, but the colouring of copper by hydrogen sulphide in the air follows the parabolic law. The thickening of the oxide layers on lead, antimony, and tin sulphides, on iron phosphide,  $Fe_2P$ , and on the arsenides,  $Co_2As$ ,  $Co_5As_2$ , and  $FeAs$ , takes place in a manner similar to that on copper-aluminium alloys. Copper phosphide behaves in an anomalous manner when the thickness of the oxide film is between 250 and 350  $\mu\mu$ , but for thinner and thicker films it follows the logarithmic law. A. R. P.

**Order of Reaction of the Reduction of Mercuric Chloride by Sodium Formate.** F. BOURION and E. ROUYER (*Compt. rend.*, 1924, **178**, 1908—1911).—The reaction between mercuric chloride and sodium formate in presence of sodium acetate has been followed kinetically by Ostwald's isolation method. 2 Mols. of mercuric chloride form a complex salt with 1 mol. of sodium

formate or acetate, and a mol. of this complex is reduced by a free mol. of sodium formate, to give a bimolecular constant for the reaction. If sufficient sodium salt is not present for the transformation of all the mercuric chloride into these complex molecules, then the termolecular reaction also proceeds,  $2\text{HgCl}_2 + \text{H}\cdot\text{CO}_2\text{Na} = 2\text{HgCl} + \text{HCl} + \text{CO}_2 + \text{NaCl}$ . S. B.

**Use of Bromate in Volumetric Analysis. IV. Preparation and Properties of Normal and Basic Mercuric Bromate.** G. F. SMITH (*J. Amer. Chem. Soc.*, 1924, **46**, 1577—1583).—Basic mercuric bromate,  $\text{Hg}(\text{OH})\text{BrO}_3$ , may be prepared by the addition of a concentrated solution of mercuric perchlorate to a hot half-saturated solution of sodium bromate in slight excess. The precipitate is quite stable in solution in 2*N*-nitric or perchloric acid owing to the existence of a complex cation,  $\text{Hg}(\text{OH})^+$ .

Normal mercuric bromate,  $\text{Hg}(\text{BrO}_3)_2$ , may be prepared by the action of equivalent quantities of mercuric perchlorate and sodium bromate both in solution in hot 3*N*-perchloric acid. It is hydrolysed in solution in water, and also to some extent in *N*-perchloric acid. The solubilities of the two bromates in nitric and perchloric acids have been determined at 25°. The basic bromate is preferable as a reagent in volumetric bromate reactions (cf. Smith, A., 1913, ii, 504, 573, 650). W. H.-R.

**Action of Potassium Hydroxide on Mercuric Iodide.** H. PÉLABON (*Compt. rend.*, 1924, **178**, 1718—1721).—The nature of the products formed when potassium hydroxide acts on mercuric iodide at 15°, and the equilibrium conditions for different concentrations of the alkali, have been studied. There is no action below a concentration of 0.3 *M*. Between 0.3 and 1.5 *M*, if excess of iodide be present, the iodomercurate,  $\text{HgI}_2\cdot 2\text{KI}$ , is formed in solution and  $\text{C}_{\text{KOH}}^2 = \text{K}\text{C}_{\text{HgI}_2\cdot 2\text{KI}}$ . At concentrations of hydroxide between 1.5 and 7 *M* the phenomena are more complex. Oxyiodides are also formed and, at the higher concentrations, a definite compound,  $\text{HgI}_2\cdot 2\text{HgO}$ , is probably obtained. Above a concentration of 11.5 *M* no more iodomercurate is obtained. With a sufficiently large excess of mercuric iodide a saturated solution of potassium hydroxide gives the compound  $2\text{HgI}_2\cdot \text{HgO}$ , whilst more dilute solutions give a solid of composition corresponding approximately with  $6\text{HgI}_2\cdot \text{HgO}$ .

All the products obtained are very sensitive to light, but are protected by the solutions in which they are formed. M. S. B.

**Action of Light on Cinnabar.** W. H. CROPP (*Proc. Austral. Inst. Min. Met.*, 1923, No. 52, 259—266).—Cinnabar occurs at Puhipuhi, N. Auckland, New Zealand, very finely disseminated through a mass of semi-porous silicious sinter and chalcedony. The latter appears to contain the mineral in the form of a red cloud which imparts a pink to red colour to the mass. On exposure to bright sunlight, the surface colour rapidly turns to bluish-grey, and this change slowly proceeds throughout the mass. Preliminary experiments indicated that the cinnabar is decomposed by the ultra-violet rays of direct sunlight into its elements. A. R. P.

**Separation of the Rare Earths by Basic Precipitation.**  
**VII. Preparation of Pure Praseodymia.** W. PRANDTL and K. HUTTNER (*Z. anorg. Chem.*, 1924, **136**, 289—294; cf. this vol., ii, 48).—After removing thorium and cerium from the earths obtained from monazite, the remaining material is converted into double ammonium or magnesium nitrates and fractionated from nitric acid, the lanthanum head-fractions being added to the neodymium tail fractions from time to time. In this way, the bulk of the neodymium is quickly separated and a crude praseodymium-lanthanum fraction obtained. This fraction is separated from magnesium nitrate, and cadmium and ammonium nitrates in large excess are added. The hot solution is treated slowly with ammonia while being mechanically stirred until several fractions are obtained; these are all dissolved in nitric acid and the process is repeated. The mother-liquors are treated with ammonium carbonate to remove all the rare earths and the cadmium ammonium nitrate solution is used again. After 7 or 8 series of fractionations, the head fractions consist entirely of pure praseodymium. The oxide obtained was of a deep black colour and corresponded almost exactly with the composition  $\text{Pr}_6\text{O}_{11}$ .  
 A. R. P.

**Search for the Element of Atomic Number 61.** W. PRANDTL and A. GRIMM (*Z. anorg. Chem.*, 1924, **136**, 283—288).—This element should be a rare earth intermediate in properties between neodymium and samarium. A large quantity of high-grade neodymium oxide from monazite was fractionated together with a quantity of a mixture of samaria, neodymia, and yttria earths from the mother-liquors of neodymium fractionation and some crude yttria earths from gadolinite, niobite, and samarskite. From 25 kg. of this material 300 g. of intermediate neodymia-samaria fraction were obtained in which any element 61 present should have been concentrated. This product was dissolved in nitric acid, the solution treated with cadmium and ammonium nitrates and subjected to fractional precipitation with ammonia, and the resulting fractions subjected to X-ray analysis. No trace of any unknown element could be detected in any of the fractions, although a good separation of the constituents of the mixture was obtained. It appears therefore that element 61 does not occur with the rare earths and may possibly not exist. If all the rare earth elements are distributed through the various groups in the periodic table in the order of their atomic numbers, element 61 falls in the manganese group, and it is noteworthy that, except for elements 85 and 87, all the missing elements, namely 43, 61, 75, and 93, occur in this group.  
 A. R. P.

**Hydrates and Hydrogels. V. Hydroxides and their Hydrates in the Different Aluminium Hydroxide Gels.** R. WILLSTÄTTER and H. KRAUT (*Ber.*, 1924, **57**, [B], 1082—1091).—Previous experiments (A., 1923, ii, 167, 493) have shown that the composition of desiccator- or vacuum-dried aluminium hydroxides throws little light on the composition of the fresh gels. A new method of desiccation depends on successive treatment



of the gels with anhydrous acetone and ether followed by preservation of the specimens for short periods in a high vacuum. The whole of the adherent water is thereby removed whilst the dehydration of the aluminium hydroxide hydrates is largely governed by the temperature of the treatments.

The action of warm aqueous ammonia on aluminium hydroxide *C* leads to considerable modification of the physical properties of the material without changing its chemical composition or causing intermolecular dehydration with formation of the polyaluminium hydroxides *A* and *B*. The latter substances are formed under the influence of hydroxyl ions from aluminium hydroxide *C* in the nascent condition, *i.e.*, before precipitation, and the isolation of pure polyaluminium hydroxides is possible only when the rate of condensation exceeds that of precipitation. On the basis of these observations, amended methods are given for the preparation of aluminium hydroxides *A*, *B*, and *C*.  
H. W.

**X-Ray Examination of Aged Metallic Hydroxides.** R. FRICKE and F. WEVER (*Z. anorg. Chem.*, 1924, **136**, 321—324).—Specimens of aluminium, chromium, and zinc hydroxides prepared in various ways were examined by the Debye-Scherrer method of X-ray analysis after standing for periods up to 4 years. Gelatinous aluminium hydroxide slowly changes with ageing into crystalline hydrargillite; if heated at 100° for some time, the freshly-precipitated gel shows a tendency to revert to microcrystalline bauxite. Chromium hydroxide, even after prolonged ageing, shows no signs of crystal structure. Zinc hydroxide immediately after drying in the air at ordinary temperatures appears to be partly crystalline; prolonged keeping results in a gradual increase in the amount of crystalline material present.  
A. R. P.

**Chemical Nature of a Colloidal Clay.** R. BRADFIELD (*Missouri Agr. Expt. Sta., Res. Bull.* 60, 1923, 60 pp.).—The colloidal material, less than 0.1 micron in diameter, was separated from a very heavy clay subsoil by means of a centrifuge. All the iron and aluminium in this material was soluble in hydrochloric acid, suggesting that it might consist of a mixture of colloidal silica, alumina, and ferric oxide, being the end-products of complete weathering. A synthetic mixture of these colloids was prepared having a similar chemical composition, but in cataphoresis experiments the synthetic sol was positive and the natural colloid negative. They differed further in that the synthetic material had a much stronger buffer action than the other and was most readily flocculated by multivalent anions in an alkaline medium, whilst the natural colloid was most sensitive to multivalent cations in an acid medium. There were also marked differences in the fractions of the two colloids soluble in dilute acid and alkali. The natural colloid was evidently a complex, easily decomposed aluminosilicate and not a mixture of the colloidal oxides.  
C. T. G.

**Density of Silicon-Iron Alloys and its Relation to Composition.** O. HENGSTENBURG (*Stahl u. Eisen*, 1924, **44**, 914—915).—The specific volume of alloys of iron containing from 25%

to 95% of silicon was determined with an accuracy of 0.7%. The curve obtained shows discontinuities at points corresponding with the compounds  $\text{FeSi}$  and  $\text{FeSi}_2$ . Although thermal investigations have given no evidence of the existence of the latter, crystallographic and chemical analysis of ferrosilicon confirms the fact of its existence at the ordinary temperature. A further discontinuity at the point 61.5% Si indicates the commencement of the separation of silicon or possibly of mixed crystals high in silicon. On the latter assumption, a further discontinuity would occur at the point 95% Si. [Cf. *B.*, 1924, 750.] C. I.

**Decomposition of Ferrous Oxide. Irregularities in Expansion due to its Instability.** G. CHAUDRON and H. FORESTIER (*Compt. rend.*, 1924, 178, 2173—2176; cf. *A.*, 1921, ii, 178).—The velocities of the two opposed reactions,  $4\text{FeO} \rightleftharpoons \text{Fe}_3\text{O}_4 + \text{Fe}$ , have been determined at temperatures in the neighbourhood of  $570^\circ$ . The decomposition of ferrous oxide was not detected below  $300^\circ$ ; it attained a maximum velocity at  $480^\circ$ , 80% being decomposed in 24 hours. Above  $570^\circ$  the reverse action was rapid. Experiments at a constant temperature ( $445^\circ$ ) showed the velocity of the decomposition to agree within 10% with the formula  $dx/dt = k(100-x)^4$ .

Dilatometric observations on ferrous oxide showed an irregularity between  $400^\circ$  and  $500^\circ$ , whilst by using mixtures of iron and the magnetic oxide the reverse reaction was similarly confirmed at  $570^\circ$ . G. M. B.

**Equilibrium of the Reduction of Nickel and Cobalt Chlorides and Bromides by Hydrogen.** II. G. CRUT (*Bull. Soc. chim.*, 1924, [iv], 35, 729—741).—The reduction of nickel chloride by hydrogen was observed in a new apparatus in which the hydrogen chloride formed is diffused rapidly into the hydrogen, the course of the reaction being followed by the variation in the pressure of these gases. At  $430^\circ$ , equilibrium is reached in this apparatus in 12.5 min., the hydrogen chloride concentration being 58%. The chlorination of nickel by hydrogen chloride takes place much more slowly, *e.g.*, equilibrium is only attained at  $430^\circ$  after 11 hours, the concentration of hydrogen chloride being 62.8%. This is considered to be due to the production of nascent hydrogen, which clings to the metal surface and retards the reaction because of its high concentration (cf. this vol., ii, 491). S. K. T.

**Preparation of Pure Chromium by Direct Reduction of Chromic Oxide with Hydrogen.** W. ROHN (*Z. Metallk.*, 1924, 16, 275—277).—Pure metallic chromium may be obtained by reduction of chromic oxide at  $1500^\circ$  in a rapid stream of hydrogen which has previously been freed from every trace of oxygen and water vapour. An apparatus for this purpose is described in which the current of hydrogen is first passed over platinum wire heated at  $1000^\circ$  to remove oxygen, then through sulphuric acid and through a spiral glass tube immersed in liquid air to remove all traces of moisture. The purified gas passes in a rapid stream over small

briquettes of chromic oxide heated at  $1500^{\circ}$  in a Heraeus tube furnace, and the issuing gas passes into the purifying apparatus again and is cooled first by the cold hydrogen from the liquid air flask before passing to that flask. A. R. P.

**Chromium Dioxide.** G. N. RIDLEY (*Chem. News*, 1924, **129**, 35—36).—A list of methods for the preparation of the compound  $\text{CrO}_2$  is given. A. A. E.

**Fluorochromates and Acid Chromates.** R. WEINLAND and H. STAELIN (*Z. anorg. Chem.*, 1924, **136**, 313—320).—By mixing solutions of the requisite quantities of the constituents the following complex chromates and fluorochromates with ethylenediamine, pyridine, quinoline, guanidine, and tetramethylammonium hydroxide have been obtained:  $2\text{CrO}_3, \text{HF}, \text{C}_2\text{H}_4(\text{NH}_2)_2$ , small, yellow columns;  $3\text{CrO}_3, \text{HF}, 2\text{C}_5\text{H}_5\text{N}$ , long, red columns;  $3\text{CrO}_3, \text{HF}, 2\text{C}_9\text{H}_7\text{N}$ , dark red;  $3\text{CrO}_3, \text{H}_2\text{O}, 2\text{C}_5\text{H}_5\text{N}$ , dark red columns;  $3\text{CrO}_3, \text{H}_2\text{O}, 2\text{C}_9\text{H}_7\text{N}$ , reddish-brown, crystalline powder;  $3\text{CrO}_3, \text{H}_2\text{O}, 2\text{CH}_5\text{N}_3$ , large, red octahedra;  $\text{H}_2\text{Cr}_2\text{O}_7, 2\text{C}_9\text{H}_7\text{N}$ , yellowish-brown, crystalline powder;  $\text{H}_2\text{Cr}_2\text{O}_7, 2\text{CH}_5\text{N}_3$ , long, reddish-yellow tablets;  $\text{HCrO}_3\text{F}, \text{C}_5\text{H}_5\text{N}$ , small, reddish-yellow columns;  $\text{HCrO}_3\text{F}, \text{C}_9\text{H}_7\text{N}$ , thin, yellow scales;  $\text{HCrO}_3\text{F}, \text{CH}_5\text{N}_3$ , orange-yellow scales;  $\text{NMe}_4\text{CrO}_3\text{F}$ , fine, orange-yellow crystals;  $\text{AgCrO}_3\text{F}$ , dark-red, insoluble powder;  $\text{TlCrO}_3\text{F}$ , brownish-yellow. A. R. P.

**Thermal Expansion of Molybdenum.** P. HIDNERT and W. B. GERO (*U.S. Bur. Standards, Sci. Paper*, No. 488, 1924).—The mean coefficient of expansion of molybdenum is  $4.9 \times 10^{-6}$  ( $25-100^{\circ}$ ) or  $5.5 \times 10^{-6}$  ( $25-500^{\circ}$ ). A. A. E.

**Electrometric Study of the Acidity of Mixtures of Molybdic and Malic Acids.** E. DARMOIS and A. HONNELAITRE (*Compt. rend.*, 1924, **178**, 2183—2185).—When the  $p_{\text{H}}$  values of a  $0.195N$ -solution of molybdic acid, measured by means of the calomel electrode, are plotted against the fraction  $f$  neutralised by ammonia, the formation of the salt  $\text{NH}_4\text{H}_3(\text{MoO}_4)_2$  is indicated. In the case of  $0.289N$ -malic acid, no acid salt is obtained. With mixtures of the acids of varying normality ( $N=0.4$  to  $3.0$ ) neutrality is only attained by the total saturation of the two acids of the mixture. All curves show an inflection which for the curve  $2N$  is at the point  $f=\frac{1}{3}$ , corresponding with the formation of an ammonium dimolybdomalate. A. COUSEN.

**Structure of Mixed Crystals.** A. E. VAN ARKEL (*Physica*, 1924, **4**, 33—41).—X-Ray examination of mixed crystals of tungsten and molybdenum (50%) and of silver and gold (25—75%) failed to support Tammann's theory (A., 1919, ii, 398, 406) that in mixed crystals the atoms are arranged in a space-lattice with definite places for the components. The spectrum of thallos bromide gave  $d_{100}=3.98 \pm 0.01 \text{ \AA.}$  and  $d=7.50$ . CHEMICAL ABSTRACTS.

**Reduction Potential of Quinquevalent Tungsten Chloride.**

O. COLLENBERG and A. GUTHE (*Z. anorg. Chem.*, 1924, **136**, 252—256).—The potential of a solution containing the compounds  $\text{KWO}_2\text{Cl}_3$  and  $\text{K}_2\text{WOCl}_5$  in equimolecular concentration in concentrated hydrochloric acid was +0.26 volt when the total concentration of tungsten was 0.143 g.-atom per litre. The curve showing the variation of this potential with a change in the ratio  $W^{IV}/W^V$  follows closely that deduced from theoretical considerations except for solutions in which the quinquevalent chloride greatly predominates. This deviation is probably due to unequal dissociation of the two chlorides.

A. R. P.

**Crystal Structure of Uranyl Nitrate Hexahydrate.**

L. PAULING and R. G. DICKINSON (*J. Amer. Chem. Soc.*, 1924, **46**, 1615—1622).—The unit of structure of uranyl nitrate hexahydrate (rhombohedral) contains four molecules of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and has  $d_{100}$  13.15,  $d_{010}$  8.02, and  $d_{001}$  11.42 Å.; it is end centred on (001). The space group symmetry is  $V_h^{17}$ , and the uranium atoms are at  $(0u\frac{1}{4})(0\bar{u}\frac{3}{4})(\frac{1}{2}\frac{1}{2}+u\frac{1}{4})(\frac{1}{2}\frac{1}{2}-u\frac{3}{4})$  with  $u=0.13$ . The above axes are assigned in accordance with the conventions of the theory of space groups. Referred to the axes used by Groth (*Chemische Kristallographie*, 1908, **2**, 142) the above-mentioned inter-planar distances are for the planes (010), (001), and (100), respectively. The conclusions of Clark (this vol., ii, 299) are shown to be unjustified.

W. H.-R.

**Revision of the Atomic Weight of Antimony. Analysis of Antimony Trichloride and Tribromide.**

O. HÖNIGSCHMID, E. ZINTL, and M. LINHARD (*Z. anorg. Chem.*, 1924, **136**, 257—282).—Pure antimony was prepared by repeatedly precipitating chloroantimonic acid,  $\text{HSbCl}_6 \cdot 4.5\text{H}_2\text{O}$ , from a solution of antimony pentachloride by saturation with hydrogen chloride, hydrolysing this compound to obtain antimonic acid and reducing this in hydrogen at 500°. The metal was converted into chloride or bromide by heating in a current of the halogen and the resulting halide was fractionally distilled, first in pure nitrogen, then in a vacuum. The silver equivalent of each halide was determined by gravimetric titration and by weighing the silver halide formed. The mean of 32 very concordant results gave 121.76 as the atomic weight of antimony, taking those of silver, chlorine, and bromine as 107.88, 35.457, and 79.916 respectively.

A. R. P.

**Preparation of Gold Crystals.**

H. R. ADAM (*J. Chem. Met. Soc. S. Afr.*, 1924, **24**, 258—260).—A 1% gold amalgam that has been maintained at 70—80° for several days leaves a residue of octahedral crystals of gold after treatment with nitric acid; these crystals are grouped together into arborescent shapes when the temperature is kept at 150° for some hours. A 2% gold amalgam after similar treatment yields long, hexagonal prisms which are very brittle and tenaciously retain mercury even after repeated digestion with nitric acid. It is suggested that the hexagonal crystals are pseudomorphs after a compound of gold and mercury, possibly  $\text{Au}_2\text{Hg}$ .

A. R. P.

## Mineralogical Chemistry.

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**Ulmic Constituents of Coal.** A. R. PEARSON (*Fuel*, 1924, **3**, 297—300).—The nitrogenous substances, ulmins, present in coal are readily oxidised to form hydrophilic colloids. The oxidation may be continued until the percentage of oxygen reaches 40—45 and the carbon : oxygen ratio is about 1 : 1. The products from various coals are similar in composition. On further oxidation of the aqueous sols with bromine and alkali, there is considerable loss of carbon and also a loss of nitrogen. Oxalic acid, bromoform, volatile nitriles, and primary amines are produced. Amorphous substances having the physical properties of resins are finally obtained. These on distillation yield phenols. There appear to be two stages in the oxidation of the ulmins, in the second of which the molecule is degraded. The existence of these two stages harmonises with a hypothesis advanced by Jones and Wheeler (*T.*, 1914, **104**, 140). In the first stage, the hydrogenated peripheral groups or side-chains of a cyclic nucleus are removed; in the second the ring system is attacked. The ultimate constitution of the nucleus is approximately the same in all coals. The formation of coke will depend on the fusibility of the coal ulmins, and this depends on their molecular complexity. Ulmins from anthracite and coking coals are most readily precipitated by sodium chloride, and have therefore the most complex nuclei. [Cf. *B.*, 1924, 699.]

T. S. W.

**Cause of Colour in Rose Quartz.** E. F. HOLDEN (*Amer. Mineral.*, 1924, **9**, 75—88, 101—108).—The colour of rose quartz is not due to the action of radioactive substances on white quartz, but to the presence of tervalent manganese, since the depth of colour increases with the manganese content; when heated at 575°, decolorisation takes place owing to a valency change in the manganese.

CHEMICAL ABSTRACTS.

**Radioactivity of some Indian Minerals.** N. A. YAJNIK and S. J. KOHLI (*J. Proc. Asiatic Soc. Bengal*, 1922, **18**, 73—74).—Uranium-ochre and samarskite were the most active, the radium content being  $21434 \times 10^{-12}$  and  $1187.2 \times 10^{-12}$  g. per g. respectively; apatite-magnetite contained  $1324.9 \times 10^{-12}$  g. per g.

CHEMICAL ABSTRACTS.

**Hafnium Content of Zirconium Minerals.** II. G. VON HEVESY and V. T. JANTZEN (*Z. anorg. Chem.*, 1924, **136**, 387—392).—The hafnium content of some zirconium minerals was found to be as follows: blue, transparent zircon from Siam, 3.5%  $\text{HfO}_2$ ; malacon from Hitterö and from Madagascar, 5.0%  $\text{HfO}_2$ ; zirkelite from Ceylon, 1.2%  $\text{HfO}_2$ ; elpidite from Narsarsuk, 0.4%  $\text{HfO}_2$ ; baddeleyite, 3%  $\text{HfO}_2$ . Thortveitite from Norway and from Madagascar was found to contain both zirconia and hafnia, the latter oxide generally predominating.

A. R. P.

**Pseudomorph of Curite.** W. VERNADSKY and C. CHAMIE (*Compt. rend.*, 1924, **178**, 1726—1728).—The crystalline form of a curite from the Belgian Congo, containing lead which is wholly of radioactive origin (Hönigschmid and Birkenbach, A., 1923, ii, 764; Richards and Putzeys, this vol., ii, 111), indicates that the mineral is probably an alteration product of pitchblende. The disproportionately large amount of uranium-lead present suggests that the original pitchblende also was a secondary mineral.

M. S. B.

**Phosphorescence of American Iceland Spar after Radium Radiation.** S. C. LIND (*Science*, 1924, **59**, 238).—Radiation of specimens of Iceland spar produced a reddish-orange phosphorescence, increasing in brilliance on rise of temperature. A. A. E.

**Density of Carbon Dioxide from Natural Limestones.** A. P. LIDOV.—(See ii, 607.)

**New Type of Aluminous Chlorite.** J. ORCEL (*Compt. rend.*, 1924, **178**, 1729—1731).—The mineral, from a serpentine and talc massif which crosses the satin schist of the valley of Comberousse, is composed of greenish-white, crystalline masses of the appearance and hardness of talc, but with a saccharoidal fracture and a spheroidal structure; *d* 2.67. Analysis:  $\text{SiO}_2$ , 27.12;  $\text{Al}_2\text{O}_3$ , 27.68;  $\text{Fe}_2\text{O}_3$ , 0.20;  $\text{FeO}$ , 1.24;  $\text{MnO}$ , 0.54;  $\text{MgO}$ , 30.96;  $\text{H}_2\text{O}$  at  $108^\circ$ , 0.01;  $\text{H}_2\text{O}$  at  $725^\circ$ , 2.65;  $\text{H}_2\text{O}$  at  $880^\circ$ , 10.17; total, 100.57. The result corresponds almost exactly with the formula  $5\text{SiO}_2, 3\text{Al}_2\text{O}_3, 9\text{MgO}, 8\text{H}_2\text{O}$ , and the mineral is therefore intermediate between magnesian prochlorites and corundophyllite. Brinton chlorite has a composition approximating to the formula  $5\text{SiO}_2, 3\text{Al}_2\text{O}_3, 8\text{MgO}, 8\text{H}_2\text{O}$ .

M. S. B.

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### Analytical Chemistry.

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**Melting-point Determination.** O. GERNGROSS and M. DUNKEL (*Ber.*, 1924, **57**, [B], 1071).—In the apparatus previously described (*ibid.*, 739), a thin wire passing through the two tubes and a wire gauze and tripod support the apparatus. R. B.

**Apparatus for Ultrafiltration.** H. BECHHOLD and L. GUTLOHN (*Z. angew. Chem.*, 1924, **37**, 494—497).—Crucibles, dishes, cylindrical filter funnels, etc. are made of porous earthenware and are coated inside with a membrane of collodion or the like. They are placed on a rubber ring on a filter-flask to which is attached a water pump. The quantity of liquid that can be filtered depends not so much on the porosity of the vessel as on the nature of the membrane, and this again depends on the manner in which it is produced. The porous material is resistant to red heat, at which the membrane burns away quietly and without ash. The apparatus

can be used with advantage in analysis, *e.g.*, for filtration of barium sulphate, aluminium hydroxide, colloidal silver, hæmoglobin, and for the removal of protective substances and electrolytes from colloidal solutions.

W. T. K. B.

**"Polydyn" Filter, which can be Heated to Redness, Suitable for Membrane Filtration (Ultrafiltration) and Quantitative Analysis.** L. ZAKARIAS (*Z. angew. Chem.*, 1924, **37**, 425).—A Gooch crucible can be utilised for ultrafiltration by introducing a filter-plate (membrane filter with cellulose acetate or unglazed porcelain) and a bottomless porcelain cylinder, and holding the whole together by means of a rubber ring and clamp. The apparatus is placed on a suction flask in the usual way.

W. T. K. B.

**[Burette for] Gas Analysis.** W. MOLDENHAUER (*Z. angew. Chem.*, 1924, **37**, 424—425).—The top of the gas burette carries two short capillary tubes and the tap is so bored that communication can be established between the tubes and between one of them and the interior of the burette.

The method of filling and using the absorption pipette in association with the burette is described.

W. T. K. B.

**Evaporation of Solutions and Liquids in Burettes.** M. G. MELLON (*Proc. Indiana Acad. Sci.*, 1922, 159—164).—Changes due to barometric pressure and relative humidities are negligible; variations in temperature cause changes in volume greater than those due to changes in vapour pressure, and in the opposite direction.

CHEMICAL ABSTRACTS.

**Use of Cool Solutions in the Jones Reductor.** G. E. F. LUNDELL and H. B. KNOWLES (*Ind. Eng. Chem.*, 1924, **16**, 723, 724).—Quantitative reductions result with the Jones reductor at room temperatures in all present applications. [Cf. *B.*, 1924, 771.]

D. G. H.

**Micro-vessel with Electrode for Determining the  $p_H$  of Blood and Body Fluids.** F. DE EDS and P. J. HANZLIK (*J. Biol. Chem.*, 1924, **60**, 355—360).—The errors liable to arise in the electrometric determination of the  $p_H$  of blood, owing to the inadvertent admission of oxygen to the vessel or to the depolarisation of the electrode by the oxyhæmoglobin, have been reduced by using a very small vessel and arranging for minimal contact between the fluid and electrode. The apparatus described requires less than 0.1 c.c. for a determination.

C. R. H.

**Indicators. IX. Azo-indicators with Asymmetric Nuclei.** A. THIEL and F. WÜLFKEN (*Z. anorg. Chem.*, 1924, **136**, 393—405).—The colour changes with variation in the hydrogen-ion concentration of solutions of derivatives of  $\alpha$ -naphthylamine in which a benzene ring is coupled by means of a diazo group to the naphthalene nucleus (*cf.* Howard and Pope, *T.*, 1911, **99**, 1333) have been investigated spectrophotometrically. With these compounds, the colour change from yellow or orange to a deep violet-blue is



extremely sharp, but in aqueous solutions the compounds are practically insoluble at hydrogen-ion concentrations near the neutral point. When acid or alkaline solutions of  $\alpha$ -naphthylamine-azobenzene-*p*-sulphonic acid or of the corresponding monophenyl substituted acid are progressively neutralised, the dyestuff is caused to flocculate gradually and the actual point at which this occurs may be ascertained by observing when the solution absorbs light of the smaller wave-lengths. Addition of protective colloids, such as sodium caseinate or ovalbumin, tends to prevent the flocculation, but does not assist in obtaining sharper end-points. Spectrophotometric measurements of the behaviour of this group of indicators have been obtained by examination of the colour changes in 50% alcoholic solution and the results are tabulated for light of different wave-lengths. The most delicate colour-changes take place in the basic dyestuffs of this group, whilst the carboxylic acids are the least delicate indicators. The  $p_H$  ranges of some members of the group are given. A. R. P.

**Indicators. X. Influence of the Solvent with Special Reference to the "Alcohol Error" of Indicators.** A. THIEL, F. WÜLFKEN, and A. DASSLER (*Z. anorg. Chem.*, 1924, **136**, 406—415).—Determinations of the isobathmic curves (absorption curves for different wave-lengths at equal acidity) of solutions of methyl-yellow, of *p*- and *o*-methyl-red, and of *o*- and *p*-helianthin in alcohol and water show that, contrary to previous statements, the nature of the solvent has an appreciable effect on the colour change, probably owing to some chemical reaction between the indicator and the supposedly indifferent solvent. The nature of this effect varies with different indicators and solvents and cannot be explained by the accepted theory of indicators. The neutral point of all the above indicators is affected by the presence of ethyl or methyl alcohol or of acetone, but only *o*-methyl-red is affected by the presence of ether. A. R. P.

**Indicator Reaction as a Source of Error in  $p_H$  Determinations.** F. W. MARSH (*Science*, 1924, **59**, 216).—The use of indicator solutions stored in glass bottles for  $p_H$  determinations gives rise to errors which cannot be eliminated by the use of the same indicator solution as for the control determination. A "spot" method of adjusting the reaction of the indicator solutions is described; the adjustment is, however, unnecessary for highly buffered solutions. A. A. E.

**Determination of  $p_H$  with One-colour Indicators in Alcoholic Solutions.** L. MICHAELIS and M. MIZUTANI (*Biochem. Z.*, 1924, **147**, 7—21).—The "reduced dissociation constant,"  $k'$ , of an indicator in non-aqueous solution is given as  $k' = a_H \cdot (F/1 - F)$ , where  $a_H = c_H \cdot f_H$  ( $f$ =activity coefficient) and  $F$ =colour intensity of a one-colour indicator (Michaelis and Krüger, A., 1922, ii, 157). Tables are given, and the method is described, for determining the  $p_H$  of alcoholic solutions using phenolphthalein, *m*- and *p*-nitrophenols, and 2:4- and 2:5-dinitrophenols as indicators without buffers. J. P.

**Wet Oxidation and Modified Volhard Method for the Determination of Chlorides in Plant-tissue Fluids.** J. V. LAWRENCE and J. A. HARRIS (*J. Amer. Chem. Soc.*, 1924, **46**, 1471—1477).—The tissue fluid is boiled with 0.1*N*-silver nitrate solution (10—20 c.c.) and nitric acid until the colour is destroyed and no solid matter remains except the silver chloride. After cooling, the excess of silver nitrate is titrated directly, without removal of the silver chloride, with standard potassium thiocyanate solution. The method is accurate, and applicable to the analysis of substances (*e.g.*, hides) of much higher protein content than saps, but is not recommended for blood analysis on account of the resistance of hæmoglobin to the action of nitric acid (*cf.* Van Slyke, this vol., ii, 271). F. G. W.

**Use of Antimony Trichloride for the Volumetric Determination of Hypochlorites, Ferri- and Ferro-cyanides.** F. FEIGL and O. SCHUMMER (*Z. anal. Chem.*, 1924, **64**, 249—255).—When a solution containing hypochlorite is treated with an excess of a standard solution of antimony trichloride, in presence of hydrochloric acid, the reduction of the hypochlorite is instantaneous. The excess of antimony trichloride is determined by back-titration with a standard solution of potassium bromate, using methyl-orange (or indigo) as indicator: (i)  $\text{NaOCl} + \text{SbCl}_3 + 2\text{HCl} = \text{NaCl} + \text{H}_2\text{O} + \text{SbCl}_5$ ; (ii)  $3\text{SbCl}_3 + \text{KBrO}_3 + 6\text{HCl} = 3\text{SbCl}_5 + \text{KBr} + 3\text{H}_2\text{O}$ ; (iii)  $\text{KBrO}_3 + 5\text{KBr} + 6\text{HCl} = 6\text{Br} + 6\text{KCl} + 3\text{H}_2\text{O}$ . The method is also applicable to the evaluation of bleaching powder. Potassium ferricyanide is completely reduced in a few minutes, in strongly acid solution, on gentle warming with excess of antimony trichloride. The resulting yellow solution renders the back-titration unsatisfactory, so the ferrocyanide is removed by precipitation with a zinc salt; the excess of antimony trichloride may be accurately ascertained with potassium bromate solution.  $2\text{K}_3\text{FeC}_6\text{N}_6 + \text{SbCl}_3 + 4\text{HCl} = \text{K}_4\text{FeC}_6\text{N}_6 + \text{H}_4\text{FeC}_6\text{N}_6 + \text{SbCl}_5 + 2\text{KCl}$ . Ferrocyanides are first oxidised to ferricyanides by potassium permanganate in presence of sulphuric acid, and the excess of potassium permanganate is removed by a few drops of oxalic acid. The resulting ferricyanide is then determined as before. A slight excess of oxalic acid does not affect the accuracy of the result. J. B. F.

**Volatility of Bromine in Solutions of Different Electrolytes and its bearing on Bromometric Analysis.** G. JANDER and H. FEIT.—(See ii, 604.)

**Use of Bromate in Volumetric Analysis.** IV. G. F. SMITH.—(See ii, 614.)

**Determination of Iodine in Food, Drink, and Excreta.** J. F. MCCLENDON (*J. Biol. Chem.*, 1924, **60**, 289—299).—The organic matter is removed by combustion in a rapid stream of oxygen. The vapours from the combustion are led through sodium hydroxide solution to absorb volatilised iodine. Finally, the iodine in this solution and in the ash from the combustion is liber-

ated, extracted with carbon tetrachloride, and determined colorimetrically. Quantities of the order of 0.01 mg. of iodine may be determined.

C. R. H.

**Volumetric Determination of Fluorine.** W. W. SCOTT (*Ind. Eng. Chem.*, 1924, **16**, 703—707).—After preliminary removal, if necessary, of phosphates or sulphates by extraction with dilute acetic acid, the material is fused with sodium carbonate, potassium hydroxide, and silica, the mass disintegrated, treated with water and hydrogen peroxide, boiled, and filtered. Calcium is determined volumetrically as oxalate in the residue. Fluorine is determined in the filtrate by precipitation with a known excess of calcium acetate and subsequent volumetric determination of the calcium remaining in solution. Alkali fluorides, dissolved in hot water, may be similarly analysed.

D. G. H.

**Determination of Total Sulphur in Neosalvarsan and "Sulpharsphenamine."** E. ELVOVE (*U.S. Pub. Health Repts.*, 1924, **39**, 750—754).—The substance is dissolved in aqueous sodium chloride, and mixed with potassium permanganate solution and hydrochloric acid. After keeping, the liquid is evaporated to dryness, the residue then being acidified and stirred with hydrogen peroxide solution. Excess of hydrogen peroxide is removed with permanganate and, after decolorising with oxalic acid and filtering, the sulphate is determined gravimetrically in an aliquot portion.

CHEMICAL ABSTRACTS.

**Analysis of Chlorosulphonic Acid.** C. MAYR (*Z. anorg. Chem.*, 1924, **136**, 238—244).—The chlorosulphonic acid content of the technical acid cannot be determined by treatment with water followed by titration of the total acidity and chlorine content, as small amounts of sulphuric and hydrochloric acids are always present. The analysis should be conducted by distilling a large quantity of the acid in a current of carbon dioxide until the temperature rises to 160°. The residue in the distillation flask is weighed, treated with water, and a portion of the solution titrated with sodium carbonate for total acidity; a second portion is neutralised with sodium hydroxide and the chlorine determined by Mohr's method. The chlorine figure is calculated to  $\text{ClSO}_3\text{H}$  and the remaining acidity is reckoned as sulphuric acid. The liquid distillate is analysed in a similar manner. Any free hydrochloric acid passes through the receivers and is collected in a Pélégot tube. [Cf. *B.*, 1924, 710.]

A. R. P.

**Volumetric Method of Elementary Analysis.** L. HACKSPILL and G. D'HUART (*Bull. Soc. chim.*, 1924, [iv], **35**, 800—803).—The method previously described (*A.*, 1923, ii, 578) gives high results for nitrogen owing to the presence of adsorbed air in the cupric oxide. This error is eliminated by oxidising the copper in oxygen. The analysis is hastened by reducing the total volume of the apparatus, and by replacing the Sprengel with a Germann-Cardoso pump. Other minor improvements are also described.

S. K. T.

**Extension of the Van Slyke Table of Factors for the Conversion of Nitrogen Gas into mg. of Amino Nitrogen.** P. F. SHARP (*J. Biol. Chem.*, 1924, **60**, 77—78).—Van Slyke's table of factors has been considerably extended and figures are given for intervals of 10 mm. over a range of barometric pressure from 520 to 780 mm. of mercury. Intermediate values can be interpolated by the use of the proportional parts included in the table.  
C. T. G.

**Ammonia Content of Blood.** S. R. BENEDICT and T. P. NASH (*Z. physiol. Chem.*, 1924, **136**, 130—133).—Polemical. The method employed by Henriques (A., 1923, i, 1250) for determining ammonia in blood is not accurate and gives very high results (cf. A., 1922, i, 191, 483). His results cannot be used to refute the authors' view that urinary ammonia results from ammonia formation in the kidney.  
D. R. N.

**Detection of Nitrous Acid.** H. STOFF (*Z. anal. Chem.*, 1924, **64**, 272—273; cf. Zlataroff, A., 1923, ii, 505).—The colour change produced by an aqueous solution of neutral red due to the presence of nitrite is not sufficiently marked to be accurate when free hydrochloric or sulphuric acid is also present. In sulphuric acid solution the presence of nitrates intensifies the colour. The reaction is also disturbed by the presence of dissolved organic compounds (oxidisable by potassium permanganate) and by ferric, ferrous, and manganous salts. In acetic acid solution, the reaction fails completely. The detection of nitrites with neutral-red succeeds without exception only in phosphoric acid solution; the limit of sensitivity is 0.2 mg.  $N_2O_3$  per litre.  
J. B. F.

**Determination of Phosphorus in Ferrovandium.** K. SWOBODA (*Oesterr. Chem.-Ztg.*, 1924, **27**, 110—113).—If the ordinary procedure for determining phosphorus is followed with ferrovandium, the ammonium phosphomolybdate precipitate will be seriously contaminated with complexes containing vanadic acid. This may be prevented by reducing the vanadic acid with metallic iron shortly before adding the molybdate reagent. The interference of arsenic is also obviated by this procedure if the first phosphomolybdate precipitate is dissolved in ammonia and reprecipitated. [Cf. B., 1924, 715.]  
A. R. P.

**Determination of Phosphorus in Blood.** M. MARTLAND and R. ROBISON (*Biochem. J.*, 1924, **18**, 765—768).—With Briggs' modification of the Bell-Doisy method it is preferable after ignition with nitric and sulphuric acids to use 2 c.c. of a 5% solution of ammonium molybdate instead of 2 c.c. of Briggs' molybdate solution. Trichloroacetic acid also produces a colour with the Briggs reagents in complete absence of inorganic phosphate. The colour is produced very slowly, and is due to an impurity of high b. p. A higher figure is obtained for the inorganic phosphates of blood even if a few minutes be allowed to elapse between

laking and precipitation of the proteins. It is also increased after anæsthesia and as a result of shock consequent upon cardiac puncture.

S. S. Z.

**Determination of Carbon Monoxide.** P. LEBEAU and C. BEDEL (*Compt. rend.*, 1924, **179**, 108—110).—The addition of phenolic substances to a suspension of cuprous oxide in sulphuric acid increases the solubility of the former and forms a solution which is a good absorbent for carbon monoxide. Thus, 1 c.c. of the filtrate from 10 g. of  $\beta$ -naphthol shaken for several hours with a suspension of 5 g. of cuprous oxide in a cooled mixture of 95 g. of sulphuric acid and 5 g. of water, after being kept for several days, decanted and preserved out of contact with air, absorbs 18 c.c. of carbon monoxide forming a complex which is quite stable up to 100°. Addition of water also causes no decomposition with loss of carbon monoxide. Dissociation of the complex ceases to be appreciable when the proportions of cuprous oxide and carbon monoxide correspond with  $\text{Cu}_2\text{SO}_4 \cdot 2\text{CO}$ . The reagent absorbs 20 times its volume of ethylene, absorbs acetylene less readily, and only very slowly reacts with oxygen. It does not readily attack mercury.

J. W. B.

**Mixed Indicator for Carbonate and Hydrogen Carbonate Titrations.** S. G. SIMPSON (*Ind. Eng. Chem.*, 1924, **16**, 709).—Using as indicator a mixture of cresol-red and thymol-blue, a sharp end-point is obtained in carbonate titrations corresponding closely with the half-neutralisation point, and methyl-orange or, better, bromophenol-blue used in the same solution shows a sharp change from blue to green on complete neutralisation. When phenolphthalein is used as the first indicator the change of colour is gradual and the titrations are inaccurate.

D. G. H.

**Alkalimetry of Zinc Ammonium Phosphate.** J. W. SPRINGER (*Z. angew. Chem.*, 1924, **37**, 482—483).—Zinc may be precipitated as zinc ammonium phosphate and this compound collected, dried, and weighed, or converted by heat into zinc pyrophosphate. Other metals (*e.g.*, calcium, magnesium, iron, aluminium, manganese) may be first removed as phosphate from a solution containing sufficient ammonia to retain the zinc salt in solution.

Zinc may be determined volumetrically by precipitation in nearly or completely neutral solution as zinc ammonium phosphate, dissolution of this in a known quantity of standard acid, and titration of the excess.

W. T. K. B.

**Determination of Copper by Zecchini's Method and its Application to the Determination of Reducing Sugars.** P. FLEURY and P. TAVERNIER (*Bull. Soc. chim.*, 1924, [iv], **35**, 794—799).—The Zecchini-Incze method of determining copper (*A.*, 1915, ii, 487) is applicable to the determination of dextrose with Fehling's solution (*cf.* this vol., ii, 425).

S. K. T.

**Determination of Mercury as Mercurous Chloride and as Metal.** L. W. WINKLER (*Z. anal. Chem.*, 1924, **64**, 262—272).—Mercury may be accurately determined, as metal, from nitric

acid solution when the amount of metal is not too small (0.5 to 1 g. per 100 c.c.). Calcium hypophosphite is recommended as precipitant although sodium or potassium hypophosphite may be used. The method is applicable in the presence of lead, cadmium, or zinc, provided the proportion of mercury is not too small, but not in the presence of copper salts, since these are also reduced by hypophosphites. If the amount of mercury present is small (0.1 to 0.5 g. per 100 c.c.) it is determined as mercurous chloride, by reduction and precipitation with phosphorous acid in presence of hydrochloric acid. This method is applicable in presence of copper salts. The precipitating solution is prepared by treating 10 c.c. of pure phosphorus trichloride with 200 c.c. of distilled water and diluting the solution to 250 c.c. J. B. F.

**Determination of Manganese by the Persulphate Method in the Presence of Hydrofluoric Acid.** J. VERNAY (*Chim. et Ind.*, 1924, **11**, 1093—1095).—The solution of the sample in nitric or sulphuric acid is treated at 80° with a solution of potassium fluoride, silver nitrate, and ammonium persulphate. After 15 mins. the solution is cooled, diluted considerably, and titrated with sodium arsenite. [Cf. *B.*, 1924, 715, and Swoboda, this vol., ii, 570.] A. R. P.

**Standardisation of Potassium Permanganate by Means of Metallic Silver.** N. A. TANANAEV (*Z. anorg. Chem.*, 1924, **136**, 193—202).—Finely-divided silver or thin silver sheet dissolves readily in an excess of a solution of iron alum with the formation of a corresponding amount of ferrous sulphate; the reaction is reversible, but under suitable conditions forms a basis for standardising permanganate solutions. The rate of solution of the silver increases with a rise in concentration of the free sulphuric acid and with the temperature. The most satisfactory conditions are obtained by shaking the requisite quantity of silver with a 5% solution of iron alum in 20% sulphuric acid in an atmosphere of carbon dioxide; towards the end of the reaction the liquid should be slowly heated to boiling. [Cf. *B.*, 1924, 734.] A. R. P.

**Standardisation of Permanganate with Various Substances.** I. M. KOLTHOFF (*Z. anal. Chem.*, 1924, **64**, 255—262).—The results obtained in the standardisation of potassium permanganate with oxalic acid, sodium oxalate, ferrous ammonium sulphate, arsenious oxide, potassium ferrocyanide, potassium iodide, and potassium iodate do not differ by more than 0.05%. J. B. F.

**Standardisation of Permanganate by Means of Different Materials.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1924, **61**, 786—789).—Potassium ferrocyanide in presence of sulphuric acid can be very accurately titrated with potassium permanganate potentiometrically; potassium iodide is equally suitable, and potassium iodate may also be used, after reduction with sulphite. S. I. L.

**Determination of Nickel in Ores and Alloys by Means of Dimethylglyoxime.** J. G. WEELDENBURG (*Chem. Weekblad*, 1924, **21**, 358—362).—The reagent gives accurate results in alcoholic solution or in aqueous sodium hydroxide solution; in this latter case, the nickel solution should be faintly acid. Arsenic and antimony do not interfere, if tartaric acid be present; tin causes the result to be too high and must be removed. Lead in small quantities is held in solution by tartaric acid, in larger quantities by ammonium acetate. Bismuth if not in large excess is held in solution by tartaric acid, chromium by tartaric acid and ammonium chloride. Silver and the alkaline-earths always interfere and must be removed. Iron and cobalt, if present together, form an insoluble dimethylglyoxime compound, but this may be prevented by reducing the iron with sulphurous acid. Ores or alloys are dissolved in aqua regia, lead and the alkaline-earth metals precipitated with ammonium sulphate, and the filtrate is treated with hydrogen sulphide; nickel is then determined in the filtrate in presence of tartaric acid and ammonium chloride.

S. I. L.

**Determination of Vanadium by Reduction with Hydrogen Peroxide and Titration with Potassium Permanganate.** A. W. HOTHERSALL (*J. Soc. Chem. Ind.*, 1924, **43**, 270—272T).—The solution is evaporated with sulphuric acid until fumes are evolved. Organic matter is destroyed by heating again with powdered potassium permanganate and the excess of the latter is removed by hydrogen peroxide. The liquid is again evaporated until fumes appear, allowed to get quite cold, and treated with hydrogen peroxide drop by drop. The vanadic acid is thus reduced to vanadyl sulphate, which, after keeping for 10 to 15 mins., causes the excess of hydrogen peroxide to be decomposed catalytically. The solution is diluted to 300 c.c., heated at 70°, and titrated with permanganate. Any solid substances separating on evaporation with sulphuric acid must be dissolved by the addition of 2 vols. of water. The cold solution is treated with hydrogen peroxide and a few crystals of potassium bromide and, after 24 hours, evaporated until fumes of sulphur trioxide are evolved. The cooled mass is dissolved in water and the solution titrated as before. Iron, copper, molybdenum, arsenic, and uranium do not interfere, but chromium causes high results to be obtained.

A. R. P.

**Detection of Bismuth in Urine and Cephalo-rachidian Fluid.** FABRÈGUE and J. BRESSIER (*J. Pharm. Chim.*, 1924, [vii], **30**, 11—12).—In the methods of Léger and Aubry traces of liberated iodine cause a yellow coloration which interferes with colorimetric determinations. A test solution is therefore prepared by dissolving 1 g. of quinine sulphate in 10 c.c. of distilled water acidified with 20 drops of glacial acetic acid, an aqueous solution of 2 g. of potassium iodide (containing no iodate or free iodine) is added, and the whole made up to 100 c.c. The organic liquid to be examined is evaporated with a small quantity of pure ammonium nitrate, and the residue incinerated and calcined. The ash is dissolved in glacial acetic acid, the solution heated on the water-bath, aqueous

acetic acid is added, the mixture filtered, and the filtrate is mixed with the test solution. Traces of bismuth can thus be readily detected and determined.

W. T. K. B.

**Determination of Organic Vapours in Gas Mixtures by Means of Active Charcoal.** F. FISCHER and C. ZERBE (*Z. angew. Chem.*, 1924, **37**, 483; cf. Berl and Wachendorff, this vol., ii, 505).—Transference of charcoal containing adsorbed benzene to a vessel of wide cross-section for the purpose of treating with steam gives less consistent results than if the steaming is carried out in the same vessel (U-tube) in which adsorption took place. This, together with possible volatilisation losses during transference, accounts for the irregularities previously observed by the present authors (cf. *B.*, 1924, 43), and not found by the authors quoted.

W. T. K. B.

**The Identification of Phenols by Means of the Spectroscope.** S. PALKIN and H. WALES (*J. Amer. Chem. Soc.*, 1924, **46**, 1488—1493).—Phenols, particularly in medicinal preparations, can be trustworthily identified, in quantities down to 0.5 mg., by spectroscopic examination of (alkaline) acetone, alcoholic, and aqueous solutions of the dyes formed by coupling the phenols with *p*-nitrodiazobenzene. The positions of the absorption bands, in the three solvents, for the dyes from phenol, *m*- and *p*-cresols, resorcinol, guaiacol, guaiacolsulphonic acid ("thiocol"), phenolsulphonic acid,  $\alpha$ - and  $\beta$ -naphthols, salicylic acid, thymol, phenolphthalein, saligenin, eugenol, and carvacrol, are tabulated and graphed.

F. G. W.

**Distinction between  $\alpha$ - and  $\beta$ -Naphthol.** H. KRAUSE (*Color Trade J.*, 1924, **14**, 87).—The sample is dissolved in absolute alcohol, cooled, and metallic sodium added until no more dissolves.  $\alpha$ -Naphthol gives a pale green colour with fluorescence, which becomes colourless although the fluorescence remains.  $\beta$ -Naphthol gives a deep royal-blue colour with an intense bluish-violet fluorescence. If more sodium is added to the  $\beta$ -naphthol solution the colour changes to olive-green, brown, and finally orange, but the fluorescence remains.

CHEMICAL ABSTRACTS.

**Detection of Picric Acid and its Reduction Products in Toxicology.** P. BIGINELLI (*Annali Chim. Appl.*, 1924, **14**, 209—222).—Methods are given for the detection of picric or picramic acid in the urine or on the clothes of individuals who have taken a dose of picric acid in order to induce an attack of sham jaundice.

T. H. P.

**Colorimetric Determination of Carbohydrates in Plants by the Picric Acid Reduction Method. I. Determination of Reducing Sugars and Sucrose.** W. THOMAS and R. A. DUTCHER (*J. Amer. Chem. Soc.*, 1924, **46**, 1662—1669).—The method of Benedict and Osterberg (*A.*, 1918, ii, 246) for the determination of sugars in urine has been modified for the determination of reducing sugars and sucrose in plant extracts. The colorimetric method is



superior to the gravimetric and volumetric methods for the determination of small amounts of sugars. More accurate values for reducing sugars are obtained by the use of mercuric nitrate in place of lead acetate as a precipitating agent to remove proteins, tannins, and amino-acids, since the former reagent removes substances having a slight reducing action on Fehling's solution and a much stronger action on the picrate-picric solution. The plant is extracted with alcohol, and an aqueous solution of the residue left on evaporation of an aliquot part is mixed with a slight excess of mercuric nitrate solution. The solution is made alkaline to litmus, filtered, and an aliquot part is treated with zinc dust and one drop of concentrated hydrochloric acid to remove the excess of mercury. After 15 minutes the sample is filtered, a portion of the filtrate mixed with the picrate-picric acid and sodium carbonate solutions, and, after dilution, kept for 20 minutes at 95°. The colour is compared with that similarly developed in a control. To determine sucrose, the latter is hydrolysed by Herzfeld's method (*Z. ver. deut. Zuckerind.*, 1888, **38**, 699) and the increase in colour after inversion determined by the above method. R. B.

**Colorimetric Determination of Carbohydrates in Plants by the Picric Acid Reduction Method. II. Determination of Starch and other "Reserve" Carbohydrates.** W. THOMAS (*J. Amer. Chem. Soc.*, 1924, **46**, 1670—1675).—Starch can be determined colorimetrically by the picric acid reduction method by conversion into dextrose and maltose with taka-diaxase (cf. Davis and Daish, A., 1914, ii, 588) without a secondary hydrolysis. Under the conditions of conversion, the ratio of dextrose to maltose is remarkably constant (2.0).

The material is gelatinised by boiling and stirring with water and the solution is incubated at 38° for 24 hours with the enzyme preparation and toluene, then boiled for 15 minutes, filtered, and the residue washed by decantation with water. The sugar is determined by the author's method (preceding abstract). To determine other "reserve" carbohydrates, the sugar-free residue is hydrolysed by boiling with water containing 0.5% of hydrochloric acid for 4 hours under a reflux condenser, neutralised with sodium hydroxide, and treated as before described. The results are relative, owing to possible destruction of dextrose by the acid hydrolysis. R. B.

**Antagonistic Action of the Trichloroacetate Ion on the Reducing Properties of Sugars.** G. DENIGÈS (*Bull. Soc. Chim. biol.*, 1924, **6**, 397—400).—Trichloroacetic acid tends to inhibit the reduction of Fehling's solution by sugars and quantitative results cannot be obtained in its presence. Investigation of the reaction showed that monochloroacetic acid, which has no such inhibiting action, is formed according to the equation,  $4\text{CuOH} + 4\text{H}_2\text{O} + \text{CCl}_3\cdot\text{CO}_2\text{H} = 4\text{Cu}(\text{OH})_2 + \text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H} + 2\text{HCl}$ , and in the strongly alkaline liquid is converted into glycollic acid. The mechanism of the reaction is explained by supposing that the copper acts catalytically, the cuprous ion formed by the action of the reducing sugar immediately reducing (dechlorinating) a corresponding

quantity of trichloroacetic acid and returning at once to the cupric state, so that no decolorisation or precipitation of cuprous oxide is observed. If addition of sugar be continued after all the trichloroacetic acid has been converted into monochloroacetic acid, reduction takes place in a normal manner. It is suggested that this reaction might be extended to other organic halogen compounds and that it might lead to a method for determining trichloroacetic acid in presence of monochloroacetic acid.

C. T. G.

**Micro-determination of Blood Sugar.** K. DRESEL and H. ROTHMAN (*Biochem. Z.*, 1924, **146**, 538—539).—The method of Hagedorn and Jensen for determining blood sugar (*A.*, 1923, ii, 265, 440) is superior to that of Bang, and no impairment of accuracy results from using an absorption paper and torsion balance, in place of a pipette, for obtaining the sample.

J. P.

**Determination of Raffinose in Sugars. Raffinose Content of Molasses.** E. SAILLARD (*Compt. rend.*, 1924, **178**, 2189—2192).—Solutions of raffinose at 20°, after inversion by Clerget's method, give a mean value of  $[\alpha] + 51.56^\circ$  for a rotation of  $+100^\circ$  of the uninverted solution. Since the values for sucrose, uninverted and inverted, are  $+100^\circ$  and  $-34^\circ$ , respectively, the sucrose content,  $S$ , and the hydrated raffinose content,  $R$ , of a solution of the mixed sugars are given by the formulæ  $S = (C - 0.4844A)/0.8556$  and  $R = (A - S)/1.57$ , where  $A$  is the direct polarisation value,  $B$  that after inversion, and  $C = A + B$ . [Cf. *B.*, 1924, 686.]

A. COUSEN.

**Spectrophotometric Determination of Pentoses.** G. SCHEFF (*Biochem. Z.*, 1924, **147**, 94—102).—Tables are given whereby the concentration of arabinose or xylose solutions may be calculated from a determination of the extinction coefficient of the band of maximum absorption ( $617.7 \mu\mu$ ), shown in amyl alcohol solution by the blue pigment formed when these pentoses are treated with Bial's orcinol reagent.

J. P.

**Detection and Determination of  $\beta$ -Hydroxybutyric Acid and Dextrose in Diabetic Urine.** A. MOLHANT (*Bull. Soc. chim. Belg.*, 1924, **33**, 261—265).—Polarimetric methods for the determination of dextrose in diabetic urine are trustworthy only in the absence of  $\beta$ -hydroxybutyric acid which is levorotatory,  $[\alpha]_D - 21.5^\circ$ . A polarimetric method for the simultaneous determination of dextrose and of  $\beta$ -hydroxybutyric acid in urine consists in removing the former by fermentation with yeast. Polarimetric measurements are taken before and after fermentation, any rotation in the latter case being due only to  $\beta$ -hydroxybutyric acid. Formulæ for calculation of the amount of dextrose and  $\beta$ -hydroxybutyric acid present are given. Further, the difference in density of the liquid before and after fermentation is directly proportional to the amount of dextrose present.

J. W. B.

**Characterisation and Determination of Small Quantities of Pyruvic Acid.** L. J. SIMON and L. PIAUX (*Bull. Soc. chim. Biol.*, 1924, **6**, 477—487).—Two methods are described: (a) 1 c.c.

of the solution containing pyruvic acid is treated with 0.5 c.c. of 40% acetic acid followed by 3 c.c. of 1% sodium nitroprusside solution. The mixture is then made slightly alkaline with ammonia, when a blue colour develops. (6) The *p*-bromophenylhydrazone is very sparingly soluble in water and can be accurately determined by titration with alkali. This method is more accurate than the former.

D. R. N.

**Action of Iodine on Fats. IV. Behaviour of Iodine-Iodic Acid Solutions.** B. M. MARGOSCHES and W. HINNER (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 349—355).—The addition of potassium iodate to iodine solutions (in alcohol, acetic acid, or aqueous potassium iodide) removes the hydrogen iodide produced by the action of iodine on fats and allows the addition of iodine to the unsaturated fatty acids to proceed quantitatively.

A. G. P.

**Behaviour of Formaldehyde. II.** N. TARUGI (*Boll. Chim. farm.*, 1924, **63**, 337—342, 369—374; cf. this vol., ii, 355).—For the determination of formaldehyde, the best method is that given by Orchard (A., 1897, ii, 288), but 1 mol. of the aldehyde precipitates, not 4, but exactly 2 atoms of silver (cf. Tollens, A., 1882, 1329; 1883, 125) from ammoniacal silver nitrate solution. The amount of reduction is, however, increased slightly by various factors, such as the action of light, so that the results are subject to a correction determined by means of a control experiment. Formic acid (46 parts) also reduces silver (108 parts). Methyl alcohol may be determined accurately by oxidation with permanganate (cf. Lockemann and Croner, A., 1915, ii, 190).

When a mixture of formaldehyde solution is heated and stirred with lime slaked in a little water in a capacious vessel over a naked flame, a violent reaction occurs at 95°, the total change being represented by the equation:  $30\text{CH}_2\text{O} + 4\text{CaO} + \text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6\text{CaO} + 2\text{C}_6\text{H}_{10}\text{O}_5 + 3\text{Ca}(\text{HCO}_2)_2 + 6\text{MeOH}$ . [Cf. B., 1924, 692.]

T. H. P.

**Detection of Aldehydes in Chloroform and Alcohol.** E. ISNARD (*J. Pharm. Chim.*, 1924, [vii], **30**, 43—48).—Silver nitrate at 70° gives a positive reaction only with chloroform containing at least 1% of aldehyde; 0.1*N*-sodium hydroxide at 70° is sensitive to a dilution of 0.005%, and solid potassium hydroxide up to 0.01%. Nessler's reagent gives a positive test up to 1 in  $2 \times 10^5$  of aldehyde. Rosaniline-hydrogen sulphite solution is the most suitable reagent, and has a sensitiveness of 1 in 5000—10,000. Silver nitrate is unsuitable for detecting aldehydes in alcohol, being non-sensitive in the cold and reduced even by pure alcohol when heated. Potassium hydroxide at 70° is sensitive to a dilution of 1 in 5000 of aldehyde in alcohol, and *m*-phenylenediamine hydrochloride up to 1 in  $10^5$ , although the latter appears to be affected by other substances besides aldehydes. Nessler's solution is not suitable in this case, but the rosaniline-hydrogen sulphite reagent is recommended. The latter is thus suitable for detecting aldehydes in ether, chloroform, and alcohol, the manipulation of the test being the same in each case.

W. T. K. B.

**Reactions between Aldehydes and Phenols.** L. VAN ITALLIE and A. HARMSMA (*Pharm. Weekblad*, 1924, **61**, 825—829).—The colours developed by addition of an aldehyde to 1% solutions of resorcinol, pyrocatechol, phloroglucinol, and pyrogallol in 4*N*-alcoholic hydrochloric acid at the ordinary temperature, together with the wave-lengths corresponding with the middle of the absorption bands, are tabulated for a very large number of aldehydes. S. I. L.

**Determination of Acetone and  $\beta$ -Hydroxybutyric Acid in small Quantities of Urine.** A. LUBLIN (*Biochem. Z.*, 1924, **147**, 187—190).—Polemical in reply to Engfeldt (this vol., ii, 428).

J. P.

**Electrometric Titration of Hydroferricyanic Acid with Potassium Iodide.** E. MÜLLER (*Z. anorg. chem.*, 1924, **135**, 265—268).—The end-point of the ionic reaction:  $2\text{Fe}(\text{CN})_6''' + 2\text{I}^- = 2\text{Fe}(\text{CN})_6'' + \text{I}_2$ , may be determined electrometrically in presence of excess of zinc ions, which remove the ferrocyanide ions as they are formed. The titration is more rapidly carried out by running the ferricyanide into the iodide than by the reverse process. S. K. T.

**Micrometric Apparatus for the Determination of Urea in Blood and other Pathological Products which contain very small Quantities.** A. MOLHANT (*Bull. Soc. chim. Belg.*, 1924, **33**, 266—268).—An apparatus for the accurate determination of urea in blood based on the measurement of the nitrogen evolved when, after treatment with trichloroacetic acid, it is decomposed with hypobromite solution, includes a divided flask which is connected to a special manometer with a long capillary side tube. On mixing the liquids the amount of nitrogen evolved is determined by measurement of the length of the column of manometer liquid forced along the capillary tube by the evolved gas, temperature and pressure corrections being made. The apparatus is calibrated by means of a standard serum containing 1 g. of urea per litre.

J. W. B.

**Group of Colour Reactions of Veronal.** W. PARRI (*Boll. Chim. farm.*, 1924, **63**, 401—404).—The colour reactions of veronal with (1) phenylhydrazine and nitroprusside, (2) a cobalt salt and an alkali, and (3) sulphuric acid and  $\alpha$ -naphthol are described. [Cf. *B.*, 1924, 767.]

T. H. P.

**Determination of Cyanamide as Dixanthylcarbamide.** R. FOSSE, P. HAGENE, and R. DUBOIS (*Comp. rend.*, 1924, **179**, 214—216).—Silver cyanamide when dissolved in nitric acid (40° B.) and maintained at 38—40° for 2 hours or at the ordinary temperature for 24 hours is quantitatively converted into carbamide nitrate. The carbamide can then be determined by making an aqueous solution just alkaline with ammonia and adding a large excess of acetic acid. A methyl-alcoholic solution of xanthidrol is then added, and after 2 hours the dixanthylcarbamide is collected, washed with alcohol, dried, and weighed.

F. G. M.

**Blood Analysis. V. Improvements in the Preparation of Uric Acid Reagent.** O. FOLIN and H. TRIMBLE (*J. Biol. Chem.*, 1924, **60**, 473—479).—Errors in the colorimetric determin-

ation of uric acid (A., 1913, ii, 162; 1922, ii, 405) are due to the presence of molybdenum in the sodium tungstate used in the preparation of the reagent. The molybdenum can be precipitated as sulphide in the presence of phosphoric acid, and the reagent so prepared gives practically no colour with resorcinol. C. R. H.

**Supposed Calcium-Nicotine Compounds.** R. W. THATCHER (*J. Amer. Chem. Soc.*, 1924, **46**, 1539—1540).—Failure to account for all the nicotine present in mixtures containing calcium salts (Graham and Carr, this vol., i, 816) is probably due to loss of nicotine by volatilisation during earlier stages of analysis, rather than to the formation of insoluble calcium-nicotine compounds, since nicotine is completely lost on exposing a mixture of nicotine sulphate and calcium carbonate to the air for a few days. F. G. W.

**Standardisation of Gelsemium.** P. S. PITTINGER (*J. Amer. Pharm. Assoc.*, 1923, **12**, 1063—1067).—A comparison of biological and chemical methods for the determination of alkaloids (gelsemine and gelseminine) in preparations of gelsemium.

#### CHEMICAL ABSTRACTS.

**Determination of Lupine Alkaloids, particularly in Lupine Seeds.** T. SABALITSCHKA and M. W. ZAHER (*Z. angew. Chem.*, 1924, **37**, 299—300).—The official method of determining the above consists in shaking the lupine powder with dilute sodium hydroxide and a mixture of ether and chloroform. The ether-chloroform extract is washed with water to remove any traces of alkali, and shaken with an excess of 0.01*N*-hydrochloric acid, the latter being finally titrated back with 0.01*N*-sodium hydroxide (1 c.c. of 0.01*N*-acid=0.00248 g. of alkaloid). This method is inaccurate, however, since a considerable quantity of alkaloid (e.g., 25%) is dissolved by the wash water. A better procedure is described whereby the material is ground to a paste with aqueous sodium hydroxide, then with calcium sulphate to produce a powdery mass, which is extracted with a mixture of equal volumes of ether and chloroform. An aliquot part of the clear extract is shaken with excess of 0.01*N*-sulphuric acid, sufficient ether being added to effect a good separation. The united washings and acid extracts are titrated back with 0.01*N*-sodium hydroxide, using methyl-red as indicator.

W. T. K. B.

**Identification of Insoluble Azo Colours on the Fibre and of Azo Pigments in Substance.** F. M. ROWE and C. LEVIN (*J. Soc. Dyers and Col.*, 1924, **40**, 218—228).—Methods are described for the identification of insoluble azo pigments by means of the products obtained when the pigment is decomposed by reduction or by treatment with fuming nitric acid, or by determination of the m. p. of the pigment. The m. p., crystalline forms, and colours in sulphuric acid solution of a large number of azo pigments prepared from  $\beta$ -naphthol,  $\beta$ -hydroxynaphthoic acid, the *m*-nitroanilide of  $\beta$ -hydroxynaphthoic acid, the  $\alpha$ -naphthalide of  $\beta$ -hydroxynaphthoic acid, and the *p*-aniside of  $\beta$ -hydroxynaphthoic acid are described.

A. J. H.

**Dyeing Processes. II. Determination of Dyes in the Dye Bath.** P. RUGGLI and A. FISCHLI (*Helv. Chim. Acta*, 1924, 7, 507—513).—The most trustworthy and generally applicable method for determining the quantity of dye in a dye-bath is by titration with a titanous salt. When possible the titration should be direct, but if excess of titanous salt must be used it is best titrated back with standard methylene-blue solution. When chrysophenine (*pp'*-diaminostilbene-*oo'*-disulphonic acid, diazotised, coupled with phenol, and ethylated) is analysed by this method it gives consistently low results. [Cf. *B.*, 1924, 554.] E. H. R.

**Micro-determination of Proteins in Blood Serum.** W. BERGER and L. PETSCHACHER (*Z. ges. exp. Med.*, 1923, 36, 258—296; from *Chem. Zentr.*, 1924, i, 505—506).—A comparison of refractometric, viscosimetric, and microchemical methods for the determination of proteins in blood sera. As a standard procedure, salting out followed by micro-Kjeldahl determination, combined with a simplified Robertson viscosimetric method, is recommended. G. W. R.

**Determination of the Protein Fractions in Serum and Plasma.** H. W. KNIPPING and H. L. KOWITZ (*Z. physiol. Chem.*, 1924, 135, 84—94).—The authors have studied most of the methods described for the separation of globulin and albumin and describe a technique which is accurate and simple, and applicable to small amounts of material. The globulin is separated from the albumin by salting out with ammonium sulphate. The method involves only two weighings. For details, reference must be made to the original paper. E. M. C.

**Determination of Pancreatic Enzymes in Duodenal Fluid by a Modified Gaultier's Method.** G. F. SPENCER (*J. Lab. Clin. Med.*, 1924, 9, 261—267).—The Lueders-Bergeim method (*Amer. J. Physiol.*, 1923, 66, 297) is accurate, simple, and rapid. There is a selective stimulation of enzyme secretion by the food. The production of trypsin, amylase, and lipase is stimulated by diets rich in protein, carbohydrate, and fat, respectively. Enzymes in duodenal fluid disappear rapidly at ordinary temperatures.

CHEMICAL ABSTRACTS.

**Colorimetric Determination of Diastase in Body Fluids.** I. COHEN and E. C. DODDS (*Brit. Med. J.*, 1924, I, 618—620).—The body fluid, suitably buffered, is incubated with diastase in the presence of a known quantity of erythrodextrin, the unchanged dextrin being determined colorimetrically by the addition of a solution of iodine and ammonium sulphate and comparison with a standard. A. A. E.

**Determination of the Potency of Insulin Preparations.** H. D. CLOUGH, R. S. ALLEN, and E. W. ROOT, jun. (*Amer. J. Physiol.*, 1923, 66, 461—484).—A study of the rabbit as a test animal. The "convulsions" test is untrustworthy. A. A. E.

## General and Physical Chemistry.

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**Width of Lines in Electric Arc Spectra at Various Pressures.** S. PROCOPIU (*J. Phys. Rad.*, 1924, [vi], 5, 220—224; cf. this vol., ii, 364).—The variation of the width of the lines of the arc spectra of zinc, cadmium, calcium, and aluminium at pressures between 1 and 760 mm. has been studied by an interferometer method. In any one series, the width of the lines increases with the order of the lines in the series, in qualitative agreement with Stark's hypothesis of the influence of the intermolecular electric field. The lines of the spark spectrum from the cathode are broader than the corresponding lines from the anode. The lines from the flame are wider than those from either the arc or the spark. G. M. B.

**Width of the Hydrogen Lines in Stellar Spectra.** E. O. HUIBURT (*Astrophys. J.*, 1924, 59, 177—180).—Combination of observations on stellar spectra with Stark's theory of the broadening of the Balmer lines of hydrogen and Saha's theory of high-temperature ionisation leads to discrepancies which may be removed by supposing that a large number of free electrons are present in the stellar envelopes. A. A. E.

**Partition of Energy in the Arc Spectrum of Mercury.** G. ATHANASIU (*Compt. rend.*, 1924, 178, 2071—2073).—Direct measurements by means of a thermopile of the radiation energy of the lines of the arc spectrum of mercury were made with a constant current and varying voltage across the lamp. The energy curves of lines of the same series are similar in form, so that the ratio of the intensities of two such rays is sensibly constant (over the range 100—300 watts), but the ratio of the intensities of two rays of different series may vary widely. L. J. H.

**The  $p$ - and  $d$ -Terms of Lithium.** F. J. VON WISNIEVSKI (*Physikal. Z.*, 1924, 25, 330—333).—A mathematical paper in which the theory developed for the helium atom (cf. this vol., ii, 361) is applied to the neutral lithium atom. It is shown that for the  $p$ -term,  $n_2 - n_1 = -1$ , in agreement with that for orthohelium. For the  $d$ -term,  $n_2 - n_1 = -3$ , which is the same for ortho- and parahelium. J. B. F.

**Spectrum of Ionised Potassium in Connexion with the Red and Blue Spectrum of Argon.** T. L. DE BRUIN and P. ZEEMAN (*Nature*, 1924, 114, 352).—Results are briefly quoted to show that the connexion between the frequency relations of the spectra of ionised potassium and argon (blue) is closer than that with argon (red). A. A. E.

**Mercury Line 2270 Å.** T. TAKAMINE and M. FUKUDA (*Nature*, 1924, 114, 382).—Of the three transitions of an electron in a  
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mercury atom,  $1S-2p_1$ ,  $1S-2p_2$ , and  $1S-2p_3$ , only the second has been observed optically. The others have only been observed by the method of Franck and Einsporn. A method is briefly described for the production of the line  $2270 \text{ \AA}$ . ( $1S-2p_1$ ) in the arc spectrum of mercury, with considerable intensity. Excitation in a condensed discharge gives a shift of  $0.1 \text{ \AA}$ . towards the red; shifts are also observed in the case of the lines  $2345 \text{ \AA}$ . and  $2564 \text{ \AA}$ . The line  $2655 \text{ \AA}$ . ( $1S-2p_3$ ) was not observed. A. A. E.

**Metastable State in Mercury Vapour.** H. W. WEBB (*Physical Rev.*, 1924, **24**, 113—128).—A determination of the life of the radiation in mercury vapour excited by electron impacts, sufficient voltage (4.9) being used to displace the valency electron to the  $2p_2$  orbit. The persistence of the radiation produced by 4.9 volt impacts in mercury vapour cannot be explained by the "imprisonment" theory of radiation, but supports the suggestion that the excited atoms assume a metastable state. According, however, to the Bohr theory, the  $2p_2$  state is not metastable. A. A. E.

**Spectrum of Helium in the Extreme Ultra-violet.** T. LYMAN (*Science*, 1924, **59**, 422).—Several new terms have been added to the  $oS-mP$  series, making seven lines in all, and a continuous spectrum extending from the limit of this series towards the extreme ultra-violet has been observed. Two members of the enhanced series  $4N(1/l^2)-(1/m^2)$  occur at  $303.6$  and  $256.3 \text{ \AA}$ . A new line which fits the relation  $oS-1\pi$  furnishes the first experimental evidence for radiation from helium involving a so-called inter-system combination. A. A. E.

**Electric Furnace Spectrum of Titanium in the Ultra-violet.** A. S. KING (*Astrophys. J.*, 1924, **59**, 155—176; cf. *ibid.*, 1914, **39**, 139).—The temperature classification of 785 lines is tabulated, with their relative intensities in the arc and at  $2000^\circ$ ,  $2250^\circ$ , and  $2600^\circ$ . New wave-length values are given for 333 furnace lines. Enhanced lines, selected by comparison with the spark spectrum, appear in this region at lower temperatures than the enhanced lines in the visible spectrum. As anticipated, admixture with potassium suppressed the enhanced lines of titanium. A. A. E.

**Fine Structure of the Nitrogen, Oxygen, and Fluorine Lines in the Extreme Ultra-violet.** I. S. BOWEN and R. A. MILLIKAN (*Phil. Mag.*, 1924, [vi], **48**, 259—264; cf. this vol., ii, 437).—By means of "hot spark" high-vacuum spectrometry, the authors are able to obtain very high resolution and precision of wave-length determinations in the region below  $1000 \text{ \AA}$ . Standards have been established in this region correct to a few hundredths Angstrom, where no such standards hitherto existed. The very strong oxygen line  $834 \text{ \AA}$ ., when analysed with sufficient resolution, shows clearly seven components, whilst the strong nitrogen line  $1085.2 \text{ \AA}$ . is revealed as a quadruplet. Since these two lines are not doublets, it is concluded that neither is due to stripped atoms. A table is given of the fine structure of all the strong lines of oxygen, nitrogen, and fluorine below  $1500 \text{ \AA}$ . The authors believe



that they have sufficient proof that their "hot spark" produces the whole series of stripped atoms  $\text{Li}_I$ ,  $\text{Be}_{II}$ ,  $\text{B}_{III}$ ,  $\text{C}_{IV}$ ,  $\text{N}_V$ ;  $\text{Na}_I$ ,  $\text{Mg}_{II}$ ,  $\text{Al}_{III}$ ,  $\text{Si}_{IV}$ ,  $\text{P}_V$ ,  $\text{Si}_{VI}$ ; as well as a series of similar atomic structure  $\text{B}_I$ ,  $\text{C}_{II}$ ,  $\text{N}_{III}$ ,  $\text{O}_{IV}$ .

J. B. F.

**Assignment of Lines and Term Values in Beryllium II and Carbon IV.** R. A. MILLIKAN and I. S. BOWEN (*Nature*, 1924, **114**, 380).—Spectral "term values" are tabulated for the stripped atoms of beryllium ( $\text{Be}_{II}$ ) and carbon ( $\text{C}_{IV}$ ); an arrangement of the stripped atoms  $\text{Li}_I$ ,  $\text{Be}_{II}$ ,  $\text{B}_{III}$ ,  $\text{C}_{IV}$ , similar to that of Paschen and Fowler for the series,  $\text{Na}_I$ ,  $\text{Mg}_{II}$ ,  $\text{Al}_{III}$ ,  $\text{Si}_{IV}$ , is then possible.

A. A. E.

**Excitation Limit of K-Series of Light Elements.** F. J. VON WISNIEWSKI (*Physikal. Z.*, 1924, **25**, 297—298).—The excitation limits of the K-series for helium, singly ionised lithium, doubly ionised beryllium, triply ionised boron, and quadruply ionised carbon are smaller than would be predicted from the values for heavier atoms (Holtzmark, *ibid.*, 1923, **24**, 225). The observed values probably correspond, not with normal atoms, but with those in which the two electrons are in a two-quantum orbit.

S. B.

**Effect of Argon on certain Spectra.** R. C. JOHNSON and W. H. B. CAMERON (*Proc. Roy. Soc.*, 1924, **A**, **106**, 195—214).—Observations have been made on the effects of the presence of argon in the discharge tube on various spectra, especially those associated with carbon. Argon, like helium, enhances the Swan and triplet systems of carbon bands; but, unlike helium, it does not seem to facilitate the appearance of the comet tail bands. The structure of the CH band is somewhat affected by argon. The chief effect on the line spectrum of oxygen is repressive. The relative intensities of the band systems obtainable from sulphur dioxide are much altered. A new band system in the region 3100—2800 Å., and degraded towards the short wave-length side, is recorded in the spectrum from sulphur vapour alone.

S. B.

**Emission Spectra of Mixed Alkali Vapours.** F. H. NEWMAN (*Phil. Mag.*, 1924, [vi], **48**, 159—163).—A series of bands in the region 6776—5485 Å. is described, which have been observed in the arc between poles of sodium-potassium alloy. The emission of these bands is ascribed to associated atoms of the two elements (cf. Barratt, this vol., ii, 138).

S. B.

**Band Spectrum of Mercury and the Dissociation of Hydrogen Molecules by Excited Mercury Atoms.** K. T. COMPTON and L. A. TURNER (*Phil. Mag.*, 1924, [vi], **48**, 360—363; cf. this vol., ii, 585).—The band spectrum of mercury is strongly developed in a Geissler discharge in a tube containing a mixture of mercury and hydrogen. The heads of the three strongest bands are of wave-lengths 4219, 4017, and 3728 Å. The band spectrum disappears when the hydrogen is pumped out. This supports

Kratzer's conclusion that the emitters of the bands are molecules of a hydride of mercury. The band appears where the concentration of excited mercury atoms in the  $2p$  states is greatest, *i.e.*, in the regions of the striated discharge, which indicates that the presence of these excited atoms is essential for the production of the bands. It is suggested that an excited mercury atom forms with a hydrogen molecule an excited hydride molecule and a hydrogen atom and does not dissociate the hydrogen into two atoms immediately, by a collision of the second kind. J. B. F.

**Band Spectrum of Boron Monoxide.** R. S. MULLIKEN (*Nature*, 1924, **114**, 349—350).—Polemical against Jevons (this vol., ii, 366, 438). Evidence is brought forward to show that the bands are due to boron monoxide, and not to boron nitride. The intensity of the bands is maximal when 0.5% of oxygen is present; a carbon arc (compounds of boron being present) gave bands of boron monoxide and trioxide in an atmosphere of oxygen or air, but not in nitrogen. The vibrational isotope effect also indicates that the bands originate from boron monoxide. The non-coincidence, for the bands having the vibrational quantum numbers  $n$  and  $n'$  both zero, of corresponding heads of the two isotopes is considered, and it is thought probable that the minimum vibrational energy of boron monoxide (and other) molecules is a half-quantum. A. A. E.

**Band Spectra of Silicon Oxide, and of the Chlorides of Silicon, Carbon, Boron, and Aluminium.** W. JEVONS (*Proc. Roy. Soc.*, 1924, **A**, **106**, 174—194).—The vacuum tube spectra of various chlorides have been examined. (i) Silicon chloride.—A new system of bands, between 3100 and 2200 Å., degraded to the short wave-length side, is attributed to silicon chloride. Bands in the same region, but degraded in the opposite direction, appear when oxygen is present. These have previously been assigned to silicon itself, but are most probably from the oxide. (ii) Aluminium chloride.—New ultra-violet bands were found at about 2600 Å., degraded towards the red. (iii) Carbon tetrachloride.—A cluster of four new bands was found at about 2780 Å., degraded towards the short wave-length side. (iv) Boron trichloride.—A complicated system of new bands was found near 2600 Å. S. B.

**Absorption Lines in the Spectrum of the Metallic Spark in Water.** E. O. HULBERT (*Physical Rev.*, 1924, **24**, 129—133).—The spectra, from 4500 to 2000 Å., of the condensed spark under water between electrodes of various metals, consist of a continuous background crossed by characteristic bright and dark lines. With aluminium, bismuth, cadmium, gold, iridium, lead, magnesium, platinum, rhodium, silver, tin, and zinc, the absorption lines were those which were reversed in the arc; with antimony, cobalt, chromium, copper, iron, molybdenum, nickel, and tungsten, there were absorption lines in addition to those listed as reversed in the arc. A. A. E.

**Absorption Spectra of Elements of the Iron Group.** E. VON ANGERER and G. JOOS (*Ann. Physik*, 1924, [iv], **74**, 743—756).—As a result of measurements of the absorption spectra in the extreme ultra-violet for iron vapour, a number of lines for each multiplet were observed, but, in the near region, only the strongest lines were found as absorption lines. Conclusions similar to those drawn by other workers with regard to the electronic arrangement in the iron atom are given (cf. Gieseler and Grotrian, this vol., ii, 287; Laporte, this vol., ii, 364). The absorption lines for iron, nickel, and cobalt vapours are tabulated. No absorption could be found for iodine vapour at 1050°. S. K. T.

**Absorption Spectra of Vapours of Lead and Tin.** N. K. SUR and R. K. SHARMA (*J. Sci. Assoc. Vizianagaram*, 1924, **1**, 121—124).—At low red heat, lead vapour gave the lines, 2833 and 2170 Å. as sharp narrow reversals; at higher temperatures, the following additional lines were reversed: 2247, 2614, 2802, 2823, 2873, 3240, 3640, 3684, 4058. The vapour of tin shows only one wave-length of 2707. J. B. F.

**Quantitative Study of Infra-red Absorption Spectra of Organic Substances.** J. LECOMTE (*Compt. rend.*, 1924, **178**, 2073—2075).—A continuation of previous work (this vol., ii, 439, 512). For substances with only one active group, the absorbing groups may be classified according to opacity. If a substance contains two or more identical groups the absorption bands are not more intense. If active groups, whether the same or different, are close together in the molecule, the region between absorption maxima is relatively clear, but if they are more separated some absorption is found here also and the bands may ultimately join. The distance between groups in ring compounds cannot be counted by carbon atoms in the same way as for chain compounds; thus groups in the para position do not behave as though they were widely separated. It is necessary to assume that a band does not correspond with vibration of the molecule as a whole, but only of such parts as are oriented in a particular way. This view is supported by the fact (observed by others) that reflection from organic liquids of infra-red radiation is feeble, for reflection depends upon the molecule as a whole. L. J. H.

**Colour and Molecular Geometry.** J. MOIR (*J. Chem. Soc.*, 1924, **125**, 1134—1141; cf. T., 1921, **119**, 1654; 1922, **121**, 1808).—The determination by Bragg (T., 1922, **121**, 2783) of the size and shape of the benzene molecule has made it possible to calculate the colour of all classes of derivatives from geometrical considerations. The position of the absorption band is governed by the shortest distance between the centres of the auxochrome and hapton (T., 1923, **123**, 2800), and also by the eccentricity of the ellipse of motion of the electron revolving round the two positive centres of force due to the atomic nuclei of the elements constituting the auxochrome and the hapton. The positions of the absorption

bands, for a number of monocyclic and dicyclic compounds, have been calculated, and are found to agree very closely with the experimentally determined values. M. S. B.

**Ultra-violet Absorption Spectra of some Derivatives of Naphthols.** S. KOMATSU, B. MASUMOTO, and S. KUMAMOTO (*Mem. Coll. Sci. Kyōtō*, 1924, (A), 7, 287—290).—The ultra-violet absorption spectra in alcoholic solution of  $\alpha$ - and  $\beta$ -naphthols, their methyl ethers, and their *ar*-tetrahydro derivatives have been examined.  $\alpha$ -Naphthol gives four bands at 3100, 3200, 3500, and 3750 Å., the latter being broad, whilst  $\beta$ -naphthol gives three at 3000, 3250, and 3700 Å. (broad). Purvis (T., 1912, 101, 1315) found only two bands for each compound. The *ar*-tetrahydro-naphthols gave for the  $\alpha$ -compound narrow bands at 3200 and 3500 and a broad band at 3700 Å., whilst the  $\beta$ -compound, in addition to these, showed a narrow band at 3000 Å. The introduction of hydrogen lessened the intensity of the narrow bands and shifted the broad bands back to the ultra-violet, thus giving a closer resemblance to the absorption spectrum of naphthalene (Baly and Tuck, T., 1908, 93, 1902).  $\alpha$ -Naphthyl methyl ether gave bands at 3150, 3250, 3450, 3550, and 3800 Å., and the  $\beta$ -compound at 3050, 3200, 3550, 3740 Å. The curves closely resemble those for the naphthols, the chief difference in both cases being that the broad band of the naphthols is broken into two by the introduction of the methyl group. The hydrogenated ethers gave three bands for the  $\alpha$ -compound and four for the  $\beta$ -compound; the influence of hydrogenation on the absorption spectra of the ethers is very similar to that found for the naphthols. S. S.

**Absorption of Violet Light by Organic Substances. IV.** L. MARCHLEWSKI and A. MOROZ.—(See i, 1006.)

**Luminescence of Condensed Gases at Very Low Temperatures.** J. C. McLENNAN and G. M. SHRUM (*Proc. Roy. Soc.*, 1924, A, 106, 138—149).—It has been suggested by Vegard (this vol., ii, 584) that the source of the green auroral line at 5577 Å. is solid nitrogen phosphorescing under electronic bombardment. Experiments are now described in which nitrogen, argon, and other gases have been solidified by liquid hydrogen, and then bombarded by the stream of electrons from a hot cathode. The phosphorescence spectrum of nitrogen under these conditions consisted of a single line at 5231 Å. Solid argon showed two lines, at 4750 and 5300 Å. The vapour above the solid was also luminous. The light emitted by nitrogen vapour included three yellowish-green lines at 5556, 5617, and 5654 Å. Argon vapour gave lines at 5648 and 5607 Å. Carbon monoxide, ammonia, oxygen, and water showed no parallel phenomena. The results do not substantiate Vegard's hypothesis, as no radiation of wave-length 5577 Å. was detected throughout the experiments. S. B.

**Light of the Night Sky.** RAYLEIGH (*Proc. Roy. Soc.*, 1924, A, 106, 117—137).—The non-polar auroral light shows the green line 5578 Å. without the negative band spectrum of nitrogen. It is

suggested that it may be a phenomena of phosphorescence, excited by the sun in the day-time and carried round by the earth's rotation as in the phosphoroscope. W. E. G.

**Photographic Determination of Fluorescence Spectra of Hæmatoporphyrin in Various Solvents.** C. DHÉRÉ, A. SCHNEIDER, and T. VAN DER BOM (*Compt. rend.*, 1924, **179**, 351—354).—Spectrophotography of fluorescence spectra of solutions of hæmatoporphyrin in various solvents has given three main types of spectra. Type I, exhibited by solutions in methyl, ethyl, and amyl alcohols, ethyl ether, ethyl acetate, acetone, and pyridine, and to some extent in normal solutions of ammonium and potassium hydroxides, shows initially a strong band in the region of the absorption band, developing by prolonged exposure into three maxima on the infra-red side and passing into an intense broad band the axis of which occurs in the infra-red. In pyridine, the strong band is at 642—618  $\mu\mu$  with maxima at 694—683, 677—666, 655—648  $\mu\mu$ , the corresponding figures in normal ammonium hydroxide being 617—606, 681—672, 666—656, 649—640  $\mu\mu$ . Type II, exhibited by solutions in normal hydrochloric, sulphuric, and tartaric acids, has three bands. The intensities of the extreme are greater than that of the intermediate band and the maximum fluorescence is on the infra-red side of the absorption band. In normal sulphuric acid, the bands are at 659—644, 629—615, and 603—590  $\mu\mu$ . Type III, shown by solutions in glacial acetic acid and to some extent in phenol, has two bands, one of which contains a minimum. In glacial acetic acid, the first band is at 669—647  $\mu\mu$ , with the minimum at 660—656  $\mu\mu$ , and the second at 616—601  $\mu\mu$ . A. E. M.

**Fluorescence of Alkaloids of the isoQuinoline and Tetrahydroisoquinoline Group.** E. BAYLE and R. FABRE.—(See i, 980.)

**Energy Liberated in Phosphorescence.** A. A. GUNTZ (*Compt. rend.*, 1924, **179**, 361—364).—A preliminary account of measurements of energy liberated by the sulphides of zinc and of zinc and cadmium containing copper to the extent of 1 part in  $10^5$  parts. Zinc sulphide showed an intensity of 0.42 energy quantum per atom of copper, whilst zinc sulphide diluted with 30% of cadmium sulphide showed an intensity of 0.11 per atom of copper. It is suggested that the maximum intensity should be about one or two quanta per atom of copper. Lenard and Hauser (*Heidelberg Akad.*, 1912, **12.4**, 33) found a value of 4 quanta per atom of bismuth in calcium sulphide, and it is suggested that the difference is due to the quadravalency of bismuth as opposed to the bivalency of copper. Activated zinc sulphide ceases to phosphoresce when cooled in liquid air, but following a second exposure at these low temperatures, the intensity of the phosphorescence is comparable with that obtained at ordinary temperatures; none of the energy of the initial activation, however, is liberated until the substance is heated. A. E. M.

**Studies in Phototropy. II. Mercury Compounds.** T. VARAHALU, A. J. RAM, and B. S. V. R. RAO (*J. Sci. Assoc. Vizianagaram*, 1924, **1**, 107—113).—The following compounds have been prepared:  $2\text{HgSHgI}_2$ ,  $\text{Hg}_3\text{S}_2\text{Br}_2$ ,  $\text{ClHgCNS}$ ,  $\text{IHgCNS}$ ,  $\text{BrHgCNS}$ ,  $\text{IHgCl}$ ,  $\text{IHgBr}$ ,  $\text{ClHgBr}$ , and it is found that all exhibit phototropic properties. They do not show phosphorescence or triboluminescence. J. B. F.

**Nature of the Radiant Energy from a Phototropically Treated Compound.** Y. VENKATARAMAIAH and A. JANAKIRAM (*J. Sci. Assoc. Vizianagaram*, 1924, **2**, 16—18).—The reversion of  $\text{HSHgCNS}$ ,  $\text{IHgCNS}$ ,  $\text{Hg}_3\text{I}_2\text{S}_2$  to their original colour, after being excited in strong sunlight, is attended with radiations capable of producing an effect on a photographic plate in the dark. J. B. F.

**Effect of Pressure on the Refractive Power of Hydrogen.** F. SCHACHERL.—(See ii, 671.)

**Quantum Theory of Dispersion.** G. BREIT (*Nature*, 1924, **114**, 310).

**Quantum Theory of Dispersion.** H. A. KRAMERS (*Nature*, 1924, **114**, 310—311).

**Scattering of Light by Krypton and Xenon.** J. CABANNES and A. LEPAPE (*Compt. rend.*, 1924, **179**, 325—327).—A continuation of previous work (*Ann. Physique*, 1921, **15**, 120). The scattering of light by these gases is not in accordance with Rayleigh's theory. The polarisation of the light scattered at right angles to the incident light is not complete and does not vary sensibly from argon to krypton. The results reveal a very slight anisotropy of the atoms of the rare gas. W. E. G.

**Scattering of Light by Very Large Colloidal Particles.** W. SHOULEJKIN (*Phil. Mag.*, 1924, [vi], **48**, 307—319).—The plane of polarisation of the scattered light as well as the character of the distribution of the dispersed energy depends on the size of the particle. With diameters less than  $\frac{1}{2}\lambda$ , the brightness of the light scattered in the direction of the incident rays is the same as the brightness in the opposite direction and polarisation is complete at an angle of  $90^\circ$  to the direction of the light. As the diameter approaches  $\lambda$  and beyond, dispersion becomes more and more asymmetrical and polarisation is everywhere incomplete; the brightness is then greatest in the direction of the incident rays. Relations are given for the scattering from large particles. W. E. G.

**Critical Opalescence.** A. ANDANT (*J. Phys. Rad.*, 1924, [vi], **5**, 193—207).—Photometric observations of the critical opalescence have been made by direct observation and by a photographic method with ether and four homologous esters. The variation of the opalescence with varying temperature, wave-length of light, etc., is described and the results are in accord with the theories of Einstein, Smoluchowski, Zernike, and Ornstein. The value of  $N$

is found to be  $58 \times 10^{22}$  and  $62 \times 10^{22}$ . The observation of the intensity of the opalescence also gives a precise method for the determination of the critical temperature and volume. G. M. B.

**Investigations on the Dependence of Rotatory Power on Chemical Constitution. XXI. The Chemical Significance of Rotatory Dispersion.** H. HUNTER (*J. Chem. Soc.*, 1924, 125, 1198—1206).—The classification of rotatory dispersion is discussed and a return to the older system, which distinguishes between normal and anomalous dispersion, is recommended. It is considered that there is no evidence that a one-term Drude equation is applicable to the rotation of organic compounds, and that any chemical significance in the two-term Drude equation probably lies in the similarity or dissimilarity of the signs. The relation between dynamic isomerism and complex rotatory dispersion is discussed. M. S. B.

**Optical Activity and the Polarity of Groups Attached to the Asymmetric Atom. I.** H. G. RULE (*J. Chem. Soc.*, 1924, 125, 1121—1134).—The rotation of an optically active compound is probably related to the electrostatic moment of the groups attached to the asymmetric carbon atom rather than to the mechanical moment postulated in Frankland's "lever-arm" theory. To test this view, a polar series showing the relative polarity of simple substituent atoms and groups, such as OH, Cl, CH<sub>3</sub>, has been drawn up on the basis of inductive capacities for long wave-lengths and electrolytic dissociation constants. A definite relationship between the position of a substituent group in the series and its influence on the optical rotation of a compound has thus been observed. Similar relationships hold for the magnetic rotation of benzene derivatives. The reciprocal effect of two groups on the electrostatic moment is seen in di-substituted benzene derivatives. Two groups of like polarity oppose one another in their effect on rotation when in the *p*-position, assist each other in the *o*-position, and have practically the same effect as a mono-substituted compound in the *m*-position. The opposite is, of course, the case for the *o*- and *p*-positions with groups of opposite polarity. This would not be possible on any theory of mechanical moment.

Other factors must necessarily be involved, including temperature and the wave-length of light employed. M. S. B.

**Spectrographic Studies on the Compton Effect.** A. DAUVILLIER (*Compt. rend.*, 1924, 178, 2076—2078; cf. this vol., ii, 581, 582).—The Compton effect which involves an increase in the wave-length of the dispersed X-radiation was based on observations of the action of *K<sub>α</sub>*-rays from tungsten or molybdenum on graphite or aluminium. Using various X-rays and a large number of diffusors, it is found that the effect is not general and fails for the heavier elements. It appears only when the selective absorption is very feeble. L. J. H.

**Analysis of Resonance Curves Observed in Potassium Vapour.** R. C. WILLIAMSON (*Physical Rev.*, 1924, **24**, 134—142).—By the use of a tube containing three copper electrodes, resonance curves have been obtained for potassium vapour, and the resonance potential found to be 1.63 volts, within 2% of the value 1.608 from spectral series. An approximate analysis of the results indicates that the value of the mean electronic free path based on the kinetic theory is too large, and that the probability of resonance occurring on collision is high. A. A. E.

**Spectra and Critical Potentials of Fifth Group Elements.** A. E. RUARK, F. L. MOHLER, P. D. FOOTE, and R. L. CHERAULT (*U.S. Bureau of Standards, Sci. Paper* 490; 1924, **19**, 463—486).—The following critical potentials have been obtained: arsenic,  $11.54 \pm 0.5$ ; antimony,  $8.5 \pm 1.0$ ; bismuth,  $8.0 \pm 0.5$  volts. The resonance potentials of arsenic and bismuth correspond with the mean excitation voltages of groups of spectral lines. Those of antimony offer difficulties in their interpretation. The absorption and thermionic discharge spectra were studied; for bismuth, the spectroscopic voltage stages were investigated in detail. The arc spectrum of arsenic is very poor in lines, a gap occurring in the visible region. This gap becomes narrower and shifts towards longer wave-lengths in bismuth and antimony. This is illustrated by energy diagrams for the three elements. From the fine structure of some of the lines, it is deduced that a new quantum number is needed, which is called the fine quantum number. The arc spectra of arsenic, antimony, and bismuth and the 14-volt lines of bismuth are classified. H. WARD.

[**Results of Electron Impacts in Gases.**] A. L. HUGHES (*Phil. Mag.*, 1924, [vi], **48**, 56—64).—The processes of dissociation, excitation, and ionisation of hydrogen by electronic impacts are discussed. The author concludes that the dissociation of hydrogen in this manner is accompanied much more often by excitation of the atoms than by their ionisation. The important variable in determining the character of, and the intensity distribution in, a spectrum is the energy of impact of the electron on the molecule.

S. B.

**Electric Discharge through Gases at Low Pressures.** J. J. THOMSON (*Phil. Mag.*, 1924, [vi], **48**, 1—33).—The phenomena of the electric discharge through gases at low pressures are explained on the following theory of the ionisation in the dark space and in the negative glow. The radiation emitted when the positive ions are neutralised at the cathode causes, by its photoelectric effect, an emission of electrons from the electrode. These electrons, falling through the whole potential difference in the dark space, constitute a beam of uniform, high speed, cathode rays. These cathode rays in their passage excite the gas in the negative glow to the emission of radiation, and this, on subsequent absorption, is responsible for the ionisation in this part of the discharge.

Positive ray observations with compounds such as benzene,



phenol, and hydrocyanic acid show that carbon has a tendency to polymerise in the negative glow, and aggregates up to  $C_5$  have been detected. S. B.

**Initial Stages of Glow Discharge in Hydrogen and Air.** K. OELKERS (*Ann. Physik*, 1924, [iv], **74**, 703—721).—Reiche's experiments (*ibid.*, 1917, [iv], **52**, 109) were repeated, his results, in general, being confirmed. The current impulses, accompanied by flashes in the discharge tube, occurred at irregular intervals and were of varying intensity, but were always more intense than stated by Reiche. The frequency and intensity of the impulses increased with increasing potential difference between the electrodes; the current flowing between the individual impulses varied similarly. As the current increased, the potential between the electrodes reached a maximum. The phenomena are practically independent of the nature of the gas. With aluminium electrodes, successive increases in potential of 2 volts caused a small glow to appear, which went out of its own accord. With other electrodes (copper, steel, silver) the current-strength oscillated greatly under a constant potential difference. Aluminium electrodes showed a much stronger potential increase for a given increase in current-strength than electrodes of the other metals. An explanation is given based on the assumption of an electric double layer resident in the gas-film on the electrodes, which is reinforced by the passage of a strong current and partly reversed by a weak one. S. K. T.

**Modified Vacuum Tubes.** J. J. MANLEY (*Phil. Mag.*, 1924, [vi], **48**, 110—112).—The external silvering of vacuum tubes is recommended, to increase the illumination in a desired direction. The attachment of efficient external electrodes is also described. S. B.

**Chance of Electrons being Ejected Photoelectrically from Atoms by X-Rays.** G. E. M. JAUNCEY (*Phil. Mag.*, 1924, [vi], **48**, 81—88).—The author concludes that the chance of an electron being ejected photoelectrically from an atom by X-rays is proportional to the cube of the wave-length of the X-rays, and to the square of the energy with which the electron is bound to the atom, provided that the wave-length of the rays is short enough to make ejection possible. S. B.

**Variation in the Resistance of Carbon and Graphite with Temperature.** B. NOYES, jun. (*Physical Rev.*, 1924, **24**, 190—199).—The resistance of carbon (from braided silk) between  $-190^{\circ}$  and  $+2000^{\circ}$  decreased linearly with increase of temperature; graphite (99% purity) showed a minimum resistance at about  $600^{\circ}$ , and the resistance then increased linearly. The presence of air (0.25 atm.) caused a decrease of about 3% in the resistance of graphite at about  $600^{\circ}$ . Above  $2000^{\circ}$ , carbon rods increase in length, and exhibit a change in the zero resistance. A. A. E.

**Electrical Conductivity and certain other Properties of Metals and Alloys on the Basis of Bohr's Theory.** K. HØJENDAHL (*Phil. Mag.*, 1924, [vi], **48**, 349—360; cf. T., 1924, **125**, 1381).—On the basis of the Bohr atom, it is shown that the

formation of a permanent diatomic compound in a metallic vapour by sharing electron orbits is impossible. It is possible, however, to form an infinite-atomic compound (the metallic state), in which an electron moves in a quantised zigzag path throughout the metal. The shape of the path, the distances between the atoms, the energy and velocity of the electron will be determined by quantum rules and will be only slightly dependent on temperature. At the absolute zero, in a perfect crystal, the paths will be regular and of a length equal to that of the crystal, and placed in a number of equivalent directions parallel to rows of atoms. The direction of the path may be broken by heat vibration of the atoms, irregularities in the crystal, and by introduction of atoms of another kind. The specific electrical conductivity is proportional to the mean length of the unbroken path. An equation showing the relation between resistance and composition is derived which is in fair agreement with experiment. The rise in resistance produced by the introduction of 1 atom of a number of metals into 100 atoms of a pure metal is approximately constant for the same metal. The velocity of the covalent electrons of iron has been calculated, using Drude's equation.

J. B. F.

**The Wiedemann-Franz Law.** I. A. EUCKEN and O. NEUMANN (*Z. physikal. Chem.*, 1924, **111**, 431—446).—Measurements have been made at 90° and 273° Abs. of the heat conductivity and electrical conductivity of antimony, bismuth, and a red brass (82% Cu, 18% Zn). In each case fine-grained and coarse-grained specimens were prepared by suitable heat treatment. The heat conductivity diminished markedly as the size of grain decreased whilst the electrical conductivity showed little change. The heat conductivity is regarded as composed of two parts, a true metallic conductivity and a non-metallic conductivity due to the crystal structure. In the limit with a very finely crystalline metal, only the metallic conductivity will come into play. By extrapolation, this limiting conductivity was calculated and it was found that when this value was inserted in the expression  $\lambda/\kappa T$  (where  $\lambda$ =heat conductivity,  $\kappa$ =electrical conductivity, and  $T$ =absolute temperature), antimony and bismuth gave figures which agreed approximately with those found for good conductors.

S. S.

**Dielectric Constants of Chlorinated Paraffins and Olefines.** P. WALDEN, and O. WERNER (*Z. physikal. Chem.*, 1924, **111**, 465—471).—The authors have constructed a new type of apparatus (to be described shortly elsewhere) employing a transmitting tube which generates oscillations of 4.5 m. wave-length. The following data obtained at 16° are given. Tetrachloroethylene  $\epsilon$ =2.37, trichloroethylene  $\epsilon$ =3.42, *cis*-dichloroethylene (b. p. 48.5°)  $\epsilon$ =3.67, *trans*-dichloroethylene (b. p. 60°)  $\epsilon$ =7.55, *s*-tetrachloroethane  $\epsilon$ =8.15, pentachloroethane  $\epsilon$ =3.76. The geometrical isomerides of dichloroethylene are thus sharply distinguished. The dielectric constants run parallel with the development of colour when salts of triphenylcarbinol etc. are dissolved in these solvents, the liquid with the highest dielectric constant giving the most intense color-

ation. The solubility of mercuric chloride in the series of chlorinated paraffins and olefines was determined and it was found that  $\epsilon/\sqrt[3]{m}$  (where  $m$  is the solubility) was nearly constant throughout the series. S. S.

**Number of  $\alpha$ -Particles emitted by Radium.** V. F. HESS and R. W. LAWSON (*Phil. Mag.*, 1924, [vi], **48**, 200—207).—The estimate of Geiger and Werner (this vol., ii, 226) of the number of  $\alpha$ -particles emitted by radium is criticised on several experimental grounds, and the authors conclude that their own earlier value (*Wien. Ber.*, 1918, **127**, 405) is near the true number. S. B.

**Radioactive Disintegration Series. II.** W. P. WIDDOWSON and A. S. RUSSELL (*Phil. Mag.*, 1924, [vi], **48**, 293—306; cf. A., 1923, ii, 819).—An unsuccessful search has been made for an isotope of radon, thoron, and acton in pitchblende, thorianite, and a preparation of radium. Theoretically, it is anticipated that only three out of four possible radioactive series exist which have members of atomic number 86 emitting  $\alpha$ -particles. The fourth, if it exists, should arise from an isotope of proto-actinium having an atomic weight of 233, pass through the missing elements 87 and 85, and end in bismuth. The principal isotopes of elements 91, 85, and 87 are calculated to be 233, 221, and 217, respectively; elements 87 and 85 are probably simple. J. B. F.

**Lead as the Last Member of the Radioactive Elements?** M. CURIE (*Rev. gén. Sci. pur. appl.*, 1923, **34**, 576—580; from *Chem. Zentr.*, 1924, i, 2089).—The author discusses the differences between the properties of the isotopes of lead. Attempts at separation by fractional crystallisation and by centrifuging were unsuccessful. G. W. R.

**Apparatus for the Extraction and Purification of Radium Emanation.** W. MUND.—(See ii, 607.)

**Mass Spectra of Zirconium and some other Elements.** F. W. ASTON (*Nature*, 1924, **114**, 273).—Zirconium gives mass lines at 90, 92, 94, and possibly 96, with intensities 10, 2, 4, (1), respectively. The masses of the isotopes are actually less than whole numbers by about 0.1 unit; the atomic weight is estimated to be 91.4 or 91.2. Cerium consists of a strong component at 140 and a weak one at 142; the principal isotopes of neodymium are 142, 144, 146, and possibly 145. Re-examination of the mass-spectrum of barium has afforded some evidence of a component at 136 in addition to the principal line at 138, but the accepted value for the atomic weight of barium, 137.37, is not thereby accounted for. The existence of  $\text{Si}^{30}$  is confirmed. The results are in broad agreement with Russell's predictions. A. A. E.

**Isotopes of Mercury and Bismuth and the Satellites of their Spectral Lines.** H. NAGAOKA (*Nature*, 1924, **114**, 245).—Polemical against Runge (this vol., ii, 446). A. A. E.

**Separation of Isotopes by Fractional Diffusion in Solutions.**

B. L. VANZETTI (*Atti I. Congr. nat. Chim. pur. appl.*, 1923, 420; from *Chem. Zentr.*, 1924, i, 1013).—By diffusion of a saturated solution of sodium chloride through a series of 8 to 10 animal or vegetable membranes separated by aqueous layers, a slight diminution in the atomic weight of the diffused chlorine was observed. The difficulty of separation by this method is attributed to the hydration of the chlorine ions. G. W. R.

**Structure of Cobalt.** H. COLLINS (*Chem. News*, 1924, 129, 107—108).—Speculative. A. A. E.

**Theory of Valency.** T. M. LOWRY (*Bull. Soc. chim.*, 1924, 4, 815—837).—A lecture delivered before the Chemical and Physical-chemical Societies of France. J. W. B.

**Relation between Crystal Habit and Crystal Lattice.** M. YAMADA (*Physikal. Z.*, 1924, 25, 289—296).—The method developed in a previous paper (*ibid.*, 1923, 24, 364) for the calculation of the surface energy of a crystal plane is applied to the three cubic lattices and to the diamond lattice. Cleavage directions in a crystal are assumed to be those which give a minimum value to the surface energy, and the cleavage figures deduced in this way are those which are accepted as typical of the various lattices. S. B.

**Photomicrographic Evidence of the Crystal Structure of Pure Cerium.** E. E. SCHUMACHER and F. F. LUCAS (*J. Amer. Chem. Soc.*, 1924, 46, 1167—1169).—Pure cerium, prepared by electrolysing very pure cerium chloride, was polished, allowed to oxidise slowly in a desiccator, and then rapidly etched with concentrated nitric acid. Photomicrographs of this surface indicate that the metal crystallises in the regular system (cubic form). There is no evidence of the hexagonal form (cf. Hull, *Physical Rev.*, 1921, 18, 89). M. S. B.

**Space Lattice of Rhombic Sulphur.** H. MARK and E. WIGNER (*Z. physikal. Chem.*, 1924, 111, 398—414).—Rhombic sulphur crystallises in rhombic bipyramids of the space group type  $V_h^{24}$ ;  $a=10.61$  Å.,  $b=12.87$  Å.,  $c=24.56$  Å. These dimensions are twice as large as those found by Bragg (*Proc. Roy Soc.*, 1914, A, 89, 575), and are based on a study of Laue X-ray patterns (A., 1923, i, 1055) coupled with a special modification of the reflection method, which is designed to allow of the determination of the plane of origin of a given line without ambiguity. The elementary cell contains 128 atoms; of these 16 at most are connected geometrically to form the crystal molecule. The centres of gravity of these groups form a rhombic diamond lattice. S. S.

**Crystal Structure of Oxalic Acid.** H. HOFFMANN and H. MARK (*Z. physikal. Chem.*, 1924, 111, 321—356).—The space lattice of anhydrous and hydrated oxalic acid has been studied by the graphical method of interpreting Laue X-ray patterns described previously (A., 1923, i, 1055). Anhydrous oxalic acid crystallises in rhombic bipyramids of the space group type  $V_h^{18}$ . The elementary

cell contains four molecules of  $(\text{CO}_2\text{H})_2$  and has the dimensions  $a=6.46 \text{ \AA.}$ ,  $b=7.79 \text{ \AA.}$ ,  $c=6.02 \text{ \AA.}$ ; no geometrical connexion can be traced between the chemical molecules in the crystal unit. A second modification of anhydrous oxalic acid has been discovered which crystallises in monoclinic needles. Hydrated oxalic acid crystallises in monoclinic prisms of the space type  $C_{2h}^5$ . The elementary cell contains 2 mols. of  $(\text{CO}_2\text{H})_2 \cdot 2\text{H}_2\text{O}$  and has the dimensions  $a=6.05 \text{ \AA.}$ ,  $b=3.57 \text{ \AA.}$ ,  $c=11.9 \text{ \AA.}$  The X-ray evidence shows that each molecule of acid is associated with 2 mols. of water; the latter is therefore in chemical combination and is not held as a separate entity in the crystal structure. S. S.

**Connexion between the (Disposition of) the Acetaldehyde Molecule in the Space Lattices of Acetaldehyde-ammonia and Metacetaldehyde.** O. HASSAL and H. MARK (*Z. physikal. Chem.*, 1924, **111**, 357—384).—Acetaldehyde-ammonia crystallises in ditrigonal scalenohedra of the space group type  $D_{3d}^5$ , for which  $r=8.17 \text{ \AA.}$  and  $\alpha=84^\circ 50'$ . The primitive elementary cell contains 6 mols. of acetaldehyde-ammonia which are arranged so as to show a geometrical connexion between the aldehyde groups within the crystal molecule. Metacetaldehyde gives tetragonal crystals belonging to the space group type  $C_{4v}^2$  or  $C_{4v}^9$ ,  $a=10.34$ ,  $c=4.10$ . The elementary cell is space-centred and contains 8 mols. of acetaldehyde; of these four at most are connected together to form the crystal molecule. The probable dispositions of the C·C·O chain in the two lattices are discussed. S. S.

**Vibration Frequencies of Salts.** W. HERZ (*Z. anorg. Chem.*, 1924, **138**, 135—136).—The equation of Lindemann (*Physikal. Z.*, 1910, **11**, 609) by means of which the vibration frequencies of elements can be calculated from their melting points, atomic weights, and atomic volumes, has been applied to the alkali halides, nitrates, and sulphates. It is assumed that the effective atomic weights are one-half the molecular weights for the halides and nitrates, and one-third for the sulphates. The data for the molecular volumes at the melting points are more accurate than those used by Lindemann, and the following frequencies are obtained, the figures requiring to be multiplied by  $10^{12}$  in each case. For the fluorides of lithium, sodium, potassium, rubidium, and caesium, 13.45, 9.80, 7.04, 4.77, 3.60; for the chlorides, 7.48, 6.37, 5.10, 3.72, 2.97; for the nitrates, 4.08, 3.68, 3.24, 2.54, 2.28; and for the sulphates, 5.88, 4.88, 4.29, 3.33, 2.69, respectively; rubidium bromide, 3.05; caesium bromide, 2.53; and for the iodides of sodium, potassium, rubidium, and caesium, 2.92, 2.93, 2.46, 2.14, respectively. W. H.-R.

**Grain-growth in Antimonial Lead.** R. S. DEAN and W. E. HUDSON.—(See ii, 682.)

**Search for Element Number 43.** C. H. BOSANQUET and T. C. KEELEY (*Phil. Mag.*, 1924, [vi], **48**, 145—147).—The X-ray spectra of a number of manganese minerals have been investigated

in the hope of detecting lines due to the missing element 43. The results were negative. S. B.

**Radius of the Hydrogen Atom in Crystals.** G. AMINOFF (*Geol. Fören. Förh. Stockholm*, 1921, **43**, 389—396; from *Chem. Zentr.*, 1924, i, 1493).—From X-ray examination of magnesium hydroxide and manganous hydroxide, the radius of the hydrogen atom is found to be 1.15 Å. and 1.05 Å., respectively. The structure of these hydroxides is expressed by the substitution, in  $\text{H}_2\text{O}\cdot\text{O}\cdot\text{H}_2$ , of the contiguous hydrogen atoms of adjacent trigonal axes by magnesium or manganese in the direction of these axes. In the curve of atomic volumes, hydrogen becomes the first element of the alkali metal group. G. W. R.

**Refraction of X-Rays in Iron Pyrites.** R. VON NARDROFF (*Physical Rev.*, 1924, **24**, 143—151).—The grating space of iron pyrites is 2.7028 Å.

**Effect of Temperature on the Regular Reflection of X-Rays from Aluminium.** E. H. COLLINS (*Physical Rev.*, 1924, **24**, 152—157).—The planes of the atoms in aluminium foil are farther apart than for the metal in bulk as a result of the rolling. The difference is not decreased by heating at 600°. W. E. G.

**Precision X-Ray Spectrometer.** W. SOLLER (*Physical Rev.*, 1924, **24**, 158—167).

**X-Ray Examination of Aged Metallic Hydroxides.** R. FRICKE and F. WEVER.—(See ii, 616.)

**Röntgenographic-Chemical Investigations.** H. STINZING (*Z. physikal. Chem.*, 1924, **111**, 157—159).—Polemical in reply to Siegbahn (this vol., ii, 581).

**Property of Swelling by Substances. Production of Fibre Diagrams by X-Ray Spectroscopy.** J. R. KATZ (*Physikal. Z.*, 1924, **25**, 321—326).—The fibres of unmercerised, weakly and strongly mercerised ramie, artificial silk from viscose, and from ammoniacal copper oxide solution, pure degummed silk, silkworm fibre and fibroin have been subjected to X-ray spectroscopical examination in the dry and wet state. From the spectrograms obtained, it is not possible to detect as the result of swelling any marked change in the lattice of the crystallite substances. It appears, therefore, that the change produced by swelling is intracellular.

J. B. F.

**Mesomorphic State and Magnetic Birefringence.** L. ROYER (*J. Phys. Rad.*, 1924, [vi], **5**, 208—219).—A discussion of the causes of the phenomena of the mesomorphic state and magnetic birefringence (cf. Friedel, A., 1923, ii, 223, 224; Cotton and Mouton, A., 1910, ii, 368). It is concluded that both are due to the presence of unsymmetrical molecules which orient themselves under the action of a magnetic field. In the case of the mesomorphic state the couple is produced by mutual action of one molecule on another.

In organic compounds, those groups which favour or augment the magnetic birefringence give rise to the mesomorphic state or enlarge its domain of stability. The influence of the double or triple bond is very marked in both cases.

W. E. G.

#### Atomic Dimensions and Gaseous Hydride Formation.

H. L. RILEY (*Phil. Mag.*, 1924, [vi], **48**, 126—128).—The author suggests that the tendency of an element to form a gaseous hydride is chiefly dependent on the diameter of the atom. Atoms of a diameter less than that of the electron orbit in the hydrogen molecule form hydrides with evolution of heat, whilst atoms which are larger either do not form a gaseous hydride, or react endothermically.

S. B.

#### Correction of the Density of Liquids for the Buoyancy of Air.

G. BARR (*J. Chem. Soc.*, 1924, **125**, 1040—1045).—The advantages of the use of a sealed counterpoise for a pycnometer (Hartley and Barrett, T., 1911, **99**, 1072), rather than a solid glass counterpoise (Wade and Merriman, T., 1909, **95**, 2174), are discussed. The densities of very volatile liquids cannot be determined with a high degree of accuracy by the pycnometer method if it is necessary to allow for large expansions or contractions. Other sources of error are considered.

M. S. B.

#### Extension of some Results of the Kinetic Theory of Gases.

Y. ROCARD (*Compt. rend.*, 1924, **178**, 2068—2071).—Theoretical.

L. J. H.

#### Molecular Attraction and Molecular Combination.

O. MAASS (*J. Franklin Inst.*, 1924, **198**, 145—159).

**Evidence of Association in Carbon Dioxide from the Joule-Thomson Effect.** F. G. KEYES (*J. Amer. Chem. Soc.*, 1924, **46**, 1584—1592).—A small fraction of polymerised molecules in a gas is not detectable from measurements of  $p$ ,  $v$ , and  $T$ , but may have a marked influence on the specific heat and Joule-Thomson effect. By an extension of the thermodynamic equation for the Joule-Thomson effect, the author obtains the equation (1)  $C_{p\mu} = 2A/RT - \beta + y/p \cdot \Delta H_p$ , in which  $y$  is the fraction of associated molecules,  $\Delta H_p$  the heat of the association reaction at temperature  $T$  and constant pressure,  $C_{p\mu}$  the product of the measured values of the Joule-Thomson effect and the specific heat at the pressure to which this effect corresponds.  $A$ ,  $R$ , and  $\beta$  are the usual constants of the equation of state. In a reaction of the type  $\text{CO}_2 \rightleftharpoons \frac{1}{2}(\text{CO}_2)_2$ , if it is assumed that chemical equilibrium exists at every stage, it can be shown that  $y = Ce^{2\Delta U_0/RT}$ .  $p/I^{5/2}$ , where  $C$  is a constant, and  $\Delta U_0$  the heat of reaction at absolute zero; this value of  $y$  can then be substituted in equation (1). Except at the three lowest temperatures, this equation is in good agreement with the results obtained by Burnett (*Phys. Rev.*, 1923, **22**, 590) for the Joule-Thomson effect in carbon dioxide, indicating that association has occurred. The equation is not, however, in agreement with the specific heat measurements of Joly (*Proc. Roy. Soc.*, 1886, **41**,

352; *Phil. Trans.*, 1891, **182**, A, 73; 1894, **185**, A, 943). The fraction of associated molecules in carbon dioxide at one atmosphere pressure is estimated as 0.004 at 220° K, 0.00075 at 270° K, and 0.000052 at 400° K. W. H. R.

**Van der Waals' Equation of State and the Liquid State of Aggregation.** I. J. BERGER (*Z. physikal. Chem.*, 1924, **111**, 129—156).—From van der Waals' equation, applied to liquids for which the external pressure is negligible compared with the cohesive force, the author derives a characteristic "constant of thermal expansion,"  $C = R a/b$ , a quantity which can be calculated from the coefficient of thermal expansion  $\alpha$  by the equation  $C = \alpha(1 + \alpha T)/(1 + 2\alpha T)^2$ . Expressed in terms of the critical temperature,  $C = 8/27T_k$ . From these equations and the volume at the boiling point, values of  $a$  and  $b$  are obtained which differ from those derived from the critical data. The relative volume,  $w = v/b$ , is the same for all non-associating liquids at the same reduced temperature ( $T/T_k$ ) within 0.5%. An equation, called the "relative equation of state," similar in form and purpose to the reduced equation of van der Waals, is put forward with  $b$  for unit of volume, the maximum internal pressure  $a/b^2$  as unit of pressure, and as unit of temperature that for which  $CT = 1$ . Hence  $(p_r + 1/w^2)(w - 1) = T_r$ . The corresponding equation of thermal expansion is empirically modified to the form  $w = 3/(1 + 2\frac{1}{12}\sqrt{1 - \frac{2}{3}T_r})$  and this fits the experimental data satisfactorily from the freezing point to the immediate neighbourhood of the critical temperature. More accurate values of  $C$ ,  $a$ , and  $b$  are then deduced from this. On applying these values to Stephan's formula for the heat of evaporation fair agreement is obtained. L. J. H.

**Proof of Nernst's Heat Theorem.** W. H. VAN DE SANDE BAKHUYZEN (*Z. physikal. Chem.*, 1924, **111**, 39—56).—Various examples which have been cited as evidence for the Nernst heat theorem are discussed in detail, and it is shown that some of those most often quoted are unsuitable for the purpose owing to uncertainty in the experimental data. The more reliable the data are, the more closely they agree with the theory. L. J. H.

**Chemical Constant of Hydrogen.** W. H. VAN DE SANDE BAKHUYZEN (*Z. physikal. Chem.*, 1924, **111**, 57—61).—The chemical constant of hydrogen is calculated in detail from the vapour pressure of the solid, the specific heat data at low temperatures, and the latent heat of fusion. It is  $C = 1.112$ . L. J. H.

**Measurement of Vapour Pressure of Gases Liquefying at Low Pressures.** E. CARDOSO, A. A. COPPOLA, and U. FLORENTINO (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 404—406; from *Chem. Zentr.*, 1924, i, 1975).—Methods are described for the purification of sulphur dioxide and for the measurement of its vapour pressure. G. W. R.

**Theory of Vapour-pressure Curves.** R. LORENZ (*Z. anorg. Chem.*, 1924, **138**, 104—108).—The vapour pressures of a liquid at



different temperatures may be compared with those of a standard liquid of similar chemical nature by means of the equations of Dühring,  $(T_2 - T_1)/(\theta_2 - \theta_1) = q$ , and of Ramsay and Young,  $T_2/\theta_2 = T_1/\theta_1 + c(T_2 - T_1)$ , where  $T_1$  and  $T_2$  are the absolute temperatures corresponding with vapour pressures  $p_1$  and  $p_2$  for the one substance, and  $\theta_1$  and  $\theta_2$  are the b. p. of the second substance at the same two pressures. The equations are identical if  $c=0$ , in which case  $q=T_1/\theta_1$ . In practice,  $p_1$  is taken as 1 atm., in which case  $T_1$  and  $\theta_1$  are the b. p. for the two liquids. The data for a large number of substances have been collected, the comparison liquids being hexane and water. For most substances, the value of  $c$  is very nearly zero, and the Dühring constant,  $q$ , is very nearly equal to  $T_1/\theta_1$ . Consequently if the vapour-pressure curve of one substance is known, the vapour-pressure curve of a second chemically similar substance may be deduced if the b. p. of the two substances are known.

W. H.-R.

**Dissociation of Cadmium Carbonate: Method of Determining Dissociation Pressures.** M. CENTNERSZWER and L. ANDRUSOW (*Z. physikal. Chem.*, 1924, **111**, 79—97).—The method consists in heating cadmium carbonate in an enclosed tube connected to a manometer; as the temperature slowly rises the pressure increases uniformly until dissociation begins to take place, when it increases much more rapidly. On cooling again, a similar break in the pressure-temperature curve occurs. By employing mixtures of an inert gas with varying proportions of carbon dioxide the dissociation temperatures for various (partial) pressures were determined. An ordinary static apparatus was also employed and yielded results in good agreement. The reaction is slow, especially the recombination, but is truly reversible and no intermediate products are formed. The dissociation pressure may be represented by the empirical equation  $\log p = -12.44 + 0.02439T$ . Applying van't Hoff's equation, the heat of dissociation is  $-43.63$  Cal.

L. J. H.

**Influence of Intensive Drying on Inner Equilibria.** A. SMITS (*J. Chem. Soc.*, 1924, **125**, 1068—1075).—This is in part a claim for priority (cf. A., 1922, ii, 358) over Lewis (this vol., ii, 98) with regard to the explanation of the effects of intensive drying as due either to a fixation of the inner equilibrium, or to a displacement of the latter followed by fixation. The existence of a fixed equilibrium has now also been confirmed experimentally by the partial separation of the components by fractional distillation (see also Baker, T., 1923, **123**, 1223).

A method is given for preparing phosphorus pentoxide so active that, in less than one year, benzene may be dried by it sufficiently to give a boiling point higher than  $87^\circ$ . The introduction of the slightest trace of water vapour causes a fall in boiling point to the normal value.

M. S. B.

**Crack Development in Glass.** E. E. SCHUMACHER (*J. Amer. Chem. Soc.*, 1924, **46**, 1772—1777).—A comparison has been made

of the tendency to crack shown by five different kinds of glass. The strain was imposed by the passage of an electric current between two terminals embedded in the specimens, and the temperature of the glass was maintained at  $300^{\circ}$  during the experiments. It was found that the glasses cracked the more readily the larger their alkali content. The electrical conductivity also increases with the proportion of alkali. S. B.

**Validity of Beer's Law for Copper Sulphate Solutions.** R. MECKE and H. LEY (*Z. physikal. Chem.*, 1924, **111**, 385—397).—Measurements have been made by photographic methods of the molecular extinction coefficient of copper sulphate solutions in the infra-red and ultra-violet. In the long-wave region, Beer's law is very nearly true, as is known to be the case in the visible region of the spectrum. For ultra-violet light ( $\lambda$  2300 to  $\lambda$  2900), the molecular extinction coefficient varies rapidly with the concentration. Cupric chloride, which is known to exhibit deviations in the visible region, shows still larger deviations with ultra-violet light. The influence of ionisation, complex formation, and hydration on the absorption of light by copper salts is discussed. S. S.

**Conductivity and Ionisation of Solutions of Potassium Iodide in Nitromethane.** J. C. PHILIP and H. B. OAKLEY (*J. Chem. Soc.*, 1924, **125**, 1189—1195).—Measurements of the electrical conductivity of potassium iodide in nitromethane have been made at different concentrations and temperatures, an audio-oscillator being used as a source of alternating current. From these, values for  $\Lambda_{\infty}$  have been deduced by Washburn's method (A., 1918, ii, 55). For any given concentration the ratio  $\Lambda/\Lambda_{\infty}$  is found to decrease with rise of temperature. Measurements of the viscosity of nitromethane show that  $\Lambda_{\infty} = k \cdot f^{0.95}$  between  $0^{\circ}$  and  $85^{\circ}$ ,  $f$  being the fluidity and  $k$  a constant. M. S. B.

**Electrical Conductance of Solutions of the Alkali Halides in Acetophenone.** J. L. R. MORGAN and O. M. LAMMERT (*J. Amer. Chem. Soc.*, 1924, **46**, 1117—1132).—The electrical conductivities of acetophenone solutions of sodium and potassium iodide and of lithium chloride and bromide have been measured at  $25^{\circ}$  in the dark. Solutions of lithium chloride obey the law of mass action over the whole range of concentrations possible (up to  $0.005616M$ ), whilst solutions of lithium bromide and sodium and potassium iodides agree with it up to concentrations of about  $0.007M$ ,  $0.0005M$ , and  $0.003M$ , respectively. By applying Kraus and Bray's general dilution formula (A., 1913, ii, 914) to the values for sodium iodide, which shows the greatest deviations from the mass law, the following equation is obtained,  $c\gamma^2/(1-\gamma) = 24.82 \times 10^{-4} + 0.140 \times (c\gamma)^{0.698}$ , where  $c$  is the concentration and  $\gamma = \Lambda_c/\Lambda_0$ . M. S. B.

**State of Division of Dyes of High Molecular Weight in Aqueous Solution.** R. ZSIGMONDY (*Z. physikal. Chem.*, 1924, **111**, 211—233).—Measurements of the osmotic pressures and freezing points of aqueous solutions of Congo-red and benzopurpurin

4B indicate that these dyes behave as non-electrolytes, or at the most are only very slightly ionised. On the other hand, conductivity measurements indicate extensive ionisation. These relations suggest that the dyes do not exist in solution as simple molecules and ions, but as strongly-ionised molecular aggregates or as micelles, and that the system is of colloidal character. Experiments on the ultra-filtration of these solutions show that benzopurpurin 4B exists in larger particles than Congo-red, but finer than any type of colloidal gold particles. Both these dyes are retained by filters which are permeable to molecules of sodium chloride, sugar, and also to the ions of the sodium salts of the intermediate fatty acids. Benzopurpurin 10B (which has the highest molecular weight of the three dyes) shows a considerably higher osmotic pressure than would be produced if the salt were non-ionised, and it readily permeates through ultra-filters which are sufficiently fine to retain the other two dyes. J. B. F.

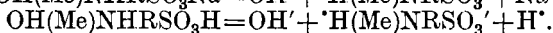
**Degree of Dissociation of Acids in Alcohol.** E. SCHREINER (*Z. physikal. Chem.*, 1924, **111**, 419—430).—The author uses the data of Goldschmidt and his collaborators (A., 1920, ii, 605) on the velocity of esterification of acids in ethyl alcohol solution to calculate the degree of dissociation of hydrochloric acid in ethyl alcohol. Dissociation is not complete at  $v=100$  and the dissociation constant  $K_0 = C_I^2 f^2 / C_n = 5 \times 10^{-2}$ , where  $C_I$  = concentration of ions,  $f$  = mean activity of  $H^+$  and  $Cl^+$ , and  $C_n$  = concentration of undissociated acid. Similar calculations for hydrobromic acid give  $K_0 = 0.4$ . S. S.

**Deduction of the Relation between the Osmotic Coefficient and the Activity Coefficient.** E. SCHREINER (*Z. physikal. Chem.*, 1924, **111**, 415—418).—The equation  $1 + C \cdot d \log f / dC = \phi + C \cdot d\phi / dC$  (where  $C$  = concentration,  $f$  = activity coefficient,  $\phi$  = osmotic coefficient), which is of importance in Bjerrum's theory of electrolytes (A., 1919, ii, 9; 1923, ii, 467), is obtained by simple thermodynamic argument of the type used by van't Hoff and Nernst. S. S.

**Constitution of Strong Electrolytes.** C. DRUCKER and G. RIETHOF (*Z. physikal. Chem.*, 1924, **111**, 1—38).—The abnormalities of strong electrolytes have been exaggerated and in any case vary so greatly for different substances that any explanation based merely on the presence of electrical charges is out of the question. An explanation is sought in the formation of complex ions such as  $Na_2^{++}$ ,  $Cl_2^{--}$ ,  $Na_2Cl^+$ , and  $NaCl_2^-$  and the law of mass action is supposed to be obeyed. It is assumed that the total number of molecules and ions may be deduced from freezing-point data (with a correction for hydration) and that the concentration of the simple ions may be calculated from *E.M.F.* measurements by Nernst's law, whilst the conductivities and transport numbers, together with assumptions relative to the nature of the complex ions present, afford a basis for the calculation of the concentrations of these ions. The data for the chlorides of the alkali metals and hydrogen are collected and new potentiometric measurements are recorded.

Experimental values are not sufficiently accurate for a quantitative interpretation, but it is considered that even in dilute solution (0.01*M*), the concentration of complex ions is not negligible, and, in consequence, the concentration of simple, non-ionised molecules is much smaller than is generally assumed. L. J. H.

**Existence of Dual Ions.** O. BLÜH (*Z. physikal. Chem.*, 1924, **111**, 251—256; cf. A., 1923, ii, 823).—In reply to the criticism of Thiel and Dassler (this vol., ii, 388), the author maintains his opinion that helianthin forms a dual ion. The author's results cannot be explained on the supposition that methyl-orange was used instead of helianthin or that the water employed contained dissolved carbon dioxide because both the sodium salt and the free acid give rise to dual ions:—



Further, the internal salt and the dual ion are not isomerides and are represented respectively by the following formulæ:— $\text{NMe}_2\text{RSO}_3\text{Na}$ ;  $\text{'HMe}_2\text{NRSO}_3\text{'}$ . The existence of dual ions is

indicated by the form of the dielectric constant curve and is not inconsistent with the colour changes shown by the acid and its salt. The red colour detected spectroscopically by Thiel and Dassler may be due to the internal salt, but it does not necessarily follow that the dual ion is also red in colour. The colour of the dual ion plays no rôle in the behaviour of helianthin as an indicator. The dipole theory is also further discussed. J. B. F.

**Equilibria between Sodium and Potassium and their Chlorides in the Fused State and the Production of Alkaline-earth-Lead Alloys.** K. JELLINEK and G. TOMOFF (*Z. physikal. Chem.*, 1924, **111**, 234—250).—The influence of lead on the equilibrium  $\text{Na} + \text{KCl} \rightleftharpoons \text{NaCl} + \text{K}$  has been studied. Mixtures of sodium and potassium chlorides were heated at 800° for various periods with either lead-sodium, lead-potassium, or lead-sodium-potassium alloys. The proportions of the reactants were varied and the product was analysed at intervals of 6 minutes. For a given mixture, the ratio of sodium to potassium in the solid phase was found to be constant. It is shown that the equilibrium of the fused salts follows the law of mass action. The chemical affinities of sodium and potassium approach equality as the temperature is raised and the heat of reaction becomes very small.

Lead-alkaline-earth metal alloys can be prepared by fusing together a mixture of about 75—85% alkaline-earth chloride and a sodium-lead alloy containing about 10% of sodium. J. B. F.

**Inter-ionic Attraction Theory of Ionised Solutes.** I. A. A. NOYES (*J. Amer. Chem. Soc.*, 1924, **46**, 1080—1097).—The theory of inter-ionic attraction, as developed by Milner, Debye, and Hückel, is critically discussed, and an expression is derived, by several independent methods, for the free energy decrease  $\Delta F$  when a gram-ion

of valency  $\nu$  is transferred from an infinite volume of a solution in which its concentration is  $c$  and in which it and other ions are present at such concentrations as correspond with  $\Sigma(c\nu^2)$ , to an infinite volume of a solution in which its concentration  $c_0$  is so small that all the ions present behave as perfect solutes. This equation is  $-\Delta F = RT \log_e c/c_0 - A\nu^2 \sqrt{\Sigma(c\nu^2)}/K^{1/5} T^{0.5}$ , where  $A$  is the product of certain constants and equals  $7.77 \times 10^{15}$  in *C.G.S.* units, and  $K$  is the dielectric constant. The limitations of the equation are pointed out.

M. S. B.

**Inter-ionic Attraction Theory of Ionised Solutes. II. Testing of the Theory with Experimental Data.** A. A. NOYES (*J. Amer. Chem. Soc.*, 1924, **46**, 1098—1116).—The last term  $-A\nu^2 \sqrt{\Sigma(c\nu^2)}/K^{1/5} T^{0.5}$  in the expression for  $-\Delta F$  (cf. preceding abstract) is equal to  $\log_e \alpha$ , where  $\alpha$  is the activation or activity coefficient. The underlying theory has therefore been tested (for a large number of different electrolytes) by activation values derived from freezing-point, electromotive-force, and solubility-effect data. Deviations from the requirements of theory are supposed to be due in part to the neglect of the size of the ions and to the increase of the dielectric constant of the water in the neighbourhood of the ions. In general, however, the activation values, especially those derived from solubility effects, are in satisfactory agreement with those calculated from the above formula.

M. S. B.

**Law of Mass Action in Ionised Systems.** W. WESSEL (*Physikal. Z.*, 1924, **25**, 270—277).—A mathematical paper on the lines of that of Debye and Hückel (*A.*, 1923, ii, 459), particular consideration being given to ionised gases.

L. J. H.

**Mutual Solubility. III. Mutual Solubility of Glycerol and Amino and Hydroxy Compounds.** R. R. PARVATIKER and B. C. McEWEN (*J. Chem. Soc.*, 1924, **125**, 1484—1492).—The solubility of a large number of organic substances in glycerol was determined by Alexéev's method (cf. *T.*, 1923, **123**, 2279). Complete solubility curves are given for glycerol-guaiacol, *m*-toluidine, and *n*-ethylbenzylamine. The law of rectilinear diameters holds fairly well for these solubility rings, and the diameters for the upper portions of the glycerol-*o*-toluidine and glycerol-pyrocatechol monoethyl ether curves lie respectively on the extensions of the diameters of the solubility rings for glycerol-*m*-toluidine and glycerol-guaiacol. The introduction of hydroxyl and (or) amino groups into an aliphatic or aromatic hydrocarbon increases its solubility in glycerol. The miscibility of glycerol with secondary and tertiary mono-amines decreases with increase in the number and size of the alkyl groups attached to the nitrogen atom. Thus glycerol has the following critical solution temperatures: with monomethylaniline 224.5°; with monoethylaniline 273°; with dimethylaniline 287°; and with diethylaniline, above 300°. The mutual affinity between certain atoms or groups in the molecules of a solvent and a solute appears to give rise to a "solution stress" tending to produce complete miscibility. The introduction of alkyl

groups decreases the solubility of carbon compounds in glycerol, the decrease being determined by the position taken up by the alkyl group. Thus whilst phenol and glycerol are miscible in all proportions, guaiacol and glycerol are only completely miscible below  $39.5^{\circ}$  and above  $83.5^{\circ}$ . The introduction of an alkyl group in the para position to an  $-\text{OH}$  or  $-\text{NH}_2$  group diminishes the solubility to a much less extent than in the ortho position, indicating that the decrease is mainly due to steric hindrance. Glycerol is miscible in all proportions with the lower members in the series of the primary alkylamines. When the amino group in an aromatic compound is in the side-chain, the miscibility with glycerol is greatly increased; thus benzylmethylamine is more soluble than monoethylaniline. Pyridine, quinoline, and heterocyclic compounds containing a ring nitrogen atom are, in general, miscible with glycerol in all proportions. A. C.

**Solubility of Salts of Uric Acid. II.** G. BARKAN (*Biochem. Z.*, 1924, **146**, 446—457).—The gelatinous sodium urate previously described by the author (*Z. Biol.*, 1922, **76**, 257) is a well-defined form representing a transition stage between the colloidal and crystalline states. No such form with well-defined solubilities is obtained in the case of potassium urate. Sodium and potassium urate gels prepared according to Schade's method (A., 1922, i, 1192) gave at  $18^{\circ}$  solubilities of  $25.7 \times 10^{-3}$  and  $32.4 \times 10^{-3}$  mol. per litre, respectively. The reduction in the solubility of urate gels when kept for some time is ascribed to a gradual increase in the size of the urate particles, and the stability of urate sols to the presence of the soluble modifications. J. P.

**Density and Hydration in Gelatin Sols.** F. E. BROWN (*J. Amer. Chem. Soc.*, 1924, **46**, 1207—1209).—A criticism of Svedberg and Stein's explanation (this vol., i, 104) of the change in density observed when gelatin is suspended in various solutions.

M. S. B.

**Densities and Viscosities of Arsenic Trisulphide Sols.** A. BOUTARIC and R. SIMONET (*Bull. Acad. Roy. Belg.*, 1924, [v], **10**, 150—154).—Stable arsenic trisulphide sols containing up to 300 g. per litre may be obtained by dissolving successive quantities of arsenious oxide and passing hydrogen sulphide through the solution after each addition, eliminating much of the water under greatly reduced pressure, and removing any large particles then present by energetic centrifuging. The density of these sols varies linearly with the concentration up to about 9%, but subsequently increases more rapidly (cf. Linder and Picton, T., 1895, **67**, 71). If  $\eta$  and  $\eta_0$  represent respectively the viscosities of the sol and of the dispersive medium, both at  $20^{\circ}$ , and  $\phi$  the ratio between the volume of the disperse substance and of the suspension, the value of  $k = (\eta - \eta_0)/\eta_0\phi$  approaches 2.5 as the dilution approaches infinity (cf. Einstein, A., 1921, ii, 19). T. H. P.

**Viscosimetry of Colloidal Solutions.** WOLFGANG OSTWALD (*Z. physikal. Chem.*, 1924, **111**, 62—78).—A defence of the capillary

viscosimeter against the criticism of Freundlich (*ibid.*, 1924, **108**, 153). Some solvated colloids do not obey the law of Hagen and Poiseuille in that the rate of flow is not proportional to the pressure. The Ostwald viscosimeter is, however, equally competent with other patterns to deal with such solutions since, by varying the head between the capillary and the exit, it can be employed to determine the variation of the rate of flow with pressure. By simple modifications it can be used for all the purposes for which the more complicated instruments were designed. Examples of its use with such solutions are given, the results being similar to those obtained by Freundlich.

I. J. H.

**Synthesis of Colloidal Micelles. The Silver Micelle.** G. REBIÈRE (*Rev. gén. Colloid.*, 1924, **2**, 105—110, 139—142).—Pure precipitated silver ground with water gives grey suspensions of low concentration and poor stability. The addition of silver oxide and of sodium hydroxide to the water gives better suspensions, but the mechanical effect of the grinding makes the particles too dense. When precipitated silver is left in contact with a solution of silver oxide (0.086 g.  $\text{Ag}_2\text{O}$  per l.) there is first a marked adsorption of the oxide, and after some weeks a reddish-violet hydrosol is obtained. At the boiling point, the formation of the sol proceeds more rapidly, but the product contains rather coarser particles. The addition of a trace of sodium hydroxide facilitates the reaction. The production of a silver sol by this method takes place in the dark and cannot be accounted for by the reduction of silver oxide by light. This latter reaction can be used to prepare silver sols by exposing a solution of silver oxide containing a trace of sodium hydroxide to ultra-violet light. The sols prepared by any of these methods show many particles in the ultra-microscope; that the micelles contain silver and silver oxide is demonstrated by the action of sulphuric acid, which causes a partial clearing of the solution, but leaves particles of silver which dissolve on the addition of potassium permanganate or nitric acid.

S. S.

**Constitution of Gaseous Ions.** J. J. NOLAN (*Physical Rev.*, 1924, **24**, 16—30).—In ionised moist air, about twenty groups of positively charged ions with mobilities between 2.24 to 1.34 have been found. These are probably composed of clusters of from 15 to 36 water molecules. Computations made on Thomson's theory of clusters are in accord with this view.

W. E. G.

**Composition of some Colloidal Gold Solutions.** P. A. THIESSEN.—(See ii, 691.)

**Determination of Surface Tension with Very Small Volumes of Liquid, and the Surface Tension of Octanes and Xylenes at Several Temperatures.** T. W. RICHARDS, C. L. SPEYERS, and E. K. CARVER (*J. Amer. Chem. Soc.*, 1924, **46**, 1196—1207).—The surface tension of water, benzene, ethylbenzene, three isomeric octanes, and *o*-, *m*-, and *p*-xylene have been determined at different temperatures by a method requiring only small quantities of liquid. The difference in the level of the liquid in the two arms of a capillary

U-tube with arms of different diameters is measured. Equations are given by which the surface tension at any intervening temperature may be calculated. Values for the "total surface energy" of unit area are also recorded. The results are in accord with the theory of atomic compressibility. M. S. B.

**Relation between Surface Tension, Density, and Chemical Composition.** S. SUGDEN (*J. Chem. Soc.*, 1924, 125, 1177—1189).

—The expression  $P = [M/(D-d)]\gamma^{\frac{1}{3}}$ , derived from the fourth root of McLeod's constant (*Trans. Faraday Soc.*, 1923, 19, 38), where  $M$  is the molecular weight,  $D$  and  $d$  are the densities of liquid and vapour respectively, and  $\gamma$  is the surface tension, may be used to calculate the critical volume, since  $P = 0.78V_c$  within 3%.  $P$  is called the parachor to signify comparative volume, and it may be expressed as a function of chemical composition. For saturated compounds, it is an additive function nearly constant for positive isomerides, definite atomic parachors being assigned to each element. Unsaturation and ring formation produce a marked effect to which definite numerical constants may also be attributed; hence the determination of the molecular parachor should assist in the solution of problems of chemical constitution. An examination of the density and surface tension of 167 compounds has given, in most cases, values for  $P$  in close agreement with the calculated values. The structure of the nitro group and of hydrogen peroxide is discussed.

M. S. B.

**Dependence of Surface Activity and Surface Tension of Solutions upon Temperature and Concentration.** P. REHBINDER (*Z. physikal. Chem.*, 1924, 111, 447—464).

—The surface tension of aqueous solutions of propionic, butyric, valeric, hexoic, and heptoic acids and of tetramethyl-, tetraethyl-, and tetrapropyl-ammonium chlorides has been determined by the methods of capillary rise and maximum bubble pressure at temperatures from 0° to 100°. The method of maximum bubble pressure is regarded as most suitable for these solutions, and with the higher fatty acids it was possible by reducing the rate of bubbling to obtain constant values, thus showing that adsorption at the new surface had reached its equilibrium value. The surface tension-temperature curves are convex to the temperature axis except in the case of substances, *e.g.*, the ammonium salts, which have only a small surface activity, when a linear relation holds as with pure water. The surface activity  $G = -\delta\gamma/\delta c$ , where  $\gamma$  = surface tension and  $c$  = concentration, is plotted against temperature and exhibits a maximum usually between 10° and 40°. The significance of the form of these curves in connexion with theories of adsorption is discussed.

S. S.

**Influence of Orientation of Surface Molecules on Surface Tension of Pure Liquids.** S. SUGDEN (*J. Chem. Soc.*, 1924, 125, 1167—1177).—Surface tension measurements of fourteen different para derivatives of benzene have been made by the maximum bubble method at different temperatures. The values found do



not show the regularities required by the hypotheses of Langmuir (A., 1917, ii, 525), and of Harkins and others (A., 1917, ii, 239) with regard to the orientation of surface molecules of liquids. The total surface energy of a substance does not appear to be determined by one particular group, brought to the surface by a special orientation, but by the chemical nature of the molecule as a whole.

McLeod's relation (*Trans. Faraday Soc.*, 1923, **19**, 38) between surface tension and density has been found to hold for all the substances examined except the amines, which are probably associated.

M. S. B.

### **Adsorption and Surface Tension at Liquid-Liquid Interface.**

J. H. MATHEWS and A. J. STAMM (*J. Amer. Chem. Soc.*, 1924, **46**, 1071—1079).—The tension at the surface of contact of water with mixtures of dimethylaniline and heptane, and of dimethylaniline and benzene, the densities of which obey the mixture rule, has been determined by the drop-weight method. The addition of dimethylaniline, which has the lower interfacial tension, causes a large fall in the tension, especially in the case of heptane. The reciprocal influence of the hydrocarbons on dimethylaniline is much less. This is ascribed to the aggregation of the constituent of lower surface tension at the surface of the drop. On the assumption that if there were no adsorption of one constituent at the interface the surface tension of the mixture would follow the mixture rule, the amount of adsorption at the surface may be calculated in moles per sq. cm. Assuming, further, that the concentration ratios are valid down to thicknesses of molecular dimensions, Gibbs' adsorption equation may be applied to the data and results in close agreement with Langmuir's adsorption theory obtained.

M. S. B.

### **Adsorption Forces and their Electrical Nature.**

B. ILIIN (*Phil. Mag.*, 1924, [vi], **48**, 193—200).—A relation between the adsorption capacity and the dielectric constant of a gas is obtained on the assumption that the forces of adsorption are electrical in nature. An expression is also developed for the heat of adsorption which is in good accord with experimental data.

S. B.

### **Adsorption from the Gas Phase at a Liquid-Gas Interface.**

II. T. IREDALE (*Phil. Mag.*, 1924, [vi], **48**, 177—193; cf. A., 1923, ii, 379).—Further observations are described of the effect of vapours on the surface tension of mercury. The surface tension decreases smoothly with increase in the partial pressure of the vapour (water, benzene, etc.) with which the mercury is in contact, up to the saturation point, at which a sudden large drop is observed. It is suggested that from an unsaturated vapour a film, one or two molecules thick, is formed on the mercury surface. From a saturated vapour a much thicker film is deposited. In attempts to measure the surface tension of mercury in a vacuum, difficulty was encountered in dealing with adsorbed water films which persisted at pressures of  $10^{-5}$  atm.

S. B.

**Adsorption by Activated Sugar Charcoal. I. Proof of Hydrolytic Adsorption.** E. J. MILLER (*J. Amer. Chem. Soc.*, 1924, **46**, 1150—1158).—Charcoal adsorbs acid from salt solutions leaving an equivalent amount of base in the solution. It thus causes hydrolytic decomposition of the salt. The effect is much more marked with salts of organic than of inorganic acids. [Cf. *B.*, 1924, 815.] M. S. B.

**Adsorption of Hydrogen by Nickel.** J. W. TERWEN (*Chem. Weekblad*, 1924, **21**, 386—389).—The variation of the maximum adsorption with temperature observed by Gauger and Taylor (*A.*, 1923, ii, 398) may be explained by assuming that an equilibrium between molecular and atomic adsorbed gas which is dependent on temperature exists in the surface layer. The heat of adsorption should therefore vary considerably with the temperature, but the data available are not sufficient to test this. Measurement by Gauger (*J. Amer. Chem. Soc.*, 1924, **46**, 674) of the frequencies of the radiations emitted by a nickel-hydrogen surface at various critical potentials also indicates that the hydrogen is present both in the atomic and molecular conditions, as well as in combination with the nickel. S. I. L.

**Heat of Wetting of Lead Sulphate.** W. A. KOEHLER and J. H. MATHEWS (*J. Amer. Chem. Soc.*, 1924, **46**, 1158—1167).—The heat of wetting of powdered lead sulphate has been found to be practically zero. The area of the surface of the powder was determined by radioactivity methods (cf. Paneth and Vorwerk, *A.*, 1922, ii, 618). M. S. B.

**Adsorption and Cataphoresis.** K. VON DER GRINTEN (*Compt. rend.*, 1924, **178**, 2083—2085).—Observations have been made on the cataphoresis of suspensions and on the effect of adding a coloured electrolyte. With a suspension of glass the speed of the particles decreases with increasing concentration of the electrolyte, and at a given concentration the direction is reversed. The adsorption per sq. cm. of surface was determined by using known quantities of glass and measuring the reduction in the concentration of the solution by means of the absorption spectrum. Below  $N/10000$ , the velocity of cataphoresis and the adsorption vary very rapidly with the concentration of the electrolyte. A maximum adsorption of  $1.6 \times 10^{14}$  molecules per sq. cm. was found; this corresponds with a unimolecular film on the surface of the glass particles. Similar results were obtained with selenium sols. L. J. H.

**Anomalous Adsorption.** J. B. SPEAKMAN (*Nature*, 1924, **114**, 352).—The adsorption isotherms for the adsorption of night-blue by wool, when obtained by colorimetric determination of the unadsorbed dye, have the same peaked form as those obtained by Biltz and Steiner (*A.*, 1910, ii, 830) for cotton and charcoal. Probably, however, the anomaly has no real existence, since the hydrochloric acid which is apparently produced during the adsorption increases the depth and alters the character of the colour of the residual liquid. A. A. E.

**Use of the Coherer to Investigate Adsorption Films.** W. G. PALMER (*Proc. Roy. Soc.*, 1924, **A**, **106**, 55—68).—Reasons are given for supposing that the electrical resistance of conductors in loose contact is due to adsorbed films of gas. The potential necessary to break down this resistance was determined for several gases with contacts of tungsten, platinum, and tungsten-carbon. It is sought to calculate from these results the heat of desorption and to draw conclusions therefrom as to the nature of the films. L. J. H.

**Sedimentation of Bentonite.** H. F. COWARD (*J. Chem. Soc.*, 1924, **125**, 1470—1474).—Bentonite, a natural silicate of aluminium, readily forms aqueous milky suspensions when allowed to stand in contact with water for a few minutes. The suspensoid is negatively charged, and is reversibly coagulated by suitable additions of electrolytes. The easy preparation of these suspensions suggests their possible use as material for colloid investigations. S. B.

**Effect of Complex Formation on Oxidation Potentials. Influence of the Cyanide Ion on the Ferrocyanide-Ferricyanide Potential.** J. A. V. BUTLER and G. P. DAVIES (*J. Chem. Soc.*, 1924, **125**, 1101—1106).—According to the thermodynamic equation for the oxidation potential of a system of two complex metallic ions, the potential should not be affected by the presence of excess of the complex-forming substance, provided that the complex ions differ only in total ionic charge and not in composition. To test this conclusion the effect of addition of excess of the cyanide ion on the ferrocyanide-ferricyanide potential has been examined. Since there is rapid oxidation of the cyanide to cyanate by the ferricyanide, readings of the potential at different intervals of time after mixing were taken, and the approximate initial value was obtained by extrapolation, correction being also made for the presence of the added potassium ion. The effect of the cyanide ion is thus found to be negligibly small, even at concentrations as high as  $2N$ .

A study of the potential of iron in ferrocyanide solutions has also been made, but no satisfactory conclusions can be drawn from it.

M. S. B.

**Normal Cathode Fall of the Glow Discharge, and the Work of Detaching Electrons at Cathodes composed of Electrolytes.** A. GUNTHER-SCHULZE (*Z. Elektrochem.*, 1924, **30**, 289—291).—An investigation of the fall of potential across the negative glow region when the discharge takes place from a cathode of aqueous electrolyte through an atmosphere of saturated water vapour. The work involved in detaching the electrons is compared with the corresponding work in the case of metals. The normal cathode fall  $V_n$  is  $423 \pm 2$  volts for ordinary solutions, and reasons are given in support of the view that this is the cathode fall for water. The potential required to detach the electrons is 4.07 volts, which is nearly equal to that required in the case of the noble metals. For solutions containing more than 45% of sulphuric acid  $V_n$  decreases with increasing concentration to a minimum of 310 volts in 75% acid, then increases to 350 volts in 100% acid. The observed

behaviour is supposed to afford evidence of the existence of different kinds of molecules in the solutions.

E. B. R. P.

**Hydrogen Overvoltage of Zinc.** G. M. WESTRIP (*J. Chem. Soc.*, 1924, **125**, 1112—1121).—The hydrogen overvoltage at a zinc cathode, as measured by the direct method, increases with current density and decreases with rise in temperature. The decrease of overvoltage with varying proportions of zinc sulphate has been determined and also the effect of different metallic impurities, copper, iron, and antimony. Antimony produces a much greater depression of overvoltage at low current densities than at high. The presence of gelatin increases the overvoltage, a maximum being reached which, at low current densities, is followed by a fall. For purposes of comparison the overvoltages at copper and brass electrodes have also been determined.

The phenomenon of overvoltage is explained by the existence of an unstable adsorption compound between hydrogen and the surface atoms of the cathode material. This spontaneously decomposes, giving gaseous hydrogen, and is to be distinguished from a chemical compound in the ordinary sense. An equation identical with Tafel's (*A.*, 1905, ii, 223) has been derived,  $\eta = a \text{ constant} + RT/2F \cdot \log D_k$ , showing the connexion between  $\eta$ , the overvoltage, and  $D_k$ , the current density. An expression has also been derived for the diminution of overvoltage with time, when the circuit has been broken. From this it is concluded that the commutator method will give lower results than the direct method, and these will vary with the speed of the commutator.

M. S. B.

**Thermal Energy of Electrons in Metals.** E. D. EASTMAN, A. M. WILLIAMS, and T. F. YOUNG (*J. Amer. Chem. Soc.*, 1924, **46**, 1184—1196; cf. ii, 681).—Values of  $C_p$ , the atomic heat at constant pressure, for a large number of metals, have been deduced from the observations of different investigators, and from these values the atomic heats at constant volume,  $C_v$ , have been calculated by means of the empirical equation,  $C_p - C_v = kT$ . For all metals  $C_v$  increases to values above  $3R$  at high temperatures. These large values of the atomic heat are attributed to the absorption of appreciable quantities of energy by loosely bound electrons and not to deviations from simple harmonic oscillation on the part of the atoms, since  $C_v$  for typical non-metals does not exceed  $3R$ , and there is no general parallelism between the excess heat capacity and certain other metallic constants whilst there is a correspondence between electropositive character and the excess heat capacity.

M. S. B.

**Kinetics of Coupled Reactions.** F. THIERSCH (*Z. physikal. Chem.*, 1924, **111**, 175—189).—A mathematical treatment of the kinetics of consecutive unimolecular reactions, in which the author makes use of nomographic methods.

J. B. F.

**Velocity of Hydrolysis of Mixed Acetals.** A. SKRABAL, E. BRUNNER, and H. AIROLDI (*Z. physikal. Chem.*, 1924, **111**, 109—128).—The velocities of hydrolysis of various mixed acetals were

measured at 25°. Dialkyl acetals hydrolyse only in acid solution, but if one or both groups be acyl the substance is of the nature of an ester and alkaline hydrolysis is possible. From the relation between the velocity coefficients for the pure and mixed acetals, it is inferred that the hydrolysis occurs in successive stages of which only the first, producing the "half-acetal," is slow. It is probable that the second stage is a direct decomposition,  $R_1R_2C(OH)(OX) = R_1R_2CO + HOX$ , rather than a true hydrolysis. In the case of acyl acetals, direct decomposition may be involved in the first stage, although in aqueous solution hydrolysis predominates. Alkyl-acyl esters are compared with Wegscheider's  $\psi$ -esters, which may be regarded as mixed acetals. Such substances hydrolyse rapidly in water without catalysis. The reactivity of individual groups and their mutual influence is discussed and compared with the corresponding relations observed in other physical properties.

L. J. H.

**Velocity of Hydrolysis of Acetals and Ketals.** A. SKRABAL and K. H. MIRTLE (*Z. physikal. Chem.*, 1924, **111**, 98—108).—The velocities of hydrolysis of ethyl acetal and ethyl ketal in the presence of varying quantities of hydrochloric acid were measured at 25°. The reactions appear to be unimolecular and the rate of hydrolysis is proportional to the hydrogen-ion concentration. When this is unity, the velocity coefficients are 60 and  $1.5 \times 10^5$ , respectively (minute as unit of time). The effect of steric hindrance is discussed with reference to its influence on the driving force and on the so-called chemical resistance.

L. J. H.

**Esterification in Presence of Silica Gel.** C. H. MILLIGAN, J. T. CHAPPELL, and E. E. REID (*J. Phys. Chem.*, 1924, **28**, 872—878).—Silica gel is a better catalyst than either thoria or titania for esterification reactions in the vapour phase. Ninety % of a mixture of the vapours of acetic acid and alcohol was esterified when passed slowly over silica gel at 150°. The authors conclude that the esterification limit must be much greater in the vapour than in the liquid phase.

S. B.

**Preparation of a Nickel Catalyst and its Reducing Activity.** M. LIETZ (*J. pr. Chem.*, 1924, [ii], **108**, 52—60).—A nickel catalyst for hydrogenation is best prepared by precipitating a 3—5% nickel sulphate solution at room temperature with sodium carbonate solution. The washed precipitate should be dried in a vacuum, and reduced at 300° with hydrogen for a minimum time depending on the quantity of catalyst. For 0.5 g. this should not exceed 30 min. The rate of absorption of hydrogen, in the reduction of sodium cinnamate, is approximately proportional to the quantity of catalyst used. The rate is increased by more vigorous shaking and is determined by the rate of diffusion of hydrogen into the metal, since changes in concentration of the sodium cinnamate have no effect on the rate of reduction.

E. H. R.

**Preparation of Palladous Oxide and its Use as a Catalyst in the Reduction of Organic Compounds. VI.** R. L. SHRINER and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, **46**, 1683—1693).—Palladous oxide, prepared by a similar method to that used for platinum oxide (Adams and Shriner, A., 1923, ii, 773) is an effective catalyst for hydrogenation. The activity was tested by its action on maleic acid (cf. Voorhees and Adams, A., 1922, ii, 558). The best temperature for the fusion of palladous chloride with sodium nitrate was thus found to be 600°. This oxide is much more active than that prepared by Schneider's method.

The reduction of aldehydes is much more readily completed with palladium than with platinum and the presence of iron is not essential. Ferrous chloride accelerates the reduction of aromatic aldehydes which contain a free hydroxyl group, but not the reduction of the ethers derived from them; in some cases it increases the time required for reduction. The influence of ferrous chloride in the reduction of benzaldehyde and salicylaldehyde has been examined in detail. The reduction with palladium differs from that with platinum in continuing until the aldehyde group has been converted into a methyl group. This further stage of reduction proceeds more slowly and in the case of benzyl alcohol is inhibited by the presence of ferrous chloride. The time of reduction is approximately proportional to the amount of the catalyst. Activation of the catalyst with oxygen accelerates the reduction of benzaldehyde, but retards the reduction of maleic acid, a similar poisoning effect being observed with platinum. The nature of the compounds to be reduced has thus an important effect, and oxygen is regarded as a promoter similar to ferrous chloride, each promoter exercising its own specific action, depending both on the catalyst and the type of compound undergoing reduction. The oxide obtained by fusing iridium chloride with sodium nitrate is not a catalyst in the reduction of aldehydes.

R. B.

**Third Report of the Committee on Contact Catalysis.** H. S. TAYLOR (*J. Physical Chem.*, 1924, **28**, 897—942).—A summary of recent investigations.

**First Law of Photochemistry.** M. C. C. CHAPMAN (*J. Chem. Soc.*, 1924, **125**, 1521—1526).—The photochemical reaction between hydrogen and oxygen has been studied with the object of testing Draper's law. The rate of combination of the gases was found to increase rather more slowly with the intensity of the incident light than is demanded by proportionality, but the author considers that the results confirm the law. This conclusion is in contradiction to that drawn by Baly and Barker (T., 1921, **119**, 653) from their work on the hydrogen-chlorine reaction.

S. B.

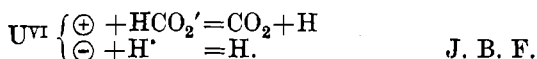
**Photochemical Studies. XVII. Photochemical Oxidation of Hydriodic Acid.** J. PLOTNIKOV (*Z. physikal. Chem.*, 1924, **111**, 171—174).—Mainly a critical review of previous work on the subject (cf. A., 1910, ii, 1020; 1920, ii, 427).

J. B. F.

**Quantum Sensitiveness of Uranyl Oxalate Photolysis.**

P. F. BÜCHI (*Z. physikal. Chem.*, 1924, **111**, 269—314).—The photolysis of oxalic acid in presence of uranyl salts is to be attributed to the decomposition of the non-ionised molecules of uranyl oxalate ( $\text{UO}_2\text{C}_2\text{O}_4$ ), or of the complex ions  $[\text{UO}_2(\text{C}_2\text{O}_4)_2]''$ . When oxalic acid is present in excess of the equimolar ratio, the velocity of decomposition is independent of the concentration of the oxalic acid, and is approximately constant. If the proportion of oxalic acid is smaller, the sensitiveness to light is, however, approximately proportional to the concentration of the oxalic acid. The great stability of the complex is indicated (a) by the quantitative equality of the velocity of decomposition for systems of uranyl sulphate, nitrate, and oxalate in presence of oxalic acid, (b) by the permanence of the complex on the addition of oxygen, hydrochloric acid, sulphuric acid, and formic acid. The photolytic decomposition follows Einstein's law, one absorbed light quantum decomposing 1 mol. of oxalic acid. In the initial stages of the decomposition of uranyl formate in sulphuric acid solution one absorbed light quantum decomposes about 0.7 mol. of formic acid. J. B. F.

**Photolysis of Uranyl Oxalate.** E. BAUR (*Z. physikal. Chem.*, 1924, **111**, 315—318; cf. preceding abstract).—In 1917, the author suggested that the photolysis of oxalic acid corresponds with the equation  $\text{H}_2\text{C}_2\text{O}_4 + 1 h\nu = \text{H}_2\text{O} + \text{CO} + \text{CO}_2$ , but subsequently (cf. A., 1919, ii, 264) expressed the view that the reaction is diquant, glyoxylic acid being formed as an intermediate product. In view of the results of Büchi, the author now concludes that the oxalic acid ion is directly decomposed into carbon monoxide and carbon dioxide with the absorption of one light quantum. It is also probable that formate photolysis likewise requires one quantum and is represented as follows :



**Influence of Light on Aqueous Solutions of Potassium Iodide, Nitrate, and Chlorate.** K. SURYANARAYANA.—(See ii, 675.)

**Photolysis of Potassium Nitrate.** C. S. ROBINSON.—(See ii, 675.)

**Constant Level Device for Water-baths.** R. BROOKS (*J. Chem. Soc.*, 1924, **125**, 1546). S. B.

**Calorimeter for Specific Heats and Heats of Vaporisation.** F. G. KEYES and J. A. BEATTIE (*J. Amer. Chem. Soc.*, 1924, **46**, 1753—1760).—A calorimeter is described, with which the specific and latent heats of vaporisation of ethyl ether have been redetermined. The heat of vaporisation was calculated from the electrical energy required to maintain a constant temperature in the calorimeter during the distillation of a known weight of liquid. In the specific heat measurements, the correction for the heat capacity of the calorimeter was eliminated by combining the observations

made with two different ether contents. The following values are given: Specific heat of ether at 12°, 0.568; and at 13.4°, 0.577. Latent heat of vaporisation at 0.1°, 90.50; at 11.8°, 88.83. Probable error 1%. S. B.

**Device for regulating Thermostats.** M. MESTREZAT and (MLLE.) M. JANET (*Bull. Soc. Chim. biol.*, 1924, **6**, 534—535).—The usual toluene-mercury gas regulator is much more sensitive if altered so that the gas passes the controlling mercury surface in the opposite direction from that usually adopted, namely from the outer wide tube into the narrow inner tube, the tip of which is ground at an angle of 45°. G. M. B.

**Simple Non-splash Ring for Use with Scheibler's Desiccators.** S. C. BRADFORD (*J. Chem. Soc.*, 1924, **125**, 1546—1547).—Splashes from sulphuric acid in a Scheibler's desiccator can be avoided by allowing a glass bell-shaped ring to rest with the narrower end downwards on the constriction of the acid reservoir. S. B.

**Receiving Apparatus for Fractional Distillation at Low Pressures.** W. F. SEYER (*J. Amer. Chem. Soc.*, 1924, **46**, 1209—1210).—A funnel, to which pieces of iron may be attached, is moved about within the apparatus, by means of a magnet, so as to direct the stream of condensing liquid to different receivers. Illustrative diagrams are given. M. S. B.

**Extraction Apparatus.** E. RUFF (*Chem.-Ztg.*, 1924, **48**, 531).—The apparatus consists of a wide tube, similar to the cylinder of a Soxhlet extractor, having a narrow tube at the bottom which passes through the cork of the extraction flask. The thimble containing the substance to be extracted is placed in the wide tube and rests on small projections on the inner wall of the tube, other projections at a higher level keeping the thimble in a central position and leaving a narrow space between it and the inner wall of the tube for the passage of the solvent vapour. A small condenser is fitted into the upper open end of the tube. W. P. S.

**Highly Sensitive Manometer.** L. HEIS (*Physikal. Z.*, 1924, **25**, 326—330).—The principle of the manometer is based on the change in pressure of a gas when subjected to a powerful magnetic field. The indicator portion of the instrument consists of two small aluminium vanes, 10 mm. apart, which are freely suspended inside an aluminium case. By means of a small mirror attached to the suspension fibre, the movement of the vanes is amplified. The whole is enclosed in an air-tight vessel. Two fine capillary tubes terminate at one end in a nozzle in the walls of the vane casing so placed that a blow or suction immediately influences the oscillation of the vanes. The capillaries are connected to two small tubular bulbs of similar capacity which can be isolated from the recorder by means of taps. One bulb is placed between the poles of a strong electro-magnet, and by switching on the electro-magnet the pressure of the gas in this bulb is suddenly increased, thereby causing a definite amount of kick in the recorder. If  $\kappa$  is the magnetic



susceptibility of the gas, and  $H$  the field strength, the pressure is increased by an amount  $\kappa H/2$ . The magnetic susceptibility of the gas is known and the instrument calibrated, and thus from the increase in pressure produced by the magnetic field, the original pressure can be calculated. In the apparatus described, for a static difference of  $2.7 \times 10^{-8}$  mm. of mercury, a throw of 1 mm. on a scale 2 m. distant is produced. The theory of the apparatus is also mathematically treated.

J. B. F.

**Lecture Table Demonstration to Illustrate that the Conductivity of a Solution is Due to its Ions.** O. O. WATTS (*J. Amer. Chem. Soc.*, 1924, 46, 1210).—An electric lamp is connected in series with a cell containing a 5% solution of barium hydroxide and with a source of alternating current; when sulphuric acid is run into the solution the luminosity of the lamp is first reduced and then increased.

M. S. B.

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## Inorganic Chemistry.

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**Effect of Pressure on the Refractive Power of Hydrogen.** F. SCHACHERL (*Pub. Fac. Sci. Univ. Masaryk*, 1923, 1—28; from *Chem. Zentr.*, 1924, i, 1154).—For the refractive index of electrolytic hydrogen at 0° and 760 mm., the value  $(n-1)=139.65 \times 10^{-6}$  was found. An increase in refractive power occurs with diminution in pressure. G. W. R.

**Atomic Dissociation of Hydrogen and Chlorine.** K. WOHL.—(See ii, 600.)

**Dissociation of Hydrogen and Nitrogen by Excited Mercury Atoms.** O. S. DUFFENDACK and K. T. COMPTON.—(See ii, 585.)

**Luminous Discharge in Chlorine.** W. A. NOYES, jun.—(See ii, 585.)

**Vapour Pressure of Liquid Chlorine.** M. TRAUTZ and W. GERWIG (*Z. anorg. Chem.*, 1924, **134**, 417—420).—The vapour pressure of liquid chlorine from a steel cylinder was measured through the temperature region  $T=194-238^{\circ}$  by static and dynamic methods, concordant results being obtained. The values differ from those of Henglein (A., 1922, ii, 760), but agree with those of Knietzsch at low and with those of Pellaton (A., 1916, ii, 245) at higher temperatures. To account for the difference in the present values and those of Henglein, it is suggested that there might be an isotopic difference in the chlorine obtained from a cylinder and that prepared chemically. The b. p. of the chlorine was  $-34.7^{\circ}/760$  mm., and the molecular heat of vaporisation at  $T=0^{\circ}$  was calculated to be  $4200 \pm 300$  cal. The vapour pressure can be expressed by the relationship  $\log p = -1160/T + 7.773$ . H. T.

**Spectrum of Fluorine.** H. G. GALE and G. S. MONK.—(See ii, 578.)

**Series Spectra of Oxygen.** J. J. HOPFIELD.—(See ii, 578.)

**Sulphur Chloride and Sulphur.** O. RUFF and H. GOLLA (*Z. anorg. Chem.*, 1924, **138**, 33—42).—The composition of a saturated solution of sulphur in sulphur chloride ( $S_2Cl_2$ ) corresponds closely with the formula  $S_4Cl_2$ . The boiling points of a series of solutions with increasing sulphur content have been determined, and the results are complicated by the fact that the b. p. of sulphur chloride itself varies with the time and the rate of heating, and is also affected by decomposition produced by corks in the apparatus. The b. p. data can be satisfactorily accounted for if it is assumed that two polythiochlorides of composition  $S_3Cl_2$  and  $S_4Cl_2$  are present, as well as  $S_8$  molecules, the solution taking place according to the reactions  $S_8 + 8S_2Cl_2 \rightleftharpoons 8S_3Cl_2$  and  $S_8 + 4S_2Cl_2 \rightleftharpoons 4S_4Cl_2$ . In solutions of high sulphur content, the dissolved sulphur is present almost entirely as  $S_4Cl_2$  and  $S_8$  molecules.  
W. H. R.

**Action of Persulphates on Metallic Cyanides.** I. BELLUCCI and B. RICCA (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 400—403; from *Chem. Zentr.*, 1924, i, 1915).—Persulphates react on heating with potassium ferrocyanide, giving hydrogen cyanide, which is partly oxidised to cyanogen.  
G. W. R.

**Fine Structure of the Nitrogen, Oxygen, and Fluorine Lines in the Extreme Ultra-violet.** I. S. BOWEN and R. A. MILLIKAN.—(See ii, 638.)

**Freezing-point Curve of the System Ammonia-Water.** L. D. ELLIOTT (*J. Physical Chem.*, 1924, **28**, 887—888).—Observations on the freezing points of mixtures of ammonia and water corroborate the existence of two crystalline hydrates of ammonia (cf. Postma, A., 1920, ii, 544).  
S. B.

**Oxidation of Ammonia to Nitric Acid.** H. G. KREUL (*Z. physik.-chem. Unterr.*, 1923, **36**, 261—262; from *Chem. Zentr.*, 1924, i, 1901).—Ferric oxide containing 5% of bismuth oxide catalyses the oxidation of ammonia to nitric acid.  
G. W. R.

**Oxidation of Hydrazine.** II. E. J. CUY and W. C. BRAY (*J. Amer. Chem. Soc.*, 1924, **46**, 1786—1795; cf. this vol., ii, 423).—The presence of oxygen is responsible for the fairly rapid decomposition of hydrazine in alkaline solutions. When alkali is added to a solution containing a hydrazine salt and excess of potassium ferricyanide, the oxidation of the hydrazine to nitrogen is quantitative, even in presence of air. The reaction can be used for the volumetric determination of hydrazine if the excess of ferricyanide is determined iodometrically. Conditions could not be found under which hydrazine is quantitatively oxidised to nitrogen by dichromate, but the reaction is realised approximately in the presence of excess of dichromate and of a moderate amount of acid.  
S. B.

**Oxidation of Hydrazine. III.** E. J. CUY, M. E. ROSENBERG, and W. C. BRAY (*J. Amer. Chem. Soc.*, 1796—1810; cf. preceding abstract, and Browne and Shetterly, A., 1909, ii, 233, 658).—The presence of the manganous salt formed during the reaction between hydrazine and potassium permanganate in acid solution is believed to be responsible for the fact that the amount of oxidising agent needed for 1 mol. of hydrazine is variable, and is always much lower than the four equivalents required for oxidation to nitrogen. A mechanism is suggested for the reaction, depending on the intermediate formation of manganic salt, and the following ionic equation is given:  $N_2H_5^+ + Mn^{+++} = NH_4^+ + \frac{1}{2}N_2 + H^+ + Mn^{++}$ . S. B.

**Oxidation of Hydrazine. IV.** E. J. CUY (*J. Amer. Chem. Soc.*, 1924, 46, 1810—1814; cf. preceding abstracts).—In the reaction between hydrazine and a ferric salt in acid solution, 1 mol. of hydrazine requires between one and two equivalents of ferric salt for oxidation. The limiting reaction may be expressed as follows:  $N_2H_5^+ + Fe^{+++} = NH_4^+ + \frac{1}{2}N_2 + H^+ + Fe^{++}$ . S. B.

**Electrolytic Preparation of Hydroxylamine.** G. PONZIO and A. PICHETTO (*Annali Chim. Appl.*, 1924, 14, 250—253).—The electrolytic reduction of sodium nitrate in presence of sulphuric acid by means of lead electrodes affords a convenient method for the preparation of hydroxylamine, which may be either isolated as hydrochloride or converted directly into dimethylglyoxime. [Cf. B., 1924, 868.] T. H. P.

**Preparation of Nitrites from Nitrates.** G. TACCHINI (*Giorn. Chim. Ind. Appl.*, 1924, 6, 275—276).—Sodium nitrate yields the nitrite in various proportions when heated with certain oxides, the best results being obtained with barium oxide or manganese dioxide. [Cf. B., 1924, 828.] T. H. P.

**Oxidation of Nitrous Acid, Hydrazine, Ammonia, and Hypophosphite by means of Permanganate.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1924, 61, 954—960).—Oxidation of nitrite to nitrate by permanganate does not occur in alkaline solution. Good results are obtained by adding the nitrite solution to a considerable excess of permanganate in presence of 4N-sulphuric acid and after 15 minutes titrating the excess with iodide and thiosulphate. Hydrazine is completely oxidised to nitrogen and water by excess of permanganate in alkaline solution, or by addition of permanganate to a boiling solution containing hydrochloric acid. Ammonia is oxidised to some extent by permanganate, the oxidation being more dependent on concentration in acid than in alkaline solution. Hypophosphite is oxidised quantitatively to phosphate by excess of permanganate in presence of sulphuric acid in 24 hours. S. I. L.

**Vapour Pressure of Liquid Nitrosyl Chloride.** M. TRAUTZ and W. GERWIG (*Z. anorg. Chem.*, 1924, 134, 409—416).—The vapour pressure of nitrosyl chloride from the f. p.  $-5.8^\circ$  to the b. p.  $61.5^\circ$  was measured by static and dynamic methods. The values obtained differ considerably from those of Briner and Pylkov

(A., 1913, ii, 317), whose nitrosyl chloride was probably contaminated with more volatile constituents. The vapour pressure can be expressed by the relationship  $\log p_{\text{mm. Hg}} = -(1332/T) + 7.867$ , and the molecular heat of vaporisation at  $T=0^\circ$  was calculated to be  $5350 \pm 300$  cal. H. T.

**Solubility of Phosphates in Relation to Hydrogen-ion Concentration.** W. R. G. ATKINS (*Nature*, 1924, **114**, 275).—Over the range  $p_{\text{H}} 7.0$ — $5.1$ , the solubility of normal phosphate calcium increases from 114 to 786 parts per million. The  $p_{\text{H}}$  value at which a precipitate is first obtained depends on the concentration of the phosphate, and precipitation is never absolutely complete, even at  $p_{\text{H}} 7.0$ . Strontium and barium phosphates give qualitatively similar curves. The solubility of magnesium phosphate is 450 parts per million at  $p_{\text{H}} 7.7$  and 1233 parts at  $p_{\text{H}} 5.8$ . The solubilities of lead, zinc, and nickel phosphates are, respectively, in parts per million: of  $\text{P}_2\text{O}_5$ , 0.97 at  $p_{\text{H}} 6.75$ ; 1.11 at  $p_{\text{H}} 6.85$ ; 11.9 at  $p_{\text{H}} 8.9$ . A. A. E.

**Band Spectrum of Boron Monoxide.** R. S. MULLIKEN.—(See ii, 640.)

**Band Spectrum of Silicon Oxide and of the Chlorides of Silicon, Carbon, Boron, and Aluminium.** W. JEVONS.—(See ii, 640.)

**Reactions of Siloxen with Halogen Compounds.** H. KAUTSKY and H. THIELE (*Z. angew. Chem.*, 1924, **37**, 540—541).—Siloxen,  $\text{Si}_8\text{H}_6\text{O}_3$ , obtained by the action of dilute hydrochloric acid on calcium silicide (Kautzky and Herzberg, *ibid.*, 1923, **36**, 508) reacts with dry hydrogen chloride or hydrogen bromide to give monochloro- or monobromo-siloxen and hydrogen. Methyl and ethyl iodides do not react with siloxen in darkness, but do so rapidly on exposure to light with formation of halogen-siloxen and methane or ethane. In the presence of water or amines, the product undergoes further change to give hydroxy or amino compounds. Other organic halides such as bromobenzene, halogen-acetic acids, etc., react in a similar manner with siloxen. F. A. M.

**Combustion of Charcoal in Oxygen.** F. C. G. MÜLLER (*Z. physik.-chem. Unterr.*, 1923, **36**, 260—261; from *Chem. Zentr.*, 1924, i, 1889—1890).—A continuation of earlier work (*Z. physik.-chem. Unterr.*, 1919, **32**, 41) on the combustion of wood charcoal in oxygen. In the first stage of combustion, carbon monoxide is formed which burns to form carbon dioxide. This is associated with a mantle of flame surrounding the burning charcoal, which disappears as combustion becomes slower. If the combustion is allowed to complete itself, a certain amount of carbon monoxide is found among the gaseous products. No carbon monoxide is found if the charcoal is withdrawn at the instant at which the mantle of flame disappears. G. W. R.

**Reactions in Phosgene [Carbonyl Chloride] Solutions.** I. A. F. O. GERMANN (*J. Physical Chem.*, 1924, **28**, 879—886).—The inorganic reactions of carbonyl chloride are discussed. The apparent

activity of this reagent is much enhanced under conditions (temperature or ultra-violet illumination) which produce appreciable dissociation into chlorine and carbon monoxide, but this complication does not arise in experiments carried out below  $200^{\circ}$  in glass vessels. Potassium iodide cannot be used to remove traces of chlorine from carbonyl chloride, as the latter gas itself reacts with the salt. The behaviour of metals with liquid carbonyl chloride is described. In some instances, the reactions appear to be limited by the insolubility of the products in liquid carbonyl chloride. The addition of aluminium chloride facilitates the solution of some metals, through the formation of a soluble double chloride. Pure aluminium dissolves only in sunlight, but is always rapidly attacked if amalgamated. S. B.

**Purification of Commercial Carbon Disulphide from Hydrocarbons.** O. RUFF and H. GOLLA (*Z. anorg. Chem.*, 1924, **138**, 31).—Excess of commercial carbon disulphide is shaken for 24 hours at  $35-40^{\circ}$  with a saturated solution of sodium sulphide. The solution of sodium thiocarbonate is treated with the calculated amount of copper sulphate solution and the resulting copper thiocarbonate decomposed with steam. The product is rectified over phosphoric oxide. W. H. R.

**Crystal Structure of Argon.** F. SIMON and C. VON SIMSON.—(See ii, 588.)

**Influence of Light on Aqueous Solutions of Potassium Iodide, Nitrate, and Chlorate.** K. SURYANARAYANA (*J. Sci. Assoc. Vizianagaram*, 1924, **2**, 12—15).—No decomposition of potassium iodide solution occurs in absence of oxygen, even when exposed to ultra-violet light. Ultra-violet light induces the decomposition of potassium nitrate and chlorate in aqueous solution with the formation of nitrite and chloride and the liberation of oxygen; the reactions are reversible. J. B. F.

**Photolysis of Potassium Nitrate.** C. S. ROBINSON (*J. Amer. Chem. Soc.*, 1924, **46**, 1834—1836).—Contrary to Anderson (this vol., ii, 408), the author claims that it is possible, with the existing data, to calculate the amount of nitrate decomposed in any interval of time. S. B.

**Solubility of Sodium Fluoride in Hydrofluoric Acid.** D. B. JEHU and L. J. HUDLESTON (*J. Chem. Soc.*, 1924, **125**, 1451—1456).—Additions of hydrofluoric acid increase the solubility of sodium fluoride, by the formation of  $\text{HF}_2'$  ions, until the solubility product of the ions  $\text{Na}^+$  and  $\text{HF}_2'$  is reached. Further additions of the acid cause a decrease in the concentration of sodium ions. The changes of solubility have been followed quantitatively. By extrapolation, the solubility of sodium fluoride in pure water is found to be 3.96 g. per 100 g. of water. This is rather lower than previous estimates. S. B.

**Diffusion of Anhydrous Sodium Sulphate among the Products of the Present Activity of Vesuvius.** G. CAROBBI and V. CAGLIOTI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], 30, 60—62).—That anhydrous sodium sulphate was formed in abundance during the eruptive phenomena resulting in the formation on Vesuvius of the laval cupola in September-October, 1922, is shown by the presence of as much as 75% of this salt in some of the stalactites of the grotto beneath the cupola. These stalactites contain also moderate proportions of sodium and potassium chlorides, lime, and manganese, and copper, aluminium, and iron salts in small amounts. T. H. P.

**System Sodium Sulphate-Magnesium Sulphate-Water.** E. H. ARCHIBALD and W. A. GALE (*J. Amer. Chem. Soc.*, 1924, 46, 1760—1771).—This system has been studied between 0° and 100°. A method for the separation of the two salts is suggested, based on the solubility diagrams obtained. S. B.

**Action of Heat in a Vacuum on Hydrated Sodium Thiosulphate and Sulphite.** PICON (*Bull. Soc. chim.*, 1924, [iv], 35, 957—959).—(See this vol., ii, 479.)

**Lithium. II. Hydrates of Lithium Iodide.** G. F. HÜTTIG and F. POHLE (*Z. anorg. Chem.*, 1924, 138, 1—16).—The system lithium iodide-water has been investigated by the vapour-pressure method previously used for the chloride and bromide (Hüttig and Reuscher, *ibid.*, 1924, 137, 155) and hydrates with 3, 2, 1, and 0.5 mols. of water are shown to exist. The "congruent melting points" (*i.e.*, the m. p. under the equilibrium water vapour pressure) are 75°, 79°, and  $\geq 131^\circ$  for the tri-, di-, and mono-hydrates, respectively, corresponding with maxima on the freezing-point curve. Eutectic quadruple points are formed by (1) the tri- and di-hydrates, (2) the di- and mono-hydrates, and (3) the mono- and hemi-hydrates, the respective data being: (1)  $t=70.5^\circ$ ,  $p=7$  mm., and composition  $\text{LiI}, 2.5\text{H}_2\text{O}$  (approx.); (2)  $t=77^\circ$ ,  $p=4.5$  mm., and composition  $\text{LiI}, 1.7\text{H}_2\text{O}$ ; (3)  $t=130^\circ$ ,  $p=6.5$  mm., and composition  $\text{LiI}, 0.9\text{H}_2\text{O}$ . Thermochemical data are calculated for the following reactions:  $\text{LiI}(\text{solid}) + 0.5\text{H}_2\text{O}(\text{vap.}) = \text{LiI}, 0.5\text{H}_2\text{O}(\text{solid}) + 10100$  cal.  $\text{LiI}, 0.5\text{H}_2\text{O}(\text{solid}) + 0.5\text{H}_2\text{O}(\text{vap.}) = \text{LiI}, \text{H}_2\text{O}(\text{solid}) + 9300$  cal.  $\text{LiI}, \text{H}_2\text{O}(\text{solid}) + \text{H}_2\text{O}(\text{vap.}) = \text{LiI}, 2\text{H}_2\text{O}(\text{solid}) + 16400$  cal.  $\text{LiI}, 2\text{H}_2\text{O}(\text{solid}) + \text{H}_2\text{O}(\text{vap.}) = \text{LiI}, 3\text{H}_2\text{O}(\text{solid}) + 16000$  cal. The data concerning the hemihydrate are incomplete. W. H.-R.

**Simple and Double Orthophosphates.** TRAVERS and (MILLE.) PERRON (*Ann. Chim.*, 1924, [x], 1, 135—183).—Addition of lithium hydroxide to orthophosphoric acid until the solution is neutral to methyl-orange results in the formation of lithium dihydrogen phosphate, but on evaporation the solution deposits crystals of trilithium phosphate and then contains free phosphoric acid. Crystals of lithium dihydrogen phosphate are, however, obtained in the presence of a sufficient excess (5%) of phosphoric acid. A solution of dilithium hydrogen phosphate may be obtained from lithium hydroxide and orthophosphoric acid, both of 0.2M-con-

centration, with phenolphthalein as indicator; in more concentrated solution, normal lithium phosphate is precipitated and all attempts to prepare a crystalline mono-acid salt failed. Addition of excess of ammonia to a solution of lithium dihydrogen phosphate in the cold precipitates *lithium diammonium phosphate*, decomposing in air with evolution of ammonia, whilst in the case of dilithium hydrogen phosphate ammonia precipitates only hydrated normal lithium phosphate. If ammonia is added to lithium dihydrogen phosphate until phenolphthalein shows an end-point, *lithium ammonium hydrogen phosphate* is formed. This is much less stable than the corresponding sodium salt and cannot be obtained crystalline by evaporation. The properties of the lithium ammonium phosphates are analogous to those of the corresponding compounds of the alkali metals. Magnesium diammonium dihydrogen orthophosphate,  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2$ , is completely dissociated in solution into magnesium hydrogen phosphate and diammonium hydrogen phosphate; addition of ammonia yields magnesium ammonium phosphate, thus differentiating the magnesium from the corresponding lithium salt. Pure magnesium hydrogen phosphate cannot be prepared by the action of the corresponding sodium phosphate on magnesium sulphate, as normal magnesium phosphate is always formed in the reaction; but by using 0.2*M*-solutions and rejecting the precipitate first formed, which consists of the salt  $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ , a pure product is obtained after shaking the liquid for some time. A description of the preparation and properties of magnesium ammonium phosphate and magnesium potassium phosphate is given. In precipitating the former for analytical purposes, the theoretical quantity or a slight excess of ammonium phosphate should be used; the sodium salt, especially when used in excess, leads to the formation of normal magnesium phosphate. The latter may, however, be converted into magnesium ammonium phosphate by the action of ammonium salts; the change, which is accelerated by rise of temperature, is accompanied by loss of magnesium to the solution. Calcium ammonium phosphate,  $\text{Ca}(\text{NH}_4)\text{PO}_4 \cdot 7\text{H}_2\text{O}$ , may be prepared similarly to the corresponding magnesium salt, but the temperature must be kept low as the substance is not stable, losing ammonia and water simultaneously at the ordinary temperature.

H. J. E.

**Simple and Double Orthophosphates.** TRAVERS and (MILLÉ.) PERRON (*Ann. Chim.*, 1924, [x], 1, 298—342; cf. preceding abstract).—Zinc dihydrogen phosphate,  $\text{Zn}(\text{H}_2\text{PO}_4)_2$  is stable only in very dilute solution; it undergoes dissociation to phosphoric acid and the normal salt at the ordinary temperature, even in moderate concentration and at 100°, at any concentration above 14.7 g. per litre, 50% is thus split up. In this behaviour, zinc resembles lithium, but not the alkaline-earth metals. When the salt is treated in dilute solution with ammonia, it yields zinc ammonium phosphate,  $\text{ZnNH}_4\text{PO}_4$ , with some  $\text{Zn}_3(\text{PO}_4)_2$  unless excess of ammonia be used. The salt  $\text{ZnHPO}_4$  does not exist. The salt  $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  is quite insoluble in water, but readily dissolves in acids, and with phosphoric



acid forms the primary salt. Zinc ammonium phosphate can also readily be obtained by precipitation from an exactly neutral solution, or by treating the normal salt, in suspension, with ammonia. It is very stable and may be washed with boiling water; it seems thus to offer advantages over the commonly used magnesium analogue in quantitative determinations of phosphorus. Zinc potassium phosphate,  $\text{ZnKPO}_4$ , may be prepared in the wet way by interaction of dipotassium hydrogen phosphate and zinc sulphate.

*Beryllium hydrogen phosphate*,  $\text{Be}(\text{H}_2\text{PO}_4)_2$ , is obtained by dissolving the oxide in a small excess over the required amount of phosphoric acid. In solution, it is dissociated, but no precipitate is thrown down, as the *double salt*,  $2\text{Be}(\text{H}_2\text{PO}_4)_2 \cdot \text{BeHPO}_4$ , is formed. Beryllium thus resembles aluminium. The salt  $\text{BeHPO}_4$  does not exist; it is entirely dissociated, and only the normal salt,  $\text{Be}_3(\text{PO}_4)_2$  is obtained, as a gelatinous precipitate. Beryllium ammonium phosphate,  $\text{BeNH}_4\text{PO}_4$ , closely resembles the zinc analogue; it is quite stable and can be applied to the determination of beryllium. Primary aluminium phosphate,  $\text{Al}(\text{H}_2\text{PO}_4)_3$ , is dissociated even in dilute solution, the secondary salt,  $\text{Al}_2(\text{HPO}_4)_3$ , being formed. Aluminium phosphate,  $\text{AlPO}_4$ , is readily obtained by appropriate precipitation; it dissolves in ammoniacal phosphate solutions, but double salts cannot be isolated. Cohen's salt (A., 1907, ii, 552) appears to be impure secondary phosphate. A characteristic reaction, useful in qualitative analysis, is expressed by the reversible equation  $3\text{H}_3\text{PO}_4 + \text{Al}_2(\text{HPO}_4)_3 \rightleftharpoons 2\text{Al}(\text{H}_2\text{PO}_4)_3$ . Solutions of the composition indicated give when boiled a dense precipitate, which rapidly dissolves again on cooling.

W. A. S.

**Fumes resulting from Chemical Reactions. I. Size of the Particles of Chemical Fumes.** H. REMY (*Z. anorg. Chem.*, 1924, **138**, 167—179).—The particles in moist fumes of ammonium chloride and sulphur trioxide consist of small drops of solutions of these substances in water. The Stokes-Cunningham formula has been used to calculate the size of these drops from observations on the rate at which the fumes sink in air. Owing to the agglomeration of the initial drops to form larger particles, the rate of fall of a freshly-prepared cloud at first increases and then finally attains a constant value. The radii of the initial drops in freshly-prepared moist fumes of ammonium chloride and sulphur trioxide are  $6.2 \times 10^{-5}$  and  $5.3 \times 10^{-5}$  cm. respectively. With time, these radii gradually increase to  $11.9 \times 10^{-5}$  and  $12.6 \times 10^{-5}$  cm., respectively.

W. H.-R.

**Ammonium Perchlorate.** P. NAOUM and R. AUFSCHLÄGER (*Z. ges. Schiess- u. Sprengstoffw.*, 1924, **19**, 121—123).—The temperature developed by the explosion of ammonium perchlorate is  $1308^\circ$  and the heat evolved  $344.5$  Cal. per kg.; the chief products of the reaction are chlorine, nitrogen, oxygen, and water vapour, but a certain amount of hydrogen chloride is also formed. The salt does not explode when heated; it decomposes slowly at  $150^\circ$  and more rapidly but quietly at a red heat, with the evolution of brown fumes containing oxides of chlorine. It is somewhat more sensitive

to shock than ammonium nitrate, and detonates more readily with a suitable detonator. Ammonium chlorate, on the other hand, is a much more unstable substance which decomposes rapidly with deflagration on heating and may be caused to explode even with a feeble detonator. The temperature of the explosion is above  $1700^{\circ}$ , and the heat evolved 537 Cal. per kg. [Cf. *B.*, 1924, 850.] A. R. P.

**Determination of the Ratio of the Combining Weights of Chlorine and Silver.** R. LORENZ and E. BERGHEIMER (*Z. anorg. Chem.*, 1924, **138**, 205—218).—Pure silver was dissolved in nitric acid, and the dissolved silver nitrate converted into chloride by the action of hydrogen chloride. The resulting silver chloride was dried in the dark and weighed with elaborate precautions. For the ratio Ag : AgCl, a mean value of 100 : 132.863 was found with a maximum error of 0.004 and a probable error of 0.0009. The results agree with those of Richards and Wells (*A.*, 1905, ii, 450).

W. H.-R.

**Ternary Systems. II. Silver Perchlorate, Aniline, and Water.** A. E. HILL and R. MACY (*J. Amer. Chem. Soc.*, 1924, **46**, 1132—1150).—The ternary eutectic of the system is at  $-58.8^{\circ}$ , and between this temperature and  $66.6^{\circ}$  nine invariant and twenty-eight univariant equilibria have been studied. The binary eutectic for silver perchlorate and aniline is at  $-6.6^{\circ}$ , and four new compounds in this system have been obtained:  $\text{AgClO}_4 \cdot 6\text{Ph} \cdot \text{NH}_2$ ,  $\text{AgClO}_4 \cdot 3\text{Ph} \cdot \text{NH}_2$ ,  $\text{AgClO}_4 \cdot 2\text{Ph} \cdot \text{NH}_2$ , and  $\text{AgClO}_4 \cdot \text{Ph} \cdot \text{NH}_2$ . All are fairly stable in the dry state at the ordinary temperature, but only the first is stable in contact with solutions. The hexa-aniline compound has a congruent m. p. at  $60.52^{\circ}$  and a transition point to the trianiline compound at  $48.3^{\circ}$ . The transition temperature of the latter is  $66.6^{\circ}$ , but the remaining two compounds are too unstable at high temperatures to allow a determination of their transition points to be made.

M. S. B.

**Fulminating Silver.** L. J. OLMER (*Bull. Soc. chim.*, 1924, [iv], **35**, 847—857).—The conditions of formation of fulminating silver are investigated in the light of the author's recent investigations (cf. this vol., ii, 410) on the solubility of silver oxide in ammonia and the rapidity of decomposition of the solution in the presence of excess of ammonia. The cases of dilute solutions containing about 0.35 g.-atom of silver per litre, and of concentrated solutions containing more than 1 g.-atom per litre are studied. In the former case, the complex  $\text{AgOH} \cdot 2\text{NH}_3$  is completely ionised, and with just sufficient ammonia to dissolve the silver oxide the solution may be kept unchanged in a sealed tube in the dark for years. Evaporation in the presence of sulphuric acid yields a more or less fulminating mixture of silver oxide and amide. With excess of ammonia, the precipitate consists mainly of silver oxide and amide, the large proportion of the former preventing detonation. Evaporation of such solutions in air at the ordinary temperature yields only silver oxide, since the presence of this compound diminishes the partial pressure of the ammonia and the solution does not follow Henry's

law, water and ammonia evaporating together and the concentration of the solution remaining constant. At  $100^{\circ}$ , however, ionisation of the complex is no longer complete, and the reaction  $\text{AgOH} \cdot 2\text{NH}_3 = \text{AgNH}_2 + \text{NH}_3 + \text{H}_2\text{O}$  takes place, the solution following Henry's law, and a deposit of fulminating silver is formed. With the more concentrated solutions, if excess of silver oxide be present, the fulminating precipitate appears the more rapidly the more concentrated is the solution, the reaction being the decomposition of the un-ionised molecules, of  $\text{AgOH} \cdot 2\text{NH}_3$  (as above). A small portion of the amide dissolves in the ammonia, yielding the nitride, which is decomposed under the catalytic influence of the glass vessel, so that fulminating silver is a mixture of silver oxide, amide, nitride, silver ammonium carbonate (by action of carbon dioxide from the air), and metallic silver. In presence of excess of ammonia, the amide dissolves, forming the nitride and, in closed paraffin wax vessels, the ammonia cannot escape and the nitride is not decomposed, but is suddenly deposited, and the least shock explodes the mixture. In glass vessels, the nitride is catalytically decomposed, a deposit of metallic silver being formed and nitrogen evolved. The silver then further catalyses the decomposition until the solution contains only 0.3 g.-atom of silver per litre. At  $100^{\circ}$ , the formation of amide and nitride is more rapid than the decomposition, and a precipitate of fulminating silver is obtained which explodes when disturbed by the first bubble of ammonia evolved. The experiments of previous investigators are explained in the light of the author's results.

J. W. B.

**Vacuum Spark Spectrum of Calcium.** J. A. ANDERSON.—(See ii, 578.)

**[Absorption Spectra of Calcium Sulphide Phosphors.]** F. SCHMIDT.—(See ii, 583.)

**Electrical Conductivity of Fused Silicates.** F. FARUP, W. FLEISCHER, and E. HOLTAN (*Chim. et Ind.*, 1924, 12, 11—15).—A series of determinations is given of the variation of the conductivity with the temperature in the case of a number of artificially prepared silicates of calcium and of calcium and aluminium at temperatures between the fusion point and  $1600^{\circ}$ . The results are of the order of magnitude of the conductivities of strong electrolytes in aqueous solution at the ordinary temperature. Increase in the content of silica or alumina is accompanied by a decrease in conductivity associated with a higher viscosity. Where crystallisation accompanied by supercooling can take place, the conductivity changes around the fusion point are more rapid than in the case of mixtures which solidify as glasses. [Cf. B., 1924, 745.]

C. I.

**Synthesis of Minerals.** P. NIGGLI (*Fortschr. Mineral. Krist. Petrogr.*, 1923, 8, 69—89; from *Chem. Zentr.*, 1924, i, 1499).—The conditions for the formation and existence of minerals in the zone of catamorphism are discussed. The systems  $\text{CaO-SiO}_2$ ,  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ ,  $\text{MgO-CaO-SiO}_2$ ,  $\text{MgO-CaO-Al}_2\text{O}_3$ ,  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  are described.

G. W. R.

**Number of  $\alpha$ -Particles Emitted by Radium.** V. F. HESS and R. W. LAWSON.—(See ii, 649.)

**Specific Heats of Magnesium, Calcium, Zinc, Aluminium, and Silver at High Temperatures.** E. D. EASTMAN, A. M. WILLIAMS, and T. F. YOUNG (*J. Amer. Chem. Soc.*, 1924, **46**, 1178—1183; cf. Lewis, Eastman, and Rodebush, *Proc. Nat. Acad. Sci.*, 1918, **4**, 25; Eastman and Rodebush, *A.*, 1918, ii, 149).—Measurements have been made of the specific heats of magnesium, calcium, zinc, aluminium, and silver, at temperatures between 100° and the m. p., with an estimated accuracy of 1%. Contrary to Swisher's observations (*Physical Rev.*, 1917, [ii], **10**, 601), the results indicate a transition point for calcium at 400°. No evidence, however, has been obtained of the transition points reported by other investigators in the case of zinc. M. S. B.

**Structure of the Basic Magnesium Carbonates.** G. R. LEVI (*Annali Chim. Appl.*, 1924, **14**, 265—274).—The results of X-ray analysis show that all basic magnesium carbonates yet described, no matter what their method of preparation, are identical with natural hydromagnesite,  $4\text{MgO} \cdot 3\text{CO}_2 \cdot 4\text{H}_2\text{O}$ . The supposed compound,  $5\text{MgO} \cdot 4\text{CO}_2 \cdot 5\text{H}_2\text{O}$ , does not exist, and the product described as  $3\text{MgO} \cdot 2\text{CO}_2 \cdot 3\text{H}_2\text{O}$  by Fritzsche (*Ann. Chim. Phys.*, 1863, **37**, 310) is not obtained under the conditions given by this author. The mineral artinite,  $2\text{MgO} \cdot \text{CO}_2 \cdot 4\text{H}_2\text{O}$ , represents a definite crystalline product with a characteristic lattice exhibiting a low degree of symmetry, which is either trimetric or monoclinic; it has not been found capable of preparation in the laboratory under any conditions yet employed. T. H. P.

**Electrolytic Deposition of Zinc, Iron, or Nickel.** P. A. GOVAERTS and P. M. WENMAEKERS (D.R.-P. 384284; from *Chem. Zentr.*, 1924, i, 1268).—In the electrolytic deposition of iron, zinc, or nickel from solutions of their sulphates in the presence of alkali thiosulphates, an organic acid is added in sufficient quantity for incipient decomposition of the thiosulphate to take place. Under these conditions, small potential differences may be used and thick, strongly adhering deposits obtained. G. W. R.

**Ageing of Zinc Hydroxide and Alkali Zincates.** R. FRICKE and T. AHRNDTS (*Z. anorg. Chem.*, 1924, **134**, 344—356).—Precipitated zinc hydroxide changes in contact with water, more quickly with dilute alkali, into a crystalline form which is less soluble and has a lower water content. This aged form is also obtained from a zincate solution by dilution or by keeping in the absence of air. From zincate solutions with a high alkali content (greater than 3N) zinc oxide and not hydroxide separates. Oxide again is obtained from zinc hydroxide in contact with concentrated alkali. Potential measurements of zinc oxide in contact with 7—13N-potassium hydroxide show that 35—95% of the zinc (calculated for primary zincate) and in 8—17.5N-sodium hydroxide 90—125% is combined, i.e., the greater part is dibasic. Cryoscopic measure-

ments in weaker alkali solutions also indicate the presence of secondary zincate. From very concentrated potassium zincate solutions, together with zinc oxide, clear, deliquescent crystals of the composition 72.5% KOH + 7.99% ZnO were obtained. Apparently these consist of a solid solution of potassium hydroxide hydrate and secondary potassium zincate. H. T.

**Effect of Temperature on the Electrolytic Potential of Cadmium Amalgams.** G. TAMMANN and C. F. MARAIS (*Z. anorg. Chem.*, 1924, **138**, 162—166).—The electrolytic potentials of a series of metallic mixed crystals depend greatly on the temperature. If the temperature is above that at which internal diffusion can occur, gradually increasing quantities of the less noble metal produce first a rapid rise in the potential followed by a much more gradual rise. Below the temperature at which diffusion can occur, all alloys containing more than 0.5 mol. of the more noble metal show the potential of the more noble metal, a sudden increase occurring at 0.5 mol. Measurements of the *E.M.F.* of a cell of the type  $\text{Hg}-\text{Hg}_2\text{SO}_4|\text{CdSO}_4\text{ solution}|\text{Cd amalgam}$ , show that diffusion occurs at  $10^\circ$  and  $-80^\circ$ , but not at  $-110^\circ$ . The internal diffusion thus stops abruptly in the neighbourhood of  $-100^\circ$ , in contrast to the more gradual change in the case of alloys of higher m. p. W. H.-R.

**Isotopes of Lead.** M. CURIE.—(Sec ii, 649.)

**Grain Growth in Antimonial Lead.** R. S. DEAN and W. E. HUDSON (*J. Amer. Chem. Soc.*, 1924, **46**, 1778—1786).—The growth of crystal grains under the influence of deforming forces has been studied in an alloy of 99% of lead and 1% of antimony, at temperatures of about  $250^\circ$ . The authors conclude that the rate of growth of the grains is proportional to the amount of alloy still available for growth, and that the number of nuclei developed increases with the deforming strain imposed. S. B.

**Potassium Iodide and Lead Salts.** W. EISNER (*Arch. Exp. Path. Pharm.*, 1924, **102**, 305—319).—Concentrations of lead acetate and potassium iodide, which in aqueous solution give a precipitate, fail to do so in the presence of serum, and form a colloidal solution. Similar results are obtained with lead acetate and sodium phosphate or carbonate in the presence of bile, lecithin solution, or serum. Previously precipitated lead iodide passes into colloidal solution in the presence of excess of serum, and lead salts of low solubility in water, when present in a colloidal solution in serum, are not precipitated by addition of potassium iodide. The rate of dialysis of lead salts in the presence of serum is increased by addition of potassium iodide, and the latter salt together with the chloride inhibits the toxic action of lead on fermenting yeast. The bearing of these results on the action of lead in the living organism is discussed. J. P.

**Deposition of Lead Salts [in Bone]. Solubilities of Lead Phosphates in Water and Lactic Acid Solution.** L. T. FAIRHALL and C. P. SHAW (*J. Ind. Hygiene*, 1924, **6**, 159—168).—Binary

lead phosphate,  $\text{PbHPO}_4$ , is soluble in water to the extent of 0.0129 g. per litre, at  $25^\circ$ ; its solubility in lactic acid solutions is always less than that of the tertiary lead phosphate. The amount of lead absorbed from lead chloride solution by bony material increases with the time of contact and with the  $p_{\text{H}}$  value of the solution; with decalcified bone and kelp charcoal true adsorption takes place, but with crushed, and with ignited, bone, there is a displacement of calcium which is not equivalent to the amount of lead adsorbed. The chloride ion is unaffected. The deposition of lead in living bone-tissue is probably not strictly analogous to the absorption in the above experiments.

S. K. T.

**Ternary System Copper-Tin-Zinc.** G. TAMMANN and M. HANSEN (*Z. anorg. Chem.*, 1924, **138**, 137—161).—The complete equilibrium diagram has been constructed for all ternary alloys containing more than 60% of copper, and for the ternary alloys on the zinc side of the system containing 40—60% of copper. The constituents of alloys containing less than 35% of zinc resemble those of the binary copper-tin alloys,  $\alpha$ ,  $\beta$ , and  $\gamma$  series of ternary mixed crystals being formed. The solubility of tin in the  $\alpha$  mixed crystals decreases with increasing zinc content. Alloys rich in copper, on cooling from the fused mass, deposit first  $\alpha$  ternary mixed crystals. If sufficient tin and zinc are present, these undergo a peritectic reaction corresponding with the change  $\alpha + \text{liquid} \rightarrow \beta$ ; this change occurs at about  $800^\circ$  in the binary copper-tin alloys, and the temperature is little affected by small amounts of zinc, but is raised by larger quantities. Alloys containing less copper deposit first  $\beta$  crystals on cooling from the fused mass, and these may undergo a peritectic reaction corresponding with the change  $\beta + \text{liquid} \rightarrow \gamma$ . The  $\beta$  and  $\gamma$  ternary mixed crystals both undergo eutectoid transformations in the solid state, corresponding with the changes (1)  $\beta \rightarrow \alpha + \gamma$ , and (2)  $\gamma \rightarrow \alpha + \delta$ . The former change occurs at about  $580^\circ$  and its temperature is little affected by increasing zinc content. The latter change occurs at  $520^\circ$  in the binary copper-tin alloys, and its temperature is raised by the addition of zinc, until, if sufficient zinc is present, the two reactions occur simultaneously,  $\beta + \gamma \rightarrow \alpha + \delta$ . The  $\delta$  phase consists of the compound  $\text{Cu}_4\text{Sn}$  and does not form mixed crystals. Alloys containing more than 35% of zinc and only small amounts of tin give rise to ternary  $\beta$  and  $\beta'$  constituents resembling those of the copper-zinc binary alloys, but the range of the ternary alloys, the constituents of which resemble those of the copper-tin system, is much the larger. The structure of the technically important alloys depends greatly on the exact conditions of cooling and heat treatment.

W. H.-R.

**Systems Cupric Sulphate-Potassium Sulphate-Water, and Cupric Sulphate-Ammonium Sulphate-Water.** R. M. CAVEN and T. C. MITCHELL (*J. Chem. Soc.*, 1924, **125**, 1428—1431).—The equilibria for these systems have been investigated at  $25^\circ$ ,  $51^\circ$ , and  $61^\circ$ . The double salts  $\text{CuSO}_4 \cdot \text{M}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{K}$  or  $\text{NH}_4$ ) are stable at all temperatures over a wide range of concentrations.

The solubility of each of the three simple salts is increased by additions of the second component, up to the point at which the double salt separates. This indicates that the double molecules can exist at considerable concentrations in solution. S. B.

**Reported Transmutation of Mercury into Gold.** F. SODDY (*Nature*, 1934, **114**, 244—245).—Atomic disruption is not necessarily involved in the transmutation, which should also be effected by attaching an electron to the mercury nucleus. A. A. E.

**Phototropy of Mercury Compounds.** T. VARAHALU, A. J. RAM, and B. S. V. R. RAO.—(See ii, 644.)

**Arrangement of Atoms in Calomel Crystals.** C. MAUGUIN.—(See ii, 588.)

**Solubility of Mercury Salts in Protein [Solutions].** S. REBELLO (*Compt. rend. Soc. Biol.*, 1923, **88**, 1331—1333; from *Chem. Zentr.*, 1924, i, 924).—Mercury, mercurous chloride, mercurous bromide, mercurous iodide, and mercuric oxide are increasingly soluble, whilst mercuric sulphide is insoluble, in protein solutions. G. W. R.

**Periodic Diffusion of Insoluble Mercury Salts in Gel Cultures.** S. REBELLO (*Compt. rend. Soc. Biol.*, 1923, **88**, 1336—1338; from *Chem. Zentr.*, 1924, i, 924; cf. preceding abstract).—Periodic formations, analogous to Liesegang rings, are given by insoluble mercury compounds in gel cultures containing ammonium sulphate and formaldehyde. G. W. R.

**Ternary Alloy System Aluminium-Cadmium-Zinc.** N. F. BUDGEN (*J. Chem. Soc.*, 1924, **125**, 1642—1660).—The chief feature of the liquidus surface of the aluminium-cadmium-zinc alloys is a deep valley joining almost linearly the eutectics at 94.4% Zn and 17.4% Zn in the zinc-aluminium and zinc-cadmium series, respectively; the temperature of the bottom of the valley falls from 380° to 268° as the cadmium replaces the zinc. The peritectic arrest line at 443° in the aluminium-zinc series occurs at 445° in the ternary alloys, whilst the line at 256°, representing the lower limit of stability of the compound  $\text{Al}_2\text{Zn}_3$ , is raised to 276° by addition of only 2% Cd to aluminium-zinc alloys. There is some indication of the formation of a ternary eutectic melting at 268°, but its composition could not be determined. Solid solutions are formed only in the cadmium and zinc corners of the space diagram and then only to a very limited extent. A. R. P.

**Compounds of Aluminium, Chlorine, and Sulphur.** O. RUFF and H. GOLLA (*Z. anorg. Chem.*, 1924, **138**, 17—32).—Aluminium chloride and sulphur chloride unite to form the compound  $\text{AlCl}_3 \cdot 2\text{S}_2\text{Cl}_2$ , which will react with chlorine to form  $\text{AlCl}_3 \cdot \text{SCl}_2$  and  $\text{AlCl}_3 \cdot \text{SCl}_4$ .  $\text{AlCl}_3 \cdot 2\text{S}_2\text{Cl}_2$  combines with sulphur to form  $\text{AlCl}_3 \cdot 2\text{S}_3\text{Cl}_2$  and  $\text{AlCl}_3 \cdot 2\text{S}_4\text{Cl}_2$ , the first of which is also produced by the reduction of sulphur chloride by aluminium. These compounds are all red liquids which cannot be crystallised, and are

practically insoluble in sulphur chloride.  $\text{AlCl}_3 \cdot 2\text{S}_2\text{Cl}_2$  has  $d_{1.784}$ , corresponding with a molecular volume of 226. The compounds are all unstable on heating, whilst, on extraction with carbon disulphide, sulphur chloride is given up and solid residues of composition  $\text{AlCl}_3 \cdot 2\text{S}_2$  or  $\text{AlCl}_3\text{S}_2$  are left, in which the remaining sulphur is more firmly held. These residues react with water with liberation of sulphur, and, as hydrogen sulphide is not formed, it is concluded that the sulphur atoms are not directly attached to the aluminium. A similar compound,  $\text{AlCl}_3 \cdot 3\text{S}$ , is formed by the reduction of sulphur chloride by excess of aluminium. These compounds are co-ordination compounds in which polythiochlorides are present (cf. this vol., ii, 672). Their relative instability compared with the corresponding compounds of sulphur tetrachloride (A., 1905, ii, 22) is due to the relatively unsymmetrical dipolar character of the  $\text{S}:\text{S}:\text{Cl}_2$  molecule compared with the symmetrical molecule of sulphur tetrachloride.

W. H.-R.

**Non-existence of the Double Sulphate,  $\text{MnK}_2(\text{SO}_4)_2$ .** G. CAROBBI and V. CAGLIOTI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], 30, 62—65).—Fusion of a mixture of manganous sulphate (2 mols.) and potassium sulphate (1 mol.) yields the compound  $2\text{MnSO}_4 \cdot \text{K}_2\text{SO}_4$ , corresponding with langbeinite,  $2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$ . The same compound is formed, together with potassium sulphate, when the two sulphates are taken in equimolecular proportions. The compound,  $\text{MnSO}_4 \cdot \text{K}_2\text{SO}_4$ , described by Mallet (T., 1900, 77, 216; 1902, 81, 1546) is, therefore, not formed under these conditions and its existence is doubtful (cf. Nacken, A., 1908, ii, 692).

T. H. P.

**Thermal Dissociation of Manganese and Magnesium Carbonates.** W. MANCHOT and L. LORENZ (*Z. anorg. Chem.*, 1924, 134, 297—316).—The gaseous pressure of manganese carbonate and the re-absorption of carbon dioxide depend on the water content of the specimen. The process is reproducible only with equal water content and can be considered as being due to hydrolysis. All precipitated manganese carbonate contains water which is retained up to complete decomposition. A specimen of manganese spar (containing 12% of magnesium carbonate) gave much lower pressures than the artificial, but if moistened reacted similarly, although to a less extent. The values obtained are lower than those for magnesium carbonate. With the latter, a perceptible pressure is obtained at  $400^\circ$ , and 1 atm. at  $540^\circ$ . This is in agreement with the value calculated from van't Hoff's equation, the heat of decomposition being taken as 60,863 cal., but is lower than that observed by Marc and Simek. No evidence was obtained with either manganese or magnesium for the existence of definite basic carbonates.

H. T.

**Reaction between Permanganate and Arsenite in Alkaline Solution.** F. FEIGL and F. WEINER (*Z. anal. Chem.*, 1924, 64, 302—322).—The reaction between potassium permanganate and arsenious oxide in alkaline solution proceeds to a definite end-point



according to the equation  $3\text{As}_2\text{O}_3 + 4\text{KMnO}_4 = 3\text{As}_2\text{O}_5 + 2\text{K}_2\text{O} + 4\text{MnO}_2$  only when there is a constant excess of permanganate. If the arsenite is in excess, the permanganate is reduced to manganous hydroxide in the complete absence of air; in the presence of air oxidation of the manganous hydroxide takes place with the formation of an indefinite mixture of oxides intermediate between  $\text{MnO}$  and  $\text{MnO}_2$ . An excess of arsenite also results in a considerable adsorption of arsenious and arsenic acids by the precipitated manganese hydroxide, and the amount of arsenic acid formed does not correspond with the oxygen consumed by reduction of the permanganate. In Reichard's method for the determination of manganese and lead peroxides involving oxidation of arsenious oxide in alkaline solution, the arsenite consumed is too high owing to the catalytic action of the lead and manganese hydroxides in promoting the oxidation of arsenious acid by the air. A. R. P.

**Search for Element Number 43.** C. H. BOSANQUET and T. C. KEELEY.—(See ii, 651.)

**Electrolytic Theory of Corrosion.** W. D. BANCROFT (*J. Physical Chem.*, 1924, 28, 785—871).—A discussion of the evidence for the electrolytic theory of corrosion. A full bibliography is given. S. B.

**Electrolytic Preparation of Pure Iron.** E. DUHME (*Wiss. Veröff. Siemens-Konz.*, 1924, 3, 39—42).—The electrolyte consists of a cold saturated solution of ferrous chloride containing magnesium chloride and free acid equivalent to less than 0.01*N*. The anode may consist of steel or even cast iron. The cathode is rotated inside a stationary auxiliary cathode on which a small secondary alternating current (of which the negative component is greater than the positive) is superimposed. A porous earthenware U-tube is arranged round the cathode and a current of air is blown through the tube. At the bottom of the cell a number of permanent magnets sealed into thin glass tubes serve to collect the particles of carbide and silicide that fall from the anode. With this apparatus, iron of more than 99.994% purity may be prepared from material containing as much as 3% C, 1% Si, and 0.4% P. [*Cf. B.*, 1924, 789.] A. R. P.

**Iron-Silicon Alloys.** P. OBERHOFFER (*Stahl u. Eisen*, 1924, 44, 979).—From his own observations and those of others, the author expresses the opinion that the range of existence of the  $\gamma$ -phase in iron-silicon alloys becomes smaller with increasing silicon content, and with alloys containing more than 5% Si disappears altogether. Further work is in progress to test this. A. R. P.

**Crystal Structure of Iron Pyrites.** R. VON NARDROFF.—(See ii, 652.)

**Water of Crystallisation of Complex Salts of Cobalt.** A. BENRATH and W. KOHLBERG (*Z. anorg. Chem.*, 1924, 138, 65—77).—The formation of definite hydrates of cobalt complex salts has been

investigated by keeping the salts over sulphuric acid solutions of known aqueous vapour pressure, and finding the compositions of the solid residues as the aqueous vapour pressure was altered. No definite hydrates are formed by chloropentamminecobaltic hexachloroiridate, hexamminecobaltic hexachloroiridate, aquopentamminecobaltic hexachloroiridate, triethylenediaminecobaltic hexachloroiridate, *cis*- or *trans*-hydroxyaquodiethylenediaminecobaltic hexachloroiridate. The hydrates previously assigned to these are in reality due to occluded or adsorbed moisture. Hexamminecobaltic sulphate forms a pentahydrate which on exposure to air loses 1 mol. of water, and on further dehydration loses 3 more mols. Hexamminecobaltic chloride and sulphate, and triethylenediaminecobaltic chloride and bromide form only trihydrates, whilst triethylenediaminecobaltic iodide forms a monohydrate. Aquopentamminecobaltic sulphate forms a trihydrate which readily gives up 2.5 mols. of water. Carbonatotetramminecobaltic sulphate and diaquotetramminecobaltic sulphate both form trihydrates. *trans*-Dinitrotetramminecobaltic hexachloroiridate forms a trihydrate which loses 1.5 mols. of water on keeping over sulphuric acid, whilst 2 mols. of water are given off at 100°. *cis*-Dichlorodiethylenediaminecobaltic hexachloroiridate forms a tetrahydrate, which, on dehydration, loses first 1 mol. and then a further 3 mols. of water; the *trans* compound forms a monohydrate. Since the majority of the hexachloroiridates are anhydrous, it is assumed that when water of hydration is present, it exists within the complex cation, whilst in the hexamine compounds it is present in the anion.

W. H.-R.

**Methods of Dissolving Chromic Oxide.** T. SABALITSCHKA and F. BULL (*Z. anal. Chem.*, 1924, 64, 322—325).—Chromic oxide, especially after very strong ignition or in the form of chromite, is incompletely soluble in fused potassium pyrosulphate even after prolonged heating. In the qualitative analysis of substances containing chromic oxide with iron and aluminium oxides, it is preferable to fuse the substance with a mixture of 2 parts of sodium carbonate and 1 part of potassium nitrate for 10 min. The mass is dissolved in water and the insoluble residue fused with pyrosulphate.

A. R. P.

**Determination of the Degree of Complexity and Complex Formation in Chromium Salts.** K. H. GUSTAVSON (*J. Amer. Leather Chem. Assoc.*, 1924, 19, 446—480).—The complex formation in solutions of chromium salts has been investigated by the method of Günther-Schulze (*A.*, 1922, ii, 504), using pure sodium permutite, and determining the chromium and alkali in the chromium permutite. The exchange of cations between various liquors proceeds rather uniformly, and for comparison of the absorption values of various chrome liquors a period of reaction of 10 to 12 hours is sufficient. On prolonged reaction hydrolysis of the chromium permutite may take place. The absorption of chromium by the permutite from chromium sulphate liquors increases with the concentration up to about 15 g. of chromic oxide per litre, and then decreases (cf.

Thomas, A., 1922, ii, 664), apparently owing to the formation of less reactive complexes. With chromium chloride solutions, the exchange increases steadily with the concentration, but the amount of chromium in the permutite is only about half that with sulphate solutions. The chromium exchange increases with the basicity in chromium sulphate solutions, but with chromium chloride it is almost independent of the basicity of the solution and tends to decrease with increasing basicity. Neutral sulphates retard the exchange from chromium sulphate liquors, and neutral chlorides exert a similar influence on chromium chloride solutions. Smaller amounts of sodium chloride or neutral sulphates increase the cation exchange from chromium chloride solutions, and the curve shows a maximum corresponding with the existence of double salts. Sodium nitrate has little retarding influence, but the exchange is enormously decreased by the presence of sodium acetate or formate. Violet modifications of chromium chloride and sulphate have a slightly higher exchange value than the green modifications in solutions of the same concentration and basicity. With chrome liquors of the same concentration, basicity, and neutral salt content, but prepared by different methods, the exchange value is a function of the precipitation figure (vol. of 0.1N-potassium hydroxide required). Sucrose and tannins depress the chromium exchange, owing to the formation of complex compounds, but "tragasol" produces only a slight effect due to the retarded diffusion of the chromium salt through the high viscosity of the "tragasol." The exchange values obtained with basic chromium chloride liquors and with neutral chromium sulphate indicate the predominance of a normal chromium cation in these solutions. In basic chromium sulphates a complex cation is present with a basicity of about 75%, three charges being associated with two atoms of chromium. R. B.

**Chromate Electrolysis without a Diaphragm.** A. LOTTER-MOSER and H. WALDE (*Z. anorg. Chem.*, 1924, **134**, 368—392).—Measurements of the efficiency of the conversion of chromate into dichromate were made using an iron wire cathode and platinum foil anode, diffusion of the denser dichromate solution being prevented either by a concentric cylindrical tube or by the use of two concentric beakers. The latter arrangement was the most satisfactory for discontinuous or continuous electrolysis. A buffer space between the anode and cathode regions similar to that obtained in the electrolysis of chromate with a diaphragm (A., 1923, ii, 736) was not observed. H. T.

**K and L Absorption and Emission Spectra of Tungsten.** C. B. CROFUTT.—(See ii, 581.)

**Electrolytic Preparation of Lower Tungsten Chlorides.** O. COLLENBERG and A. GUTHE (*Z. anorg. Chem.*, 1924, **134**, 317—326).—By treating alkali tungstate mixed with about 10% of alkali carbonate, the latter serving to give a porous finely divided form of hydrate which is readily soluble, with strong hydrochloric acid, a solution of sexavalent tungsten containing the complex anion,

$\text{WO}_2\text{Cl}_3'$ , was obtained. This solution, on electrolysis with a platinum cathode and current density  $D_k=0.032$ , was reduced to the slightly soluble quinquevalent form,  $\text{WOCl}_3'$ . Using a lead cathode and with  $D_k=0.064$ , reduction to the trivalent form took place, the potassium salt,  $\text{K}_3\text{W}_2\text{Cl}_9$ , being isolated in the form of small, yellowish-green crystals. H. T.

**Passive Tin.** R. STEINHERZ (*Z. Elektrochem.*, 1924, **30**, 279—286).—The relations between the polarising currents and the potentials assumed by tin electrodes in acid solutions furnish an experimental definition of passivity. This is attained, if at all, at potentials which vary with the nature and concentration of the acid. As the anodic polarisation of tin is increased, the current at first increases with the potential (measured against a 0.1*N*-calomel electrode), reaches a maximum at a "critical potential"  $E_c$ , above which the tin is said to be passive, and thereafter decreases. If these potentials are read while the current is passing, and the size of the electrode is limited to about 1 mm.<sup>2</sup>, they can be reproduced to about  $\pm 0.05$  volt. In approximately 0.1*N*-solutions, hydrochloric acid gives a sharp maximum at +0.09 volt, hydrofluosilicic acid a rounded one at +0.45 volt. The values for sulphuric, hydrobromic, and hydriodic acids are -0.05, -0.01, and -0.18, respectively. The graphs of  $E_c$  against concentration are characteristic. They usually reach a minimum between  $C=0.1$  and 0.2 and may then rise, e.g., to +0.20 in the case of sulphuric acid from  $C=0.65$  upwards. A critical potential is not found in the cases of nitric, iodic, perchloric, and acetic acids. Mixtures of hydrochloric and perchloric acids show a regular transition between the two characteristic curves. Rotation of the electrode in hydrochloric and sulphuric acids raises  $E_c$ , and stannic acid is formed. Passive, as well as the active, tin is quantitatively dissolved in the stannous state. Therefore the above definition of passivity is not in accordance with that often adopted, e.g., by Schmidt (A., 1923, ii, 732). The brown coating observed by Goldschmidt and Eckardt (A., 1906, i, 825) is not a necessary concomitant of this kind of passivity.

E. B. R. P.

### Behaviour of Titanic Acid towards Hydrochloric Acid.

A. M. MORLEY and J. K. WOOD (*J. Chem. Soc.*, 1924, **125**, 1626—1636).—The solubility in hydrochloric acid of  $\alpha$ -titanic acid, prepared by addition of ammonia to titanium tetrachloride at 25°, first increases with the concentration of the hydrochloric acid to a maximum of about 11 millimols. per litre in 0.1*N*-acid, then falls to a minimum of about 1 millimol. per litre in 0.2*N*-acid. This behaviour corresponds with the gradual peptisation of the titanic acid, followed by a rapid salting out of the colloid; further increase of the concentration of the hydrochloric acid results in a true solution of the titanic acid and the solubility then increases regularly with the normality of the acid.  $\beta$ -Titanic acid, prepared by the action of ammonia on titanium tetrachloride at 100°, behaves in a very similar manner, but is much less soluble. The maximum colloidal solubility occurs in 0.5*N*-hydrochloric acid and the minimum in

1.5*N*-acid, showing that the particles of the  $\beta$ -acid are much more complex than those of the  $\alpha$ -acid. With increasing age of solution, the amount of  $\alpha$ -titanic acid retained both in colloidal and in true solution slowly decreases, whereas the solubility of the  $\beta$ -acid slowly increases with age. The results of the research in general show that titanium hydroxide is amphoteric and behaves in a similar way to stannic hydroxide towards acids (cf. Collins and Wood, *T.*, 1922, 121, 441).  
A. R. P.

**Mass Spectra of Zirconium and some Other Elements.** F. W. ASTON.—(See ii, 649.)

**Atomic Weight of Zirconium.** F. P. VENABLE and J. M. BELL (*J. Amer. Chem. Soc.*, 1924, 46, 1833—1834).—Anomalies in the authors' investigations on the atomic weight of zirconium (*A.*, 1907, ii, 479) are now explained by the presence of hafnium as an impurity in the materials they employed.  
S. B.

**Adsorption by Zirconium Oxide Gels. III. Hydrogen Peroxide, Hydrochloric Acid, and Perchloric Acid.** E. WEDEKIND and H. WILKE.—(See ii, 594.)

**Revision of the Atomic Weight of Germanium. I. Analysis of Germanium Tetrachloride.** G. P. BAXTER and W. C. COOPER, jun. (*Proc. Amer. Acad. Arts Sci.*, 1924, 59, 235—255).—Germanium was extracted from zinc oxide residues by solution in hydrochloric acid, precipitation as sulphide, roasting, and reduction with hydrogen. The crude metal, containing arsenic as the principal impurity, was converted into the tetrachloride, which was separated from arsenic trichloride by fractional distillation in a vacuum. The atomic weight of germanium so obtained, 72.60, is compatible with Aston's observations on the relative abundance of the isotopes 74, 72, and 70.  
CHEMICAL ABSTRACTS.

**Dielectric Constant of Germanium Tetrachloride.** M. E. LEAR (*J. Physical Chem.*, 1924, 28, 889—890).—The dielectric constant of germanium tetrachloride has been determined by Drude's method to be 2.65 at 30°.  
S. B.

**Partition of a Metal between Two Liquid Metallic Phases.** G. TAMMANN and P. SCHAFMEISTER (*Z. anorg. Chem.*, 1924, 138, 219—232).—The partition coefficients determined by Wright (*A.*, 1893, ii, 15, 415, 522; 1894, ii, 419) are reviewed and some new determinations described. If the dissolved metal forms no compounds with either of the liquid phases, the partition coefficient is of the order 1, and this may sometimes also be the case if a compound is formed with one of the liquid phases only. In the partition of antimony between liquid zinc-lead, zinc-bismuth, and aluminium-lead, the following partition coefficients have been determined: 535°,  $[Sb]_{Zn}:[Sb]_{Pb}=1.28$ ; 550°,  $[Sb]_{Zn}:[Sb]_{Bi}=0.66$ ; 725°,  $[Sb]_{Al}:[Sb]_{Pb}=2.22$ . In these cases, compounds  $Sb_2Zn_3$  and  $SbAl$  are formed but no compounds with lead or bismuth. The partition coefficient of antimony between any two of the above metals is of the same order as the ratio of the solubilities of the

compound  $\text{Sb}_2\text{Zn}_3$  (or  $\text{SbAl}$ ) in the two liquid metals concerned, and these solubility curves have been determined. In general, however, if a compound is formed with one liquid phase only, a high partition coefficient is obtained, the dissolved metal going largely into the liquid with which it forms a compound. Examples of this type for which the partition coefficients have been determined are the partition of silver between zinc-lead, zinc-bismuth, aluminium-lead, aluminium-bismuth, zinc-thallium, and aluminium-thallium; of gold between zinc-bismuth, aluminium-bismuth, and zinc-thallium; of copper between zinc-lead, zinc-bismuth, aluminium-lead, and aluminium-bismuth. The partition coefficient of silver between zinc and lead varies greatly with the temperature, being of the order 300 at  $540^\circ$ , but only 5 at  $750^\circ$ , indicating the importance of a low temperature in the desilverisation of lead (Parkes' process). When the dissolved metal forms compounds with both liquid phases, the partition coefficient may be of the order 1 as in the partition of magnesium between aluminium-lead or aluminium-bismuth, or the coefficient may have a high value as in the partition of gold between zinc-lead or aluminium-lead, where the gold goes largely to the zinc and aluminium respectively. In many cases, the coefficient also varies with the concentration of the dissolved metal.

W. H.-R.

**Bivalent Bismuth. II.** E. NEUSSER (*Z. anorg. Chem.*, 1924, **138**, 180—188).—The heat evolved in the reaction between hydrochloric acid and the so-called bismuth suboxide (this vol., ii, 559) has been measured, as well as the solubility of the latter in aqueous sodium hydroxide solution, and the specific magnetic susceptibility. In all three cases, the numerical values are indistinguishable from those given by a mixture of 1 mol. of bismuth trioxide and 1 atom of metallic bismuth, indicating that the so-called compounds of bivalent bismuth have no real existence.

W. H.-R.

**Sensitiveness of Gold Hydrosol to Ammonia.** P. A. THIESSEN (*Z. anorg. Chem.*, 1924, **134**, 357—367).—The sensitivity of phosphor-gold hydrosol ( $\text{Au}_p$ ) to ammonia is shown to be due to the presence of unreduced gold compounds in the sol. Ethereal solutions of gold salts which are the most sensitive are only with difficulty reduced by phosphorus and subsequent treatment with other reducing agents, *e.g.*, hydrazine considerably reduces the sensitiveness. The colour of the hydrosol depends on the amount of unreduced compounds present. With large amounts, it is blue (*cf.* purple of Cassius) and with small amounts red. From the blue sol, electrolytes, *e.g.*, sodium chloride, precipitate a gel consisting of a mixture of gold and gold oxide; ammonia, on the other hand, precipitates a mixture of gold and gold fulminate, the latter forming the active coagulating agent.

H. T.

**Composition of some Colloidal Gold Solutions.** P. A. THIESSEN (*Z. anorg. Chem.*, 1924, **134**, 393—408).—The red hydrosol produced by the reduction of alkaline gold solutions with formaldehyde is free from any oxidation products of gold, the ultramicros

consisting of pure metal; the blue hydrosol produced by partial reduction is a mixture, the ultramicros containing gold and gold oxide. Contrary to the conclusions of Pauli (A., 1921, ii, 246), there is no evidence for the existence of compounds between gold and water in the coagulates of these sols, the water which is given off at temperatures up to  $600^{\circ}$  being mechanically held. Since the blue hydrosol has a different actual composition and space configuration from that of gold sol, the optical phenomena observed by Steubing (A., 1908, ii, 600) are not in disagreement with the theory of Mie (*Ann. Physik*, 1908, [iv], 25, 377). H. T.

**Anodic Oxidation of Gold. II. Properties of Auric Sulphate.** F. JIRSA and H. JELINEK (*Z. Elektrochem.*, 1924, 30, 286—289).—The solubility of auric hydroxide in sulphuric acid of various concentrations has been further investigated (cf. Jirsa and Buryánek, A., 1923, ii, 80, 173). The potentials of the electrode reaction  $\text{Au} \rightleftharpoons \text{Au}^{+++}$  were determined. Auric hydroxide, produced by anodic corrosion as previously described, was dissolved in hot concentrated sulphuric acid. The solubility of the auric hydroxide produced by the hydrolysis of such solutions varies from 0.063 to 0.000016 g.-at. of gold per litre as the concentration of the sulphuric acid varies from 18.7 to 0.53*N* ( $t=18^{\circ}$  to  $19^{\circ}$ ). From the results with the more dilute acid, the solubility product,  $[\text{Au}^{+++}][\text{OH}']^3=9.0 \times 10^{-46}$ . The potential of a gold electrode in *N*-sulphuric acid containing 0.00003 g.-at. of gold against a hydrogen electrode in the same acid is 1.311 volts; hence  ${}_0E_h$  for  $\text{Au} \rightleftharpoons \text{Au}^{+++}$  is +1.39 volts. This value may be used to calculate  $E_h$  in solutions of known gold concentration up to about 12*N*-acid; above this concentration, the calculated values are lower than the experimental, probably since an interposed solution of potassium sulphate no longer nullifies the diffusion potentials. The potentials of concentration chains of auric ions in the same sulphuric acid solutions were measured, and agreed well with those calculated on the assumption of tervalent gold. E. B. R. P.

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### Mineralogical Chemistry.

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**Stony Meteorite from Anthony Harper County, Kansas, and a Recently Found Meteoric Iron from Mejillones, Chili.**  
G. P. MERRILL (*Proc. Nat. Acad. Sci.*, 1924, **10**, 306—312).—The Kansas meteorite belongs to the group of grey chondrites and contains 20.9% of metallic constituent distributed in granules and threads throughout a stony matrix which consists essentially of ferrous and magnesium silicates. The Mejillones iron contains Fe 93.4%, Ni 5.8%, and Co 0.46%, and is almost identical in composition with the meteoric iron from Alpine, Texas (*Proc. U.S. Nat. Mus.*, 1922, **61**, [4]). S. S.



**Meteoric Iron from Four Corners, San Juan County, New Mexico.** G. P. MERRILL (*Proc. Nat. Acad. Sci.*, 1924, 10, 312—318).—This large meteorite, weighing 25 kg., is a granular octahedral nickel-iron (Fe = 89.3%, Ni = 9.6%, Co = 0.59%) with enclosures of angular fragments of silicates in which olivine, pyroxene, and feldspar were found. The structure is unusual, but resembles that of the coprapo meteorite examined by Meunier (*Meteorites*, Fremy's "Encyclopédie Chimique," 1884, 152). S. S.

**Meteoric Iron from the Desert of Adrar in Morocco (Mauretania).** A. LACROIX (*Compt. rend.*, 1924, 179, 309—313).—The meteoric iron constitutes a new type of siderite with a silicate content of about 20%. The metallic fraction contains Fe, 91.41; Ni, 4.45; Co, 0.25; Mn, 0.04; Cu, trace; S, 3.77; P, 0.08%, representing nickel-iron=89.03, pyrrhotite=10.38, and schreibersite=0.59, the nickel-iron containing Fe, 94.7; Ni, 4.97; Co, 0.28; Mn, 0.04; and Cu, trace. The silicate fraction contains SiO<sub>2</sub>, 53.96; Al<sub>2</sub>O<sub>3</sub>, 2.56; FeO, 16.58; MnO, 0.51; MgO, 23.97; CaO, 1.84; Na<sub>2</sub>O, 0.43; K<sub>2</sub>O, 0.15, representing feldspars (not identified)=8.7, hypersthene=86.8, and peridot=4.5. The whole conforms to the measured  $d$  5.28. A. E. M.

**Kempite, a New Manganese Mineral from California.** A. F. ROGERS (*Amer. J. Sci.*, 1924, [v], 8, 145—150).—This was found as small, emerald-green crystals with pyrochroite, hausmannite, rhodochrosite, etc., in a large boulder of manganese ore near San José, California. The crystals are orthorhombic ( $a:b:c=0.677:1:0.747$ ); hardness  $3\frac{1}{2}$ ,  $d$  2.94;  $n(\alpha)=1.684$ ,  $n(\beta)=1.695$ ,  $n(\gamma)=1.698$ . The mineral is soluble in hydrochloric acid with evolution of chlorine. Three partial analyses on small amounts of material gave (insoluble deducted):

Mn.	Cl.	H <sub>2</sub> O.	O.	Total.
50.59	16.41	11.60	[21.40]	100.00

This agrees with the formula Mn<sub>4</sub>Cl<sub>2</sub>O<sub>6</sub>.3H<sub>2</sub>O. No other known mineral has the composition of a manganese oxychloride.

L. J. S.

**New Minerals.** A. SCHWANTKE (*Forsch. Min. Krist. Petr.*, 1923, 8, 90—100; from *Chem. Zentr.*, 1924, i, 1349).—Physical and chemical data are given for new minerals discovered or described during the preceding year. G. W. R.

**Sodium Cycle and Modern Geo-chemical Problems.** J. H. GOODCHILD (*Chem. News*, 1924, 129, 155—156.)

**Synthesis of Minerals.** P. NIGGLI.—(See ii, 680.)

## Analytical Chemistry.

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**Micro Melting-point Apparatus.** J. F. CLEVINGER (*Ind. Eng. Chem.*, 1924, **16**, 854—855).—An apparatus for the determination of the m. p. of minute quantities of crystalline substances melting at temperatures up to 400° consists of a heating unit and an object unit. The former, which is electrically heated, is connected to the latter by a horizontal conducting plate. The provision of an air chamber below the conductor and the covering of the brass container with asbestos board permit the crystals under examination to be melted on an object slide and viewed through a microscope. Temperature lag effects are avoided by slow heating. C. I.

**Gravimetric Microchemical Technique.** L. DIENES (*J. Biol. Chem.*, 1924, **61**, 73—76).—The difficulties attendant on the use of a micro-filter in micro-gravimetric analysis may be avoided by carrying out the precipitation and washings in a small weighed centrifuge tube of special design. C. R. H.

**Capillary Analysis.** R. DUBRISAY (*Chim. et Ind.*, May, 1924 [special number], 121—124).

**Modification Facilitating the Use of a Lunge Nitrometer and allowing its General Application.** G. RIVIÈRE and G. PICHARD (*Bull. Soc. chim.*, 1924, [iv], **35**, 901—902).—By means of a 3-way stopcock and bulb (60—70 c.c.) fitted below the graduated portion of a Lunge nitrometer it is possible, before taking the reading, to remove the mixture of sulphuric acid and mercuric sulphate which is formed during the volumetric determination of a nitrate without any loss of gas or entry of air. Similarly, illuminating gas may be analysed by the successive absorption of carbon dioxide, oxygen, ethylenic hydrocarbons, and carbon monoxide, the absorbent being removed after each measurement. J. W. B.

**Apparatus for Measuring the Volume of Gas Evolved from a Reaction.** G. P. PAMFIL (*Compt. rend. Soc. Biol.*, 1923, **88**, 924—925; from *Chem. Zentr.*, 1924, i, 1239).—An apparatus adapted for use with a constant-temperature bath for measuring the volume of gas evolved on adding a reagent to a substance. G. W. R.

**Turbidimetric Determination of Precipitates.** P. L. HIBBARD (*Ind. Eng. Chem.*, 1924, **16**, 804—805).—A modified colorimeter is described which affords a rapid means for the determination of any ion which will give a colourless granular precipitate, by measurement of turbidity. The instrument requires calibration for each precipitate and the conditions of precipitation must be standardised, the accuracy obtainable being 5—10%. [Cf. *B.*, 1924, 813.] C. I.

**Platinised Alundum Cathodes in Electroanalysis.** W. G. FRANCE and T. S. ECKERT (*Ind. Eng. Chem.*, 1924, **16**, 802—803).—Platinised alundum is not a satisfactory substitute for platinum gauze as cathode in the determination of metals by electrodeposition. [Cf. *B.*, 1924, 813.] C. I.

**Rapid Electrolytic Analysis in an Apparatus with a Rotatory Anode.** BERTIAUX (*Bull. Soc. chim.*, 1924, [iv], **35**, 1030—1039).—The analysis is carried out in a cell in which a perforated, cylindrical anode of platinum-iridium alloy is rotated within a fixed cathode of similar shape and material. S. K. T.

**New Methods of Volumetric Analysis. VI.** K. JELLINEK and W. KÜHN (*Z. anorg. Chem.*, 1924, **138**, 81—103).—Prussian blue, in the form of mixed saturated solutions of ferric chloride and potassium ferrocyanide, is a suitable indicator for the titration of an acid by an alkali,  $\text{Fe}_4^{III}[\text{Fe}^{\text{II}}(\text{CN})_6]_3 + 12\text{KOH} = 3\text{K}_4\text{Fe}(\text{CN})_6 + 4\text{Fe}(\text{OH})_3$ . The most accurate results are obtained if the acid solution is heated to about  $60^\circ$  before the alkali is added. Stannous chloride or alkali sulphite may be determined by titration with a standard solution of hydrogen peroxide, using starch and potassium iodide as an indicator, together with a few drops of solutions of ferrous ammonium sulphate and cupric sulphate to accelerate the reaction between the hydrogen peroxide and the starch iodide. Stannous chloride may also be titrated with hydrogen peroxide or ferric chloride, using ferric thiocyanate as an indicator. Boiling acidified potassium dichromate solution may be titrated with thio-sulphate solution using methylene-blue as an indicator:  $\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{Na}_2\text{S}_2\text{O}_3 + 7\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 3\text{Na}_2\text{S}_4\text{O}_6 + 3\text{Na}_2\text{SO}_4 + 7\text{H}_2\text{O}$ . The dichromate solution should be heated to about  $60^\circ$ , and the thiosulphate added quickly until the yellow colour is very faint; the solution is then heated to boiling, the methylene-blue added, and the titration completed. This reaction may be used as the basis of a "chromimetry," and reducing agents such as sodium sulphide may be determined by oxidation by excess of the dichromate, and the unchanged dichromate then titrated with thio-sulphate. Sodium arsenite in slightly acid solution may be determined by titration with sodium hypochlorite, using starch and potassium iodide as an indicator:  $\text{NaOCl} + \text{Na}_3\text{AsO}_3 = \text{NaCl} + \text{Na}_3\text{AsO}_4$ . The hypochlorite is added to the arsenite solution at about  $40^\circ$ . This reaction may be used to determine powerful oxidising agents such as dichromate and permanganate, by allowing the latter to oxidise excess of arsenite solution. W. H.-R.

**New Methods of Volumetric Analysis. VII.** K. JELLINEK and W. KÜHN (*Z. anorg. Chem.*, 1924, **138**, 109—134).—Potassium permanganate is a very satisfactory indicator for the titration of solutions of zinc salts by means of potassium ferrocyanide in the presence of ammonium chloride, and in slightly acid solution; the pink colour disappears as soon as the ferrocyanide is in excess, owing to oxidation to ferricyanide. Small quantities of copper do not interfere. Zinc and manganese in boiling solution may be

titrated with standard sodium sulphide solution, phenolphthalein being used as an indicator. The quantity of sulphide solution required is a constant excess of 8.0% in the case of zinc, and 6.0% in the case of manganese. Aluminium or lead in solution may be determined by titration with disodium hydrogen phosphate with methyl-red as an indicator:  $9\text{Na}_2\text{HPO}_4 + 2\text{Al}_2(\text{SO}_4)_3 = 2\text{Al}_2(\text{HPO}_4)_3 + 3\text{Na}_2\text{HPO}_4 + 6\text{Na}_2\text{SO}_4$ ;  $3\text{Pb}(\text{NO}_3)_2 + 4\text{Na}_2\text{HPO}_4 = 3\text{Pb}(\text{HPO}_4)_2 + \text{Na}_2\text{HPO}_4 + 6\text{NaNO}_3$ . The solutions are, however, best standardised empirically as the amount of phosphate used is slightly in excess of that demanded by the equations. Using methyl-red as an indicator, lead may be determined by titration with disodium hydrogen arsenate or trisodium arsenate; (i)  $\text{Pb}(\text{NO}_3)_2 + \text{Na}_2\text{HAsO}_4 = \text{Pb}(\text{HAsO}_4) + 2\text{NaNO}_3$ ; (ii)  $2\text{Na}_3\text{AsO}_4 + 3\text{Pb}(\text{NO}_3)_2 = \text{Pb}_3(\text{AsO}_4)_2 + 6\text{NaNO}_3$ . In the second reaction, the amount of arsenate used in the titration is always 1.2% less than that demanded by the equation. Mercuric chloride is so slightly dissociated that, if sodium chloride solution is added to a mercuric salt solution containing a drop of silver nitrate, precipitation of silver chloride occurs until nearly all the mercuric salt is converted into undissociated chloride. It is not, however, possible to develop a quantitative method based on this reaction, or in the similar cases of mercuric and zinc cyanides.

W. H. R.

**Determination of the Hydrogen-ion Concentrations of Acid Solutions with the Aid of the Glass Electrode.** A. L. VON STEIGER (*Z. Elektrochem.*, 1924, 30, 259—263).—A continuation of the work of Haber and Klemensiewicz (A., 1909, ii, 785) and Hughes (A., 1923, ii, 114). The electrodes of thin glass were formed in steam containing hydrogen chloride and kept in the acid solutions used, *i.e.*, hydrochloric acid and Sørensen citrate standards of  $p_{\text{H}}$  about 1 to 5. The potentials across these were measured with the binant electrometer. The mean difference between the readings of the electrode in solutions of  $p_{\text{H}}$  1.07 and 4.94 against a saturated potassium chloride-calomel electrode was 0.2174 volt, agreeing to about 1% with the calculated difference. With the aid of the electrode thus calibrated, the  $p_{\text{H}}$  values of other citrate and hydrochloric acid solutions were found and agreed to about 1% with those found by the hydrogen electrode.

E. B. R. P.

**Determination and Value of  $\pi_0$  in Electrometric Measurements of Hydrogen-ion Concentrations.** S. P. L. SÖRENSEN and K. LINDERSTRÖM-LANG (*Compt. rend. Trav. Lab. Carlsberg*, 1924, 15, [6], 1—40).—Detailed proposals for the standardisation of the method accord in the main with those of Clark. The *N*- or 3.5*N*-potassium chloride-calomel electrode is recommended as the standard, several such electrodes being frequently compared with each other and with a hydrogen electrode with electrode liquid 0.01*N*-hydrogen chloride and 0.09*N*-potassium chloride. Bjerrum's extrapolation method is recommended for the elimination of the diffusion potential. The importance of distinguishing between concentration and activity is emphasised and the

terms  $a_H$ ,  $pa_H$ , and  $a\pi_0$  are proposed for the quantities on the Lewis-Bjerrum activity theory corresponding with  $C_H$ ,  $P_H$ , and  $\pi_0$ , respectively. The standard value of the *E.M.F.* of the cell  $Hg|HgCl, 0.1N-KCl|N-H^+|H_2, Pt$  has been redetermined and calculated by the ordinary conductivity method to be  $\pi_0$  at  $18^\circ$ , 0.3380 volt, and by the activity method to be  $a\pi_0$  at  $18^\circ$ , 0.3357 volt (the electrode liquid in this case having *N*-activity of hydrogen ions).

G. M. B.

### Titrimetric Determination of Hydrogen-ion Concentrations.

C. RISCH (*Biochem. Z.*, 1924, **148**, 147—149).—A simple method for determining  $p_H$  between 8 and 9 (*e.g.*, in sea-water) involves matching the colour given by the test solution with phenolphthalein with that of distilled water to which a measured volume of 0.01*N*-potassium permanganate is added. Curves are given from which the  $p_H$  may be read directly.

J. P.

**Detection of Bromide and Iodide Ions in the presence of other Ions giving Precipitates with Silver Nitrate.** G. P. PAMFIL and M. WONNESH (*Z. anorg. Chem.*, 1924, **138**, 199—204; cf. Pamfil, this vol., ii, 497).—Bromide or iodide solutions give a precipitate when added to a solution of silver chloride and hexamethylenetetramine containing just sufficient ammonia to give a clear solution. A similar solution of silver bromide gives a precipitate with iodides only. These reactions are very sensitive, and are not affected by the presence of other ions giving precipitates with silver nitrate, with the exception of the cyanide ion.

W. H.-R.

**Microchemical Determination of Perchlorate.** A. PAMFILOV and W. JOFINOV (*Chem.-Ztg.*, 1924, **48**, 541).—Perchlorate in the presence of chlorate and chloride may be detected as follows: a few drops of the solution are neutralised with solid sodium hydrogen carbonate and, after addition of a few small crystals of rubidium chloride, evaporated to dryness on the object glass of a microscope. The residue is dissolved in a drop or two of very dilute permanganate solution and the liquid is evaporated until a crust forms at the edges. The formation of rose-coloured mixed crystals of rubidium perchlorate and permanganate may be observed if only 0.1% of perchlorate was present in the original solution. With practice the process may be used to give approximate quantitative results.

A. R. P.

**Determination of Sulphurous Acid, Thiosulphate, and Sulphide by means of Permanganate.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1924, **61**, 841—846).—In each case, the oxidation to sulphate is complete only when considerable excess of permanganate is used in strongly alkaline solution; after 2 minutes the excess is determined iodometrically. In neutral or acid solution, the oxidation is incomplete, even after keeping 24 hours with a large excess of permanganate.

S. I. L.

**Distillation Method of Separating Selenium from Tellurium.** V. LENHER and D. P. SMITH (*Ind. Eng. Chem.*, 1924, **16**, 837—838).—A working procedure is given for the separation of selenium from tellurium by distillation from a sulphuric acid solution with a current of gaseous hydrogen chloride in which selenium chloride is volatile. The condenser connexion should be very close to the top of the distilling flask through which the gas inlet tube is fused, otherwise selenium tetrachloride will condense in the intervening portion. The distillate is collected in water and elementary selenium precipitated by passage of sulphur dioxide. The tellurium in the residue is determined by the method of Lenher and Homberger. Accurate results are obtained with mixtures of the two elements in any proportions. C. I.

**Determination and Separation of Rare Metals from Other Metals.** IV. **Volumetric Determination of Tellurium and its Gravimetric Separation from Selenium.** L. MOSER and R. MIKSCH (*Monatsh.*, 1924, **44**, 349—363).—Tellurium as tellurous acid may be determined volumetrically with stannous chloride by a modification of Brauner's method (*ibid.*, 1890, **11**, 526), the reduction being conducted in an atmosphere of carbon dioxide. A volumetric method is described, depending on the oxidation of tellurous acid with potassium dichromate in neutral solution. Tellurous acid cannot be determined by oxidation with potassium permanganate in acidified solutions, but accurate results may be obtained in alkaline solution by cooling to 8—10° after the oxidation and slowly acidifying, with continuous stirring, with dilute sulphuric acid. Excess of 0.1N-oxalic acid solution is then added and after warming to 50° the excess is titrated with permanganate. Satisfactory results are also obtained in alkaline solution in the presence of sodium chloride (cf. Gooch and Peters, A., 1900, ii, 45). Reduction of tellurous acid with titanous chloride gives unsatisfactory results, owing to the formation of hydrogen telluride, and titration with acidified potassium bromate, sodium iodate, and alkaline hydrogen peroxide were also untrustworthy. Telluric acid may be determined iodometrically by reduction with either hydrobromic acid or hydrochloric acid (cf. A., 1904, ii, 613) in the apparatus previously described for selenious acid (A., 1918, ii, 451), air being excluded by a stream of carbon dioxide. Simultaneous reduction with hydrazine hydrochloride and sulphurous acid (Gutbier and Huber, A., 1914, ii, 575) and precipitation as tellurium dioxide (Browning and Flint, A., 1909, ii, 934) are the best gravimetric methods for determining tellurium. Of the known methods for the gravimetric separation of tellurium and selenium, Browning and Flint's method (precipitation of tellurium dioxide by hydrolysis in very weak acetic acid solution) was found to be the most satisfactory. A new method of separation is described based on the different behaviour of selenious and tellurous acids towards hydriodic acid. The selenious acid is reduced and elementary selenium precipitated, whilst the tellurium remains in solution as the double salt,  $2\text{KI} \cdot \text{TeI}_4 \cdot 2\text{H}_2\text{O}$ . To prevent the formation of colloidal

selenium, which absorbs iodine, the solution is added gradually to the boiling potassium iodide solution, the selenium then collecting at the bottom of the flask in a crystalline form. R. B.

**Determination of Nitrogen in the Wet Combustion Method for Carbon.** A. K. ANDERSON and H. S. SCHUTTE (*J. Biol. Chem.*, 1924, **61**, 57—61).—The wet combustion method of Gortner (*A.*, 1917, i, 311) has been extended to the determination of nitrogen by making the solution alkaline after the digestion with sulphuric acid and potassium dichromate and then proceeding as in an ordinary Kjeldahl determination. In presence of chloride the method gives low results, so that hydrochloric acid must be removed by aëration in presence of hot sulphuric acid before the addition of the dichromate. C. R. H.

**Use of Permutite in Separating and Determining Ammonia in Urine.** A. KOLB (*Chem.-Ztg.*, 1924, **48**, 557).—One c.c. of urine is shaken for a short time with 2 g. of moistened, finely granular permutite free from slimy material. Water is added and the permutite, which then contains all the ammonia in the urine, is washed several times by decantation. Five c.c. of 10% sodium hydroxide solution are added followed by 10 c.c. of Nessler's reagent, and the colour of an aliquot part of the liquid is compared with a standard ammonia solution under the usual conditions (cf. Folin and Bell, *A.*, 1917, ii, 268). A. R. P.

**Determination of Ammonia by means of Sodium Hypobromite.** M. B. DONALD (*Analyst*, 1924, **49**, 375—378).—The most accurate method ( $\pm 0.1\%$ ) is a modification of that of Artmann and Skrabal (*A.*, 1907, ii, 196). The ammonium salt solution is slowly added to the sodium hypobromite solution, shaken, kept for 5 minutes, acidified with hydrochloric acid, and an aqueous solution of potassium iodide added. The solution is diluted to 250 c.c., and the iodine titrated with thiosulphate. D. G. H.

**Determination of Nitrate by the Method of Grandval and Lajoux.** K. SCHERINGA (*Pharm. Weekblad*, 1924, **61**, 995—998).—Traces of acid in presence of organic material cause decomposition of the nitrate, hence an alkaline solution is preferred. The phenolsulphonic acid should be not more than a week and not less than 24 hours old. If chlorides are present, an amount of sodium chloride equivalent to the amount found in the sample should be added to the standard; results very much more accurate than those obtained by Frederick (*A.*, 1919, ii, 371) are obtained in this way. The green colour obtained with freshly prepared phenolsulphonic acid appears to be due to the action of chloride and nitrate together on phenol still uncombined. For a large number of routine determinations, Massink's modification of Frederick's method ("Het Water," 1919) is most suitable. S. I. L.

**Simple and Double Orthophosphates. II. Applications to Analyses.** TRAVERS and (MILLER) PERRON (*Ann. Chim.*, 1924, [x], **2**, 43—70).—Phosphoric acid may be determined accurately by precipitation with magnesium chloride in a neutral solution

containing ammonium salts, ammonia being added after the precipitation, but if the magnesium chloride is added to a strongly ammoniacal phosphate solution, some normal magnesium phosphate is formed, and the mixture should be boiled in order to convert this into magnesium ammonium phosphate. About twice the theoretical amount of magnesium chloride is sufficient, even in the presence of ammonium citrate. The precipitate is best titrated with hydrochloric acid, using methyl-orange or methyl-red as indicator. In the determination of magnesium, the formation of normal magnesium phosphate is avoided by precipitating with diammonium hydrogen phosphate and then adding ammonia.

The solubility of calcium phosphate in solutions of ammonium citrate is not due to the formation of a double phosphate as suggested by Herzfeld and Feuerlein (A., 1881, 940), but to the formation of calcium citrate by double decomposition (cf. Grupe and Tollens, A., 1880, 825). The precipitation of zinc ammonium phosphate in neutral solution is suitable for the determination of both zinc and phosphoric acid, unless the latter has been separated in the form of phosphomolybdate. Phosphoric acid may be determined in the presence of beryllium by fusing the solid with fusion mixture, boiling with water, and filtering; the phosphoric acid remains in the filtrate. In the absence of aluminium, beryllium may be precipitated as beryllium ammonium phosphate by adding a large excess of diammonium hydrogen phosphate to a neutral solution, and then adding ammonia. Aluminium may be precipitated as phosphate by the addition of twice the theoretical amount of disodium hydrogen phosphate to a faintly acid solution, the resulting mixture being made exactly neutral to methyl-orange. Aluminium may be separated from phosphoric acid by making the solution alkaline with sodium hydroxide, and precipitating the phosphoric acid as normal barium phosphate. (Cf. ii, 676, 677.)

W. H.-R.

**Modification of Molybdic Acid Method for Determination of Inorganic Phosphorus in Serum.** S. R. BENEDICT and R. C. THEIS (*J. Biol. Chem.*, 1924, **61**, 63—66).—By certain changes in the preparation of the reagent and by heating during colour production, the intensity of the colour obtained in the modification by Briggs (A., 1922, ii, 718) of the method of Bell and Doisy (A., 1920, ii, 769) for the determination of phosphorus in blood is considerably increased and the colour is more stable. C. R. H.

**"Lead Method" of Separating Phosphoric Acid in Qualitative Analysis.** D. BALAREV and M. DOTSCHEWA (*Z. anorg. Chem.*, 1924, **138**, 79—80).—In the authors' method (A., 1922, ii, 525) for the separation of phosphoric acid by means of lead nitrate, the acetic acid used in the separation may be oxidised by the nitrate or nitric acid, with the formation of organic acids of which the sodium salts are sparingly soluble in ammoniacal solution. Lead acetate is now used in place of lead nitrate; no indicator need then be added in order to adjust the hydrogen-ion concentration.

W. H.-R.



**Determination of Carbonates in Highly Coloured Liquids.**

H. B. DUNNICLIFF (*Analyst*, 1924, **49**, 426—428).—The liquid, followed by sulphuric acid and a small proportion of "paroline," is introduced through a nitrometer into a bulb placed in a water-bath and connected at its opposite end by pressure tubing with a mercury reservoir. The evolved carbon dioxide is passed up into the nitrometer, its volume read, and the weight of carbonate per 100 c.c. of liquid calculated from the formula  $K(V-v)(P-B-c)/(273+T)$ , where  $V$  is the volume in c.c. of gas,  $v$  the correction for dissolved air,  $P$  the observed pressure,  $B$  the water-vapour pressure at the laboratory temperature  $T^\circ$ ,  $c$  the correction for temperature of mercury column, and  $K$  is 0.006846. [Cf. *B.*, Oct.]

D. G. H.

**Determination of Carbonyl Chloride in Gas Mixtures.**

G. BREDIG and A. VON GOLDENBERG (*Gas- u. Wasserfach*, 1924, **67**, 490—491).—Gas mixtures containing hydrogen chloride, carbonyl chloride, and carbon dioxide are first shaken with a little water (to absorb the hydrogen chloride) and then with a measured volume of *N*-potassium hydroxide, which absorbs both the carbonyl chloride and carbon dioxide. Carbonyl chloride reacts readily with alkali, viz.,  $\text{COCl}_2 + 4\text{KOH} = 2\text{KCl} + \text{K}_2\text{CO}_3 + 2\text{H}_2\text{O}$ , and the determination is completed by adding a known excess of hydrochloric acid and titrating back with 0.1*N*-barium hydroxide.

W. T. K. B.

**Volumetric Determination of Potassium as Hydrogen Tartrate.** KLAPPROTH (*Kali*, 1923, **17**, 343—345; from *Chem. Zentr.*, 1924, i, 1565).—Potassium tartrate is precipitated with formic acid and the excess of acid is determined volumetrically. The precipitate is treated with calcium carbonate and the resulting calcium tartrate decomposed by sodium carbonate. G. W. R.

**Iodometric Determination of Sodium.** H. MÜLLER (*Biochem. Z.*, 1924, **147**, 356—357).—A reply to criticisms of the author's method by Bálint and Petow (this vol., ii, 500). J. P.

**Analysis of Sodium Sulphide.** E. CRESPI (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 488—491; from *Chem. Zentr.*, 1924, i, 1977).—In the analysis of sodium sulphide, iodometric titration may be used after preliminary carbonation by means of a current of carbon dioxide, whereby hydrogen sulphide is removed and the thiosulphate is unaltered. G. W. R.

**Determination of Calcium, Magnesium, and Phosphorus in Animal Substances.** L. DIENES (*J. Biol. Chem.*, 1924, **61**, 77—90).—Modifications are described in the methods previously used by the author (*A.*, 1919, ii, 427) for the determination of small quantities of calcium, magnesium, and phosphorus. Duplicate determinations in the cases of calcium and magnesium agree to within 0.001 mg. C. R. H.

**Precipitation of Magnesium as Phosphate from Solutions containing Tartaric Acid in the Presence of Aluminium.**

E. WILKE-DÖRFURT (*Wiss. Veröff. Siemens-Konz.*, 1924, **3**, 9—11).—Further tests of the previously described method for separating

magnesium from aluminium by precipitation as phosphate from ammoniacal tartrate solutions (*ibid.*, 1921, **1**, 85) show that, contrary to the statements of Hahn (*Chem.-Ztg.*, 1922, **46**, 536) and others, good results are obtained when more than 1% of magnesium is present in the alloy. The results, on the whole, tend to be a little too high.

A. R. P.

**Iodometric Determination of Magnesium as Magnesium Ammonium Arsenate.** M. KLINGENFUSS (*Z. anorg. Chem.*, 1924, **138**, 195—198).—Magnesium may be determined volumetrically by adding its solution to a boiling 0.1N-arsenate solution containing ammonia and ammonium chloride. The mixture is boiled until the precipitated magnesium ammonium arsenate has coagulated, and is then left for 3 hours, and the precipitate filtered off. The unchanged arsenate in the filtrate is then determined by adding potassium iodide and hydrochloric acid to the solution, allowing the latter to remain for 30 minutes, and then titrating the liberated iodine with thiosulphate. The difficulty of preparing a standard arsenate solution (cf. Gooch and Morris, A., 1900, ii, 686) may be overcome by dissolving a weighed quantity of arsenic trioxide in dilute aqueous sodium hydroxide, and oxidising the solution by heating with hydrogen peroxide on a water-bath. The excess of hydrogen peroxide is then destroyed by boiling and the solution made up to the required volume.

W. H.-R.

**Determination of Magnesium in Aluminium, Zinc, and Lead Alloys.** B. FETKENHEUER and A. KONARSKY (*Wiss. Veröff. Siemens-Konz.*, 1924, **3**, 19—21).—Magnesium may be separated from large quantities of aluminium, zinc, or lead by taking advantage of the solubility of the hydroxides of these metals in potassium hydroxide and the insolubility of magnesium hydroxide in this solvent. For aluminium and zinc, only the theoretical amount of potassium hydroxide is necessary, whilst lead requires twice that amount. The magnesium hydroxide is purified by solution in hydrochloric acid and removal of the impurities by means of ammonia, ammonium chloride, and ammonium sulphide. [Cf. B., 1924, 791.]

A. R. P.

**Colorimetric Determination of Small Quantities of Lead and Copper in Drinking Water.** C. PYRIKI (*Z. anal. Chem.*, 1924, **64**, 325—330).—In the determination of small quantities of copper and lead in water by Winkler's method, correct results are obtained for copper only if the difference between the amount of standard lead solution required to match the copper and lead combined and that required for the lead alone (cyanide being added to dissolve the colloidal copper sulphide) is multiplied by 0.813, as copper sulphide is more intensely coloured than lead sulphide. [Cf. B., 1924, 845.]

A. R. P.

**Determination of Copper and Tin in Copper-Tin Alloys.** A. T. ETHERIDGE (*Analyst*, 1924, **49**, 371—374).—Copper is separated

from a sulphuric acid solution by electrolysis, sufficient acid being present to retain the tin completely in solution and prevent precipitation by hydrolysis. The tin is subsequently precipitated as stannic sulphide, which is ignited, and the resulting oxide weighed. [Cf. *B.*, 1924, 750.]

D. G. H.

**Separation of Copper from Platinum Metals.** W. H. SWANGER and E. WICHES (J. Amer. Chem. Soc., 1924, 46, 1814—1818).—A quantitative separation of copper from the platinum metals is not afforded by extraction with nitric acid of the sulphides, whether these are previously ignited or not. Extraction of the unignited sulphides with 3% hydrogen peroxide solution effects a rough separation, but the procedure recommended is the precipitation of the copper as cuprous thiocyanate in presence of sufficient sulphur dioxide and acid to prevent the precipitation of the thiocyanates or sulphites of the platinum metals.

S. B.

**Determination of Iron by means of Permanganate in the presence of Hydrochloric Acid.** W. MANCHOT and F. OBERHAUSER (Z. anorg. Chem., 1924, 138, 189—194).—The error caused by the liberation of chlorine cannot be prevented, but may be accurately allowed for by determining its magnitude, by either of the following methods. (1) The ferrous salt solution is titrated with permanganate in the usual manner, and potassium bromide is then added. The bromine liberated is determined by the addition of excess of arsenious acid, the unchanged arsenious acid being titrated with standard bromine solution, using indigo-carmin or styphnic acid as indicator. (2) The reduced ferrous salt solution is treated with potassium bromide and then with excess of permanganate, and the liberated bromine determined as before. In both cases the addition of phosphoric acid is advisable in order to keep the solution colourless. The iron should be reduced to the ferrous state by means of sulphurous acid or finely-divided cadmium, and not by hydrogen sulphide. In the presence of hydrochloric acid, ferrous solutions may also be determined by treatment with excess of dichromate solution, and then with potassium bromide, the liberated bromine being determined as above.

W. H.-R.

**2 : 4-Dinitrosoresorcinol as a Delicate Reagent for Ferrous Salts.** M. GOLDSTÜCK (Chem.-Ztg., 1924, 48, 629).—A solution of 2 : 4-dinitrosoresorcinol in boiling water gives a bluish-green precipitate in neutral or faintly acid solutions of ferrous salts containing 0.02 mg. of iron in 10 c.c. If small quantities of ferric salts are also present the solution becomes bright green. Copper is the only metal that interferes with the test.

A. R. P.

**Titration of Ferric Chloride with Thiosulphate.** K. JELLINEK and L. WINOGRADOV (Z. anorg. Chem., 1924, 138, 78).—Full practical details are given for the authors' method (A., 1923, ii, 871) for the titration of ferric chloride with thiosulphate [Cf. *B.*, 1924, 814.]

W. H.-R.

**Electrometric Titration of Nickel and Cobalt with Potassium Cyanide.** E. MÜLLER and W. SCHLUTTIG (*Z. anorg. Chem.*, 1924, **134**, 327—343).—Nickel and cobalt in solution can be determined electrometrically, using a silver electrode and the reverse potential method of Müller and Lauterbach (A., 1922, ii, 875),  $e_u\text{Ni} = -0.25$  volt, and  $e_u\text{Co} = -0.49$  volt, or by running the nickel and cobalt solutions into potassium cyanide until a jump in the potential is obtained. This point in the case of nickel corresponds with the commencement of the change,  $\text{Ni}(\text{CN})_4'' + \text{Ni}'' \rightarrow 2\text{Ni}(\text{CN})_2$  and for cobalt with the change  $2\text{Co}(\text{CN})_5''' + 3\text{Co}'' \rightarrow 5\text{Co}(\text{CN})_2$ .

H. T.

**Electrometric Titration of Chromic Acid using (a) the Hydrogen Electrode or (b) the Oxygen Electrode.** H. T. S. BRITTON (*J. Chem. Soc.*, 1924, **125**, 1572—1582).—A hydrogen electrode which gives satisfactory results in chromic acid solution was prepared by depositing a coarse, thin layer of platinum black from a solution containing lead acetate and a platinum salt on a highly polished piece of platinum foil. With this electrode and also with the usual oxygen electrode, titrations were made of solutions of chromic acid against a standard alkali, and fairly concordant results were obtained. The degree of dissociation of the first hydrogen ion in 0.02475*M*-chromic acid solution at 18° was found to be 95% and the second dissociation constant  $\text{HCrO}_4' \rightleftharpoons \text{H}^+ + \text{CrO}_4''$  was found to be of the order of  $4.4 \times 10^{-7}$ . From the results obtained electrometrically it would appear that, when phenolphthalein is used as indicator in the titration of chromic acid against an alkali, the end-point as shown by the indicator occurs a little before the true end-point. No evidence could be obtained to show that chromic acid in solution has the formula  $\text{H}_2\text{Cr}_2\text{O}_7$ .

A. R. P.

**Hydrolysis of Quadrivalent Titanium Sulphate Solutions as the Basis of a Separation of Titanium and Aluminium in Solution in Sulphuric Acid.** L. KAYSER (*Z. anorg. Chem.*, 1924, **138**, 43—64).—The hydrolysis of solutions of quadrivalent titanium sulphates of composition approximately  $3\text{TiO}_2.4\text{SO}_3.15\text{H}_2\text{O}$ , and  $4\text{TiO}_2.5\text{SO}_3.12.5\text{H}_2\text{O}$ , and also of some double sulphates with ammonium has been investigated. The conductivities of these solutions at 25° generally increase with time, but the exact nature of these variations depends greatly on the concentration of titanium salt, the acidity of the solution, and the presence of other salts. In solutions with considerable excess of sulphuric acid, the conductivity first decreases to a minimum and then gradually increases. No appreciable change in  $p_{\text{H}}$  could, however, be detected during the hydrolysis, contrary to the theories of Tian (A., 1922, ii, 362) and of Wagner (A., 1913, ii, 200, 765). The increase in conductivity may possibly be due to adsorption effects.

At higher temperatures, the hydrolysis takes place according to the reaction  $\text{TiO}'' + 2\text{OH}' + \text{H}_2\text{O} = \text{Ti}(\text{OH})_4$ , but a little basic sulphate is also formed and can only be decomposed by very pro-

longed washing. After 1 hour at  $100^{\circ}$ , hydrolysis is complete if  $p_H$  is greater than about 1.5 or 1.6, the speed of hydrolysis being affected by the presence of other salts. If aluminium is present, hydrolysis at  $100^{\circ}$  will result in the partial precipitation of aluminium if  $p_H > 1.7$ , but in a narrow zone of hydrogen-ion concentration in the neighbourhood of  $p_H = 1.6$ , it is possible to precipitate the whole of the titanium, whilst the aluminium remains in solution. A separation of the two metals based on this fact is described, in which the two metals are first precipitated together by ammonia and the mixed precipitate is dissolved in a known amount of sulphuric acid, the solution being diluted to give the required  $p_H$  and then heated at  $100^{\circ}$  to precipitate the titanium. [Cf. *B.*, 1924, 814.]

W. H.-R.

**Colour Reaction for Zirconium and Fluorine.** J. H. DE BOER (*Chem. Weekblad*, 1924, **21**, 404—405).—The colours given by various metals in presence of alizarinsulphonic acid are completely discharged by a large excess of hydrochloric acid except the reddish-violet colour given by zirconium, which changes gradually through orange to yellow if a very great excess is employed. Addition of fluorides to the orange solution at once discharges the colour.

S. I. L.

**Determination of Antimony.** A. ECKE (*Chem.-Ztg.*, 1924, **48**, 537).—Antimony dissolves in warm hydrochloric acid containing a cupric salt, an equivalent quantity of the latter being reduced:— $\text{SbCl}_3 + 2\text{CuCl}_2 = \text{SbCl}_5 + 2\text{CuCl}$ . The solution should be prepared in an atmosphere of carbon dioxide, and subsequent titration of the cuprous salt with standard permanganate solution gives a measure of the quantity of antimony present. Lead interferes with the determination, since it also reduces the cupric salt. In the case of an alloy containing antimony, tin, lead, and copper, a portion of the sample is dissolved in hot sulphuric acid; the cooled solution is treated with hydrochloric and tartaric acids, and neutralised with sodium hydroxide solution, using phenolphthalein as indicator. The solution is then acidified with tartaric acid, sodium hydrogen carbonate solution is added, and the solution titrated with 0.1N-iodine solution.

W. P. S.

**Rapid Electrolytic Determination of Bismuth and its Use in the Analysis of Bismuth Ores and Products.** K. SEEL (*Z. angew. Chem.*, 1924, **37**, 541—543).—An accurate method for determining bismuth is described, in presence or absence of lead, based on the methods of Sand (T., 1907, **91**, 373; 1908, **93**, 1572; A., 1910, ii, 66, etc.) and of Fischer (A., 1909, ii, 521), using a controlled cathode-potential. The bismuth solution containing dextrose and nitric acid is electrolysed at  $60$ — $70^{\circ}$  with an initial current density up to 2 amps. per sq. cm. and a cathode potential of 0.5 volt; the current density sinks gradually to 0.2—0.1 amp. per sq. cm., the potential being allowed to rise to 0.8—0.85 volt. The cathode is then washed, dried, and weighed in the usual manner. Lead begins to be deposited on the cathode when the potential reaches

0.95 volt, the anode also being coated with lead peroxide. The results are usually 0.1% too high, but are otherwise consistent and accurate, the separation from lead being very satisfactory.

F. A. M.

**Separation of Rhodium from Platinum.** E. WICHES (J. Amer. Chem. Soc., 1924, 46, 1818—1833).—The customary separation of rhodium from platinum by means of ammonium chloride is unsatisfactory. The method recommended for this separation is the precipitation of the rhodium as hydroxide by various reagents. Sodium hypobromite may be used; but a procedure, fully described, employing barium carbonate is the most satisfactory. S. B.

**Examination of Ether for Anæsthetic Use.** F. WISCHO (Pharm. Monatsh., 1923, 4, 195—196; from Chem. Zentr., 1924, i, 948).—Jorisson's reagent (0.4 g. of vanadic acid in 4 c.c. of sulphuric acid and 96 c.c. of water) gives a red colour with ether if peroxides are present. Aldehydes and unsaturated alcohols give a blue colour on keeping. G. W. R.

**Electrometric Determination of Formaldehyde.** E. MÜLLER and W. Low (Z. anal. Chem., 1924, 64, 297—302).—In the presence of an excess of sodium carbonate, formaldehyde reduces silver nitrate quantitatively to metallic silver at the ordinary temperature and is itself oxidised to sodium formate. The excess of silver salt, which is then in the form of carbonate, may be determined by neutralisation of the solution with sulphuric acid followed by electrometric titration with potassium chloride, using a silver indicator electrode or, preferably, by direct electrometric titration (without neutralisation) with potassium iodide. [Cf. B., 1924, 847.]

A. R. P.

**Colorimetric Determination of Phenols in Urine.** R. GOIFFON and F. NEPVEUX (Compt. rend. Soc. Biol., 1923, 89, 1213—1214; from Chem. Zentr., 1924, i, 1070).—Directions are given for the determination of phenols in urine by a method based on that of Rakestraw (A., 1923, ii, 587) for phenols in blood. G. W. R.

**Qualitative Tests of some Photographic Developers.** A. ROSSI (Sci. techn. ind. phot., 1923, Nov.; Ind. Chim., 1924, 11, 217).—Coloured rings and uniform colorations are obtained as follows when 10—20 drops of very dilute aqueous formaldehyde are added to a solution in concentrated sulphuric acid, with subsequent mixing: quinol and "metol" (N-methyl-p-aminophenol sulphate), brown, blackish-brown; pyrogallol, carmine, reddish-brown; pyrocatechol, both wine-red; "genol," green, none; diaminophenol, none, brownish-grey; p-aminophenol, none. On addition of 10% of sodium hydroxide and 1 c.c. of 10% mercuric chloride solutions to 0.2 g. in 5 c.c. of water, the following reactions are obtained: "genol," a turbidity, then a precipitate becoming yellow, green, bluish-green, and olive; quinol, yellow precipitate becoming brick-red, brown, and brownish-grey; "metoquinone," a yellow precipitate becoming dark yellowish-grey, then olive-yellow.

CHEMICAL ABSTRACTS.

**Attempt to extend Mitchell's Colorimetric Method to the Determination of Pyrocatechol Tannins.** P. H. PRICE (*Analyst*, 1924, **49**, 361—366).—Pyrocatechol, protocatechuic acid, and catechin give constant, but not comparable, results with Mitchell's method (A., 1923, ii, 188). Since the ratios pyrocatechol : gallic acid and protocatechuic acid : gallic acid were both found to be 100 : 57, additional evidence is afforded that the carboxyl group in protocatechuic acid does not dilute the pyrocatechol nucleus. The pyrocatechol tannins cannot be determined by Mitchell's process. It is pointed out that in order to obtain a violet coloration two hydroxyl groups in the ortho position are always necessary.

D. G. H.

**Determination of Sugar in Blood by Bang's Method.** P. A. COPPENS (*Nederl. Tijdschr. Geneeskunde*, 1924, **68**, I, 153—155; from *Chem. Zentr.*, 1924, i, 1568).—Directions are given for the preparation of copper and calcium chloride-uranyl acetate solutions for use in a modified Bang method for the determination of sugar in blood.

G. W. R.

**Determination of Sugar in Urine by means of Fehling's Solution with Methylene-blue as Internal Indicator.** J. H. LANE and L. EYNON (*Analyst*, 1924, **49**, 366—371).—Neutralised and defecated urine is mixed with Fehling's solution, boiled for 1 minute, and 10 drops of a 1% aqueous solution of methylene-blue are added. Known quantities of urine are then added until complete decolorisation results on boiling for 15 seconds. The results agree with those of Gerrard's cyano-cupric method, but are lower than those obtained by Pavy's method.

D. G. H.

**Determination of Dextrose in Blood.** A. CRUTO (*Rass. Clin. Therap. Sci. aff.*, 1924, **23**, 6—8; from *Chem. Zentr.*, 1924, i, 2291).—Directions are given for the determination of dextrose in blood by a method depending on the liberation of iodine from potassium iodide in an alkaline solution containing copper sulphate, and subsequent determination of the iodine by titration with thio-sulphate.

G. W. R.

**Microchemical Methods for Distinguishing between Glycogen and Dextrin.** E. M. CALVINO (*Riv. di Biol.*, 1923, **5**, 486—496; from *Chem. Zentr.*, 1924, i, 2291).—With a 0.5% solution of "Orseillin BB" in 90% ethyl alcohol, glycogen gives a red coloration, whilst erythrodextrin gives no coloration.

G. W. R.

**Titration of Organic Acids (in Urine).** M. LABBÉ, H. BITH, and F. NEPVEUX (*Presse méd.*, 1923, **31**, 505—506; from *Chem. Zentr.*, 1924, i, 1425).—When dimethylaminoazobenzene is used as indicator instead of "Orange IV," as recommended by Van Slyke and Palmer, values are obtained for organic acids which are only 60% of the true amount.

G. W. R.

**Addition of Bromine to Fats and Oils and the Determination of the Bromine Value.** T. SABALITSCHKA and K. R. DIETRICH (*Pharm. Ztg.*, 1924, **69**, 742—743).—The bromine values of oils and

fats determined by the increase in weight of a thin film of the oil or fat exposed to bromine vapour (cf. Oestermann, *B.*, 1924, 719) are accurate and correspond with the iodine values only if daylight be excluded during the determination. In sunlight, the values are considerably too high, and in diffused daylight they are about 1% too high, owing to the formation of brominated substitution products.

P. M.

**Determination of the Acetyl Value of Fats.** R. BIAZZO (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 448—467; from *Chem. Zentr.*, 1924, i, 2030).—Two new methods are described for the determination of the acetyl value of fats: (a) the acetyl value is derived from the increase in weight on acetylation with acetic anhydride, after removal of excess of the anhydride; (b) acetylation is carried out with chloroacetyl chloride and the acetyl value derived from the amount of chlorine determined volumetrically.

G. W. R.

**Determination of Cholesterol in Blood.** S. L. LEIBOFF (*J. Biol. Chem.*, 1924, **61**, 177—180).—The blood (0.25 c.c.) is absorbed on a filter-paper which is extracted in a small continuous extraction apparatus with chloroform. The cholesterol in solution is then determined colorimetrically.

C. R. H.

**Colorimetric Determination of Carbamide.** Y. NAKASHIMA and K. MARUOKA (*Deut. Arch. klin. Med.*, 1924, **143**, 318—324; from *Chem. Zentr.*, 1924, i, 2191—2192).—Carbamide is determined in blood-serum, after removal of proteins, by means of the bluish-red colour produced with a solution of furfuraldehyde and stannous chloride in 30% hydrochloric acid.

G. W. R.

**Colorimetric Determination of Carbamide with Urease.** K. YANAGI (*J. Amer. Med. Assoc.*, 1924, **82**, 1169—1171).—Large differences are not observed on comparison of the colorimetric method of Nakashima and Maruoka (see preceding abstract) with the urease methods of Van Slyke and Cullen and of Bahlmann, except when abnormally large quantities of carbamide are present in the blood-serum.

CHEMICAL ABSTRACTS.

**Determination of Phenols in Blood.** R. C. THEIS and S. R. BENEDICT (*J. Biol. Chem.*, 1924, **61**, 67—71).—Phenols are determined colorimetrically in the protein-free filtrate obtained from blood by the method of Folin and Wu (*A.*, 1919, ii, 308), by means of *p*-nitrobenzenediazonium chloride, which gives an orange colour with phenols in presence of sodium carbonate. Experiments with blood to which known amounts of phenol have been added show the possible error to be  $\pm 10\%$ . Normal human blood contains 1—2 mg. per 100 c.c. of free phenols, and, in some cases, small quantities of conjugated phenols.

C. R. H.



## General and Physical Chemistry.

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**Magnetic Resolution of the Scandium Lines.** S. GOUDSMIT and P. ZEEMAN (*Nature*, 1924, **114**, 432—433).—Preliminary measurements of the magnetic resolution of some scandium lines agree with calculations based on the assumed validity of Landé's  $g$ -formula, but probably there are also some terms for which the ordinary formula does not apply. Unless the results are vitiated, *e.g.* by the simultaneous action of different outer electrons, the single  $3s$ -electron must be the emitting electron of the neutral scandium atom, and in the ionised scandium atom there is no  $3s$ -electron, or it is in this case also the emitting electron. A. A. E.

**Vacuum-arc Spectrum of Sodium.** I. H. BARTELS (*Z. Physik*, 1924, **25**, 378—401).—A new vacuum sodium arc is described, capable of burning in two forms. In the first form, it burns with a yellow zone, merging into a green mantle which completely fills the vessel; shortly before all the sodium is vaporised, the arc changes into the second form, becomes deep yellow, and burns without separation into zones. The relative intensities of the lines in the two forms of arc and in the green mantle have been measured. S. K. T.

**Low-voltage Arc Spectra of Copper and Silver.** A. G. SHENSTONE (*Nature*, 1924, **114**, 501).—By the use, in a vacuum, of a three-electrode arrangement, spectrograms of the ultra-violet arc spectrum of silver vapour have been obtained entirely free from spark lines. The only lines appearing are the first two pairs of the principal series; new wave-length measurements have been made. The arc in copper vapour at 8 volts gives a large number of lines terminating with a single line at  $2024\cdot33 \text{ \AA.}$ , the value calculated for  $1S-2\pi_1$ , but there can be no line of comparable intensity corresponding with  $1S-2\pi_2$ . A. A. E.

**Low-voltage Excitation of the Spectrum of Cæsium.** A. L. HUGHES and C. F. HAGENOW (*Physical Rev.*, 1924, [ii], **24**, 229—233).—By the use of a device ensuring an equipotential source of electrons, a nickel cylinder over an alundum tube heated internally by a tungsten spiral, the appearance has been observed of the lines in the principal series of cæsium in the order, and practically at the potential, required by Bohr's theory. The evidence obtained in the diffuse and sharp series was also in favour of stepwise excitation of the various lines. A. A. E.

**Excitation of the Spectra of Monatomic Gases.** G. DEJARDIN (*Ann. Physique*, 1924, [x], **2**, 241—327).—A detailed account of investigations on the excitation of the spectra of mercury, helium, argon, krypton, and xenon by electrons of varying velocity. Most of the results have already been published (*A.*, 1923, ii, 47; VOL. CXXVI. ii. 27

this vol., ii, 284). The following values in volts are found for the ionisation potentials: helium,  $19.7 \pm 0.2$  (resonance potential),  $24.5 \pm 0.2$  at which both orthohelium and parhelium lines appear simultaneously; mercury,  $10.4 \pm 0.2$ ,  $20 \pm 0.5$ ,  $30 \pm 1$ ,  $44 \pm 2$ ; argon,  $11.5 \pm 0.2$ ,  $15.2 \pm 0.2$ ,  $19 \pm 0.5$ ,  $34 \pm 0.5$ ,  $70 \pm 2$ ; krypton,  $9.7 \pm 0.2$ ,  $12.7 \pm 0.2$ ,  $15.5 \pm 0.2$ ,  $28.25 \pm 0.5$ ,  $59 \pm 2$ ; xenon,  $8.9 \pm 0.2$ ,  $10.9 \pm 0.2$ ,  $13 \pm 0.5$ ,  $24.25 \pm 0.5$ ,  $51 \pm 2$ . The order of the appearance of lines in the groups which are characterised by these threshold potentials is confirmed by experiments with the oscillating electrodeless discharge. S. S.

**Spectra of Isotopes.** P. DAS (*Bull. Calcutta Math. Soc.*, 1923, **13**, 183—190).—An expression for the separation between homologous lines in the spectra of isotopes is evolved and applied to the sharp singlet series of helium. CHEMICAL ABSTRACTS.

**Term Structure of Multiplets.** A. LANDÉ and W. HEISENBERG (*Z. Physik*, 1924, **25**, 279—286).

**Extension of the X-Ray Doublet Laws into the Field of Optics.** I. S. BOWEN and R. A. MILLIKAN (*Physical Rev.*, 1924, [ii], **24**, 209—222; cf. this vol., ii, 638, 639).—Evidence is available that many of the strongest lines in hot spark spectra are due to "stripped atoms," i.e., atoms devoid of valency electrons except that which emits the radiation by jumping between energy levels. For the *L*-doublets due to atoms with but one *L*-electron,  $\text{Li}_I$ ,  $\text{Be}_{II}$ ,  $\text{B}_{III}$ , and  $\text{C}_{IV}$ , the relativity formula for X-ray doublets,  $\Delta\nu = k(z-s)^4$  holds, as also for *L*-doublets attributed to atoms stripped of all but three *L*-electrons. The values of *s* decrease from 2.02 for lithium to 1.86 for carbon, these giving quantitatively the influence on the effective nuclear charge of the addition of electrons in the valency shells. For triplets, values of *s* for atoms stripped of all but two or four *L*-electrons agree reasonably well with those for 1, 3, or 5 *L*-electrons. The formula is also applicable to the *M* series. The extension of the X-ray doublet laws to the whole optical region provides a new method of predicting spectra and of determining the state of ionisation of atoms emitting certain lines.

A. A. E.

**Some Conspicuous Successes of the Bohr Atom and a Serious Difficulty.** R. A. MILLIKAN and I. S. BOWEN (*Physical Rev.*, 1924, [ii], **24**, 223—228).—The successful application of the theoretical relativity formulæ to the doublets in optical spectra (cf. preceding abstract) means considerable simplifications in the classification of lines in the X-ray and optical regions. Thus it implies the identification of the  $L_I$ ,  $L_{II}$ ,  $L_{III}$  X-ray levels with the  $s$ ,  $p_2$ ,  $p_1$  terms of optical series, respectively. This would make  $p_2 p_1$  correspond with  $2_1 2_2$  orbits (whereas they are always both assigned to the  $2_1$  orbits) and would also assign both *s* and  $p_2$  to the  $2_1$  orbits, and must be so taken if their differences are to be explained on a relativity basis. These changes are, however, vital to the Bohr theory of the interpenetration of orbits. It would appear to be necessary either to abandon altogether relativity

causes and effects in electronic orbits, or to introduce into atomic models a dissymmetry not heretofore contemplated, and to conclude that the orientation of the orbit with respect to the atom body has a much more powerful effect on the screening constant  $s$  than has the shape of the orbit (azimuthal number). W. E. G.

**Absolute Intervals of Optical Doublets and Triplets.**

A. LANDÉ (*Z. Physik*, 1924, **25**, 46—57).—The relationship of the optical  $p$ -term doublets with the  $X$ -ray doublets (cf. Landé, this vol., ii, 511) becomes still more marked when the absolute intervals of the optical doublets and triplets are considered. An interval formula has been deduced, by an extension of Sommerfeld's theory of the relativity  $L$ -doublets, taking into account the complexity due to the approach of the electron to the nucleus at one part of its orbit. In spite of the empirical value of the formula, a relativity interpretation of optical doublets and triplets does not seem possible. Neither is an interpretation of the formula to be reached by a consideration of magnetic forces. M. S. B.

**Secondary Spectrum of Hydrogen.** P. DAS (*Bull. Calcutta Math. Soc.*, 1922, **14**, 13—17).—A model of the hydrogen molecule assumes that two nuclei describe closed orbits round an electron placed at their centre of gravity, the other electron describing some orbit at a comparatively large distance from the complex structure. Inter alia, a close relation between the secondary spectrum and the Balmer lines results. CHEMICAL ABSTRACTS.

**Structure of the Second Positive Group of Nitrogen Bands.**

P. LINDAU (*Z. Physik*, 1924, **25**, 247—252; cf. Mecke and Lindau, this vol., ii, 510).—An apparatus is described by which measurements of wave-lengths may be made more quickly than by the usual precision method, and with equal accuracy. M. S. B.

**Origin of the First and Second Positive Groups of the Nitrogen Band Spectrum.**

M. DUFFLEUX (*Compt. rend.*, 1924, **178**, 1966—1968).—An electric discharge passed through nitric oxide and nitrogen peroxide has confirmed the view that the first positive group of the nitrogen band spectrum is emitted by the molecule and the second by the atom (cf. this vol., ii, 134). If nitric oxide be allowed to travel slowly through the discharge tube it emits the second group of nitrogen bands immediately on entry, as well as bands characteristic of the oxides. As the gas approaches the end of the tube, the oxide bands disappear, being replaced by the first group of nitrogen bands. The phenomena observed in the nitrogen peroxide tube are more complicated, but again the second group is seen at the beginning of the tube, whilst the first does not appear until near the exit. These results are explained by supposing that the oxides decompose to give atomic nitrogen which emits the second group, this being followed by the formation of nitrogen molecules which emit the first group of bands. M. S. B.

**Origin of the so-called Cyanogen Band.**

E. FREUNDLICH and E. HOCHHEIM (*Z. Physik*, 1924, **26**, 102—105).—When nitrogen

is heated in a graphite tube furnace at  $2100^{\circ}$  the cyanogen band  $3883 \text{ \AA}$ . is strongly developed, but this band does not appear if the graphite tube is replaced by one of tungsten. This is contrary to the view of Grottrian and Runge that these bands are due to nitrogen (cf. Kratzer, A., 1922, ii, 4; Barratt, A., 1920, ii, 569).

S. K. T.

**Emission Spectra of Organic Compounds.** W. H. McVICKER, J. K. MARSH, and A. W. STEWART (*J. Amer. Chem. Soc.*, 1924, **46**, 1351—1358; cf. T., 1923, **123**, 817).—The Tesla-luminescence spectra of a number of organic compounds were examined. Usually a characteristic spectrum was obtained for each compound, although there is a general resemblance between the spectra of allied compounds. The benzene ring system is one of the most delicate producers of Tesla-luminescence spectra. Heterocyclic compounds, e.g., furfuraldehyde, thiophen, pyrrole, and pyridine, gave no emission, although the pyridine nucleus when attached to a benzene ring, as in quinoline, exerted a marked influence on the spectra.

H. T.

**Absorption Spectrum of [Liquid] Bromine.** P. BOVIS (*Compt. rend.*, 1924, **178**, 1964—1966).—Measurements have been made of the opacity to light of different wave-lengths of bromine in extremely thin layers. A table is given showing the optical density (logarithm of the ratio of the intensity of the incident ray to the intensity of the transmitted ray) for different wave-lengths, of a layer of liquid bromine  $1 \mu$  thick. The maximum optical density, 0.673, is reached at the wave-length  $0.417 \mu$ , which is practically the same wave-length at which Ribaud (A., 1920, ii, 3) found the maximum optical density for bromine vapour. The same mass of bromine in the gaseous form, however, has an optical density less than half the value for the liquid.

M. S. B.

**Absorption of Near Infra-red Radiation by Alums.** S. HIGUCHI (*Sci. Rep. Tohoku Imp. Univ.*, 1924, **12**, 359—363).—The absorption spectrum of various aluminium, chromium, and thallium alums in the infra-red shows two intense bands at  $3.30$ — $3.52 \mu$  and  $3.00$ — $3.10 \mu$ , the characteristic vibration of crystal water thus being different from that of ordinary water in agreement with Schäfer and Schubert (A., 1916, ii, 505).

A. R. P.

**Attempted Identification of Absorption Bands by Quantitative Measurements with Molecular Compounds.** I. G. SCHEIBE, F. MAY, and H. FISCHER (*Ber.*, 1924, **57**, [B], 1330—1336).—The allocation of the bands of a complicated absorption spectrum to separate linkings or groups is generally effected by comparison within homologous series, but, not infrequently, slight chemical alterations cause such profound modifications in the spectra that the method becomes useless. It is proposed, therefore, to utilise for this purpose the more gradual changes occurring in molecular compounds, including solvates. The experimental procedure is described in detail. The application of the method to

mixtures of acetone with chloroform, mesityl oxide, and aniline with nitrobenzene is described. H. W.

### Absorption Spectra of Vanadium, Titanium, and Scandium.

H. GIESELER and W. GROTRIAN (*Z. Physik*, 1924, **25**, 342—366).—The absorption lines for the vapours of vanadium, titanium, and scandium at 2000° are tabulated. For the first two elements, it is concluded that, in the normal state (represented by the orbits  $F_{3/2}$  in the quartet series system, and  $F_2$  in the triplet series system, respectively), the most loosely held electron in the atom circulates in an azimuthal four-quantum orbit. The normal state for scandium is represented as a  $D$ -term in the doublet series system. S. K. T.

### Absorption of Ultra-violet Rays by Carbon Disulphide.

G. BRUHAT and M. PAUTHENIER (*Compt. rend.*, 1924, **179**, 153—155).—With the help of a Fabry-Buisson microphotometer, the extinction coefficient for carbon disulphide has been measured for certain rays of the ultra-violet absorption band between 2500 and 4000 Å. A curve is given showing the variation of  $\kappa$  with  $\lambda$ , a maximum value for  $\kappa$  being reached when  $\lambda$  is approximately 3250 Å. M. S. B.

**Spectrographic Study of Vegetable Alkaloids. Absorption of Ultra-violet Rays by Alkaloids of the isoQuinoline and Morphine Groups.** P. STEINER.—(See i, 1096.)

**Law of Decrease of Fluorescing Power as a Function of Concentration.** F. PERRIN (*Compt. rend.*, 1924, **178**, 1978—1980; cf. J. Perrin, *ibid.*, 1923, **177**, 469).—It has been shown, from theoretical considerations, that, since the fluorescing power,  $\phi$ , of a solution increases to a limiting value  $\phi_0$  as the concentration  $c$  is decreased to zero, the connexion between fluorescing power and concentration is represented by the equation  $\phi = \phi_0 e^{-kc}$ , where  $k$  is a constant. This has been verified experimentally for a number of fluorescing substances. Since the fluorescence observed is proportional to the product of the concentration and the fluorescing power, that is, to  $ce^{-kc}$ , it will reach a maximum at a concentration  $c_m = 1/k$ . This optimum concentration has been calculated for the substances under consideration. M. S. B.

**Luminescence of Solidified Gases and its Application to Cosmical Problems.** L. VEGARD (*Compt. rend.*, 1924, **179**, 151—153).—A continuation of previous work (this vol., ii, 584). Solid nitrogen, after excitation by cathode or positive rays below 35.5° Abs., shows a residual luminescence which may continue for hours. On slowly raising the temperature, the nitrogen undergoes a change of form at 35.5° Abs., and the stored energy is emitted as  $N_1$ ,  $N_2$ , two bands in the red, and two in the violet. Above 35.5° Abs. solid nitrogen shows only a feeble luminescence on excitation. Solid ammonia, nitrous oxide, and oxygen show scarcely any effect. W. E. G.

**Chemiluminescence of the Iodide of Millon's Base.** A. PETRIKALN (*Z. Physik*, 1924, **25**, 292—298).—The iodide of Millon's base decomposes, at about 350°, with a blue luminescence, which

consists of a line spectrum of excited mercury atoms, corresponding with the transitions  $1s-2p_1$ ,  $1s-2p_2$ , and  $1s-2p_3$ , together with a band spectrum of mercurous iodide, having two powerful bands at 4500 and 3440 Å. and a weaker one farther on in the ultra-violet. The line,  $2p_2-2s$ , which was expected, was not found. The observed spectrum is in harmony with the decomposition energy of the compound (70 kg.-cals.).

S. K. T.

**Spectroscopic Study of the Cathodo-luminescence of Fluorite.** F. G. WICK (*Physical Rev.*, 1924, [ii], **24**, 272—282).—The spectra of natural fluorites consist of sharp bands superimposed on broad diffuse bands, the former being intensified and the latter weakened if the specimen is first heated at 600°. Fusion in an oxidising flame causes superficial conversion into oxide, with consequent change of colour and the appearance of many new narrow bands. On comparison of the tabulated results with the cathodo-luminescence spectra, obtained by Urbain, of calcium oxide and fluoride containing rare earth impurities, it is evident that the bands are due chiefly to samarium, dysprosium, europium, gadolinium, and terbium. It is suggested that an atom of the rare earth replaces an atom of the material used as diluent, and forms an integral part of the regular crystal lattice of the latter; the sharpness of the lines is accounted for by the constraint exercised on its vibrations by the neighbouring atoms.

A. A. E.

¶ **Refractivity and the Molecular Phase Hypothesis.** I. E. C. C. BALY and R. A. MORTON (*J. Physical Chem.*, 1924, **28**, 659—667).—The Sellmeyer dispersion formula has been modified by the introduction of the molecular phase hypothesis (Baly, A., 1920, ii, 460). The resulting formula is  $(n-1)(V_1+V_2+V_3+\dots) = V_1N_1/(\nu_1^2-\nu^2) + V_2N_2/(\nu_2^2-\nu^2) + V_3N_3/(\nu_3^2-\nu^2) + \dots$ , where  $V_1$ ,  $V_2$ , and  $V_3$  are the relative volumes of the phases present,  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ , their characteristic frequencies,  $N_1$ ,  $N_2$ , and  $N_3$ , constants characteristic of the phases, and  $n$  the refractive index. Since the phase frequencies are integral multiples of the fundamental frequency of the molecule,  $\nu_1$ ,  $\nu_2$ , etc. may be written  $a\nu_x$ ,  $b\nu_x$ , etc., where  $\nu_x$  is the fundamental frequency. This formula has been shown to give values for the refractive indices in very close agreement with those determined experimentally for chlorine, bromine, and ozone. If correct, it defines the number, nature, and relative volumes of the phases present in a gas, gives more accurate values for the characteristic absorption bands than can be arrived at by direct measurement, and leads to an accurate determination of the energy quantum characteristic of the molecule.

M. S. B.

**Rotatory Dispersion of Tartaric Acid.** T. M. LOWRY and P. C. AUSTIN (*Nature*, 1924, **114**, 430—431).—Polemical with Astbury (this vol., i, 939; A., 1923, i, 178).

A. A. E.

**Rotatory Dispersive Power of Organic Compounds. XI. Molecular Weight of Ethyl Tartrate and the Origin of Anomalous Rotatory Dispersion in Tartaric Acid and its Derivatives.** T. M. LOWRY and J. O. CUTTER.—(See i, 1040.)

**Rotatory Dispersive Power of Organic Compounds. XII. Octyl Alcohol and Octyl Oxalate.** T. M. LOWRY and E. M. RICHARDS.—(See i, 1029.)

**Optical Superposition. V. *d*-sec.-Octyl *i*-Tartrate.** T. S. PATTERSON and C. BUCHANAN.—(See i, 1041).

**Electromagnetic Theory of Optical Activity and MacCullagh's Postulate.** H. CHIPART (*Compt. rend.*, 1924, 178, 1969—1971).—A mathematical paper showing the significance of MacCullagh's postulate with reference to the question of the propagation of an electromagnetic disturbance in a medium of unlimited extent, and the relation of the latter to the study of refraction and reflection.  
M. S. B.

**Polarised Resonance Radiation [of Sodium and Mercury] in Weak Magnetic Fields.** R. W. WOOD and A. ELLETT (*Physical Rev.*, 1924, [ii], 24, 243—254; cf. *ibid.*, 234—242, and *Proc. Roy. Soc.*, 1923, A, 103, 396).—A beam of plane polarised light is focussed on a bulb containing the vapour at low pressure and the polarisation of the resonance radiation determined photographically.  
W. E. G.

**Polarisation of Sodium Resonance Radiation in Magnetic Fields.** E. GAVIOLA and P. PRINGSHEIM (*Z. Physik*, 1924, 25, 367—377).—The  $D_1$  line is unpolarised in a magnetic field.  
W. E. G.

**Ionisation Potential of Positive Ions.** J. FRANCK (*Z. Physik*, 1924, 25, 312—316).—Ionisation on collision between atoms and slow-moving positive ions of the same element can occur if the minimum kinetic energy is equal to one and a half times the work of ionisation. The probability that the process takes place with this minimum kinetic energy is, however, exceedingly small, and a high ion concentration would be necessary to produce any perceptible effect. When collision occurs between a positive ion of one element and an atom of another element, the difference between the energies of ionisation of the colliding atoms can also contribute to the ionisation. An explanation of the "pseudo-vacuum," occurring in very pure specimens of the rare gases, is given, based on the preceding considerations. S. K. T.

**Discharges from Points in Gases, and so-called Dark Discharges.** J. ZELENY (*Physical Rev.*, 1924, [ii], 24, 255—271).—A study of the variation of luminosity with current for air and hydrogen chloride, of the initial stages in discharges from points in air, and of the luminous effects of point discharges in air and helium.  
A. A. E.

**Effect of the Silent Electric Discharge on Gases.** R. H. GEORGE and K. A. OPLINGER (*Proc. Indiana Acad. Sci.*, 1923, 77—84).—A study was made of the sparking potentials in oxygen and nitrogen from fine tungsten points, in the presence and absence of interposed plates.  
CHEMICAL ABSTRACTS.

**Thermoelectrical and Actinoelectrical Properties of Molybdenite.** W. W. COBLENTZ (*U.S. Bureau of Standards*, 1924, 19, (486), 375—418).—The thermoelectric power of different samples of molybdenite measured against copper ranges from about +700 to -1040 microvolts. Light-sensitive spots are shown by certain samples of the mineral, and when exposed to thermal radiation of short wave-lengths, an actinoelectric effect is shown by the development of an *E.M.F.* which has a maximum value for wave-lengths between 0.65 and 0.9  $\mu$ .

The photoelectric effect, manifested by a change in resistance when the molybdenite crystal is subjected to an impressed potential and exposed to light, is produced by radiation of wave-lengths 0.3 to 2  $\mu$ , and may be positive or negative, according to the wave-length of the exciting radiation.

H. M. D.

**Bohr's Atomic Theory and Electrical Conductivity.** O. FEUSSNER (*Z. Physik*, 1924, 25, 215—219; cf. Vegard, A., 1918, ii, 94).—It has been pointed out that the maxima of atomic electrical conductivity appear in those elements in which Bohr's theory of atomic structure postulates the formation of a new outer electron ring containing one electron. Further, the most pronounced maxima are obtained when the next lower principal quantum ring is completed, either by transference from the new ring, as in copper, silver, and gold, or by completion of the old rings before a new one is begun, as in the alkali metals. Certain exceptions are found. In three cases, chromium, molybdenum, and tungsten, the rule appears undoubtedly to be broken, unless a redistribution of the electrons, so as to bring only one in the outer ring, is to be considered possible (cf. Gieseler, this vol., ii, 285).

M. S. B.

**Dielectric Constant of Germanium Tetrachloride.** M. E. LEAR.—(See ii, 690.)

**Hall Effect with Bismuth in Weak Fields.** E. ADINOLFI (*Atti R. Accad. Lincei*, 1924, [v], 33, i, 500—504).—The coefficient of the Hall effect for bismuth varies linearly with the strength of the magnetic field and exponentially with the temperature.

T. H. P.

**Electron Theory of the Hall Effect.** L. PAGE (*Physical Rev.*, 1924, [ii], 24, 283—285).—The constant free path electron theory of the Hall effect leads to a normal (negative) effect, and not to a zero effect (Eldridge, *ibid.*, 1923, 21, 131), so that the theory fails to explain experimental results.

A. A. E.

**Electron Theory of the Hall Effect.** J. A. ELDRIDGE (*Physical Rev.*, 1924, [ii], 24, 286).—Page's criticisms (preceding abstract) are accepted, but they do not affect the fact that a positive or negative effect may be obtained by varying the velocity distribution among the electrons.

A. A. E.

**Atomic Moments.** P. WEISS (*J. Phys. Radium*, 1924, [vi], 5, 129—152).—The validity of the calculation of atomic magnetic moments, (*a*) from the saturation (of magnetisation) values at low



temperatures and (b) from the constants of Curie, is discussed. Gadolinium sulphate is the only substance to which both methods have been applied and the results are concordant. From the values for many metals, paramagnetic gases, and salts both solid and in solution, the figure 1126 is deduced for the fundamental magneton (instead of 1123.5 formerly given). This is nearly equal to the fifth part of the value deduced from Bohr's theory, but the difference is probably outside experimental error, although the quintuple magneton appears to play an important rôle. L. J. H.

**Magnetic Moments of Atoms.** W. GERLACH and A. C. CILLIERS (*Z. Physik*, 1924, 26, 106—109).—Silver, copper, and gold atoms in the normal state have a magnetic moment equal to that of one Bohr magneton; the moment of the thallium atom is smaller, whilst the lead atom is not magnetic in the normal state. These results are in agreement with the quantum theory (cf. Stern, *ibid.*, 1921, 7, 249). The results obtained with bismuth could not be explained theoretically. S. K. T.

**Range of  $\alpha$ -Rays from U I and U II, and the Validity of the Geiger-Nuttall Relation.** B. GUDDEN (*Z. Physik*, 1924, 26, 110—116).—By measurement of the pleochroic halos of fluorspar (cf. Joly, *Phil. Mag.*, 1907, 13, 381) the range in air,  $R$ , of  $\alpha$ -rays from U I and U II is found to be 2.68 and 2.76 cm., respectively, to within 1%. Geiger and Nuttall's linear relation between the disintegration constant,  $\lambda$ , and  $R$ , is consequently only approximately true over a very limited range of  $R$ , and in the region of strong deviation (low values of  $\lambda$ ) a new value of  $\lambda$  for U II is calculated,  $1.8 \times 10^{-16}$  sec.<sup>-1</sup>, which is smaller than that hitherto accepted. S. K. T.

**Quantum Theory of Radioactive Disintegration.** A. SMEKAL (*Z. Physik*, 1924, 25, 265—278).—The quantum mechanism previously proposed (cf. *ibid.*, 1922, 10, 275) is now shown to give a complete explanation, on the principles of Bohr's theory, of all the  $\beta$ -ray spectra definitely known. Rosseland's criticism (cf. *ibid.*, 1923, 14, 173) is unfounded. The relationships between the nuclear levels in radium-B and radium-C (cf. this vol., ii, 138) are explained from the close analogy between the  $\gamma$ - and X-ray spectra. S. K. T.

**Large Quantum  $\gamma$ -Rays and the Photoelectric Origin of the Natural  $\beta$ -Spectrum of Radium.** J. THIBAUD (*Compt. rend.*, 1924, 179, 165—167).—Previous experiments on the  $\beta$ -ray spectrum of radium-C (cf. this vol., ii, 515) have shown it to be probable that the  $\beta$ -rays emitted by radium-C are of photoelectric origin, due to the action of the  $\gamma$ -rays. This conclusion has now been confirmed by examining the secondary  $\beta$ -radiation excited in a number of other metals by the  $\gamma$ -rays of radium. From all these metals,  $\gamma$ -rays cause the emission of electrons from the  $K$  level, and, for the heavier metals, from the  $L$  level, and the energies of these electrons obey the same quantum law as the radiations excited by X-rays. When radium is in contact with

another element, two similar  $\beta$ -ray spectra are obtained, one, the natural  $\beta$ -ray spectrum of the radium, being about four times as intense as the other, which is due to the electrons emitted by the non-radioactive substance. This bears out the opinion that the atom emitting the  $\gamma$ -ray has the best chance of absorbing it with the emission of a  $\beta$ -ray.

There was no indication, on the photographic plates, of a photoelectric effect corresponding with the  $E$  ray of the natural spectrum.  
M. S. B.

**Measurement of Feeble Radioactivity and the Radio-activity of Alkali Metals and Some Other Substances.** G. HOFFMANN (*Z. Physik*, 1924, 25, 177—199; cf. A., 1920, ii, 575; 1922, ii, 184).—Two sensitive methods are described for the determination of a feeble  $\beta\gamma$ -radiation. By the first method disturbances due to an accompanying  $\alpha$ -radiation are avoided by placing the ionisation chamber at a sufficient distance from the radiating substance. The second method may be used when an  $\alpha$ -radiation is absent, or is so slight that the  $\beta\gamma$ -radiation between two impulses can be measured with sufficient accuracy. A feeble  $\alpha$ -radiation may also be measured, or a feeble  $\beta$ -radiation not measurable by the first method. In each case the ionisation chamber is filled with a gas free from emanation, and the ionisation current may be varied by varying the pressure. These methods have been applied to the study of the radioactivity of the alkali metals. The activity of sodium and caesium is found to be negligible. The ratio of the activity of potassium to rubidium by method I is 1 : 4, but by method II, 1 : 7.6. By the first method the ratio of the activity of potassium to the  $\beta\gamma$ -activity of uranium is 1 : 460. Lead which had been undisturbed for 140 years had an  $\alpha$ -activity about equal to that of copper, but ordinary lead has an activity about 10 times as great. Samples of coloured fluorspar were also examined. The activity of a pale-green variety, expressed as radium content, was  $0.27 \times 10^{-12}$  g. per g., whilst that of a dark violet sample was  $2.24 \times 10^{-12}$  g. The latter had a strong odour. The application of the apparatus to the determination of radium by the  $\gamma$ -ray method, and to the study of atmospheric radioactivity, is also described.  
M. S. B.

**Preparation of Line Sources of Radium-C.** G. H. HENDERSON (*Nature*, 1924, 114, 503).—The efficiency of the usual method of preparing an active line source of radium-C is increased fourfold by enclosing a thin cylindrical sheath of iron or nickel in the tube, the sheath being in contact with the mercury which is positive, and the sealed-in platinum wire negative. With 200 volts, an efficiency of over 50% can be obtained.  
A. A. E.

**Internal State of the Earth in Relation to its Radioactivity.** A. P. SOLOW (*J. Phys. Radium*, 1924, [vi], 5, 153—160).—A mathematical paper relating the internal temperature of the earth to hypothetical distributions of radioactive materials. L. J. H.

**Variations in the [Quantity of] Heat Liberated by Radium Bromide.** J. H. LE BEL (*Compt. rend.*, 1924, 179, 160—161).—The temperature of 0.01 g. of radium bromide when placed in a Dewar vessel has been measured over long periods of time. Variations of the order of 3% are found to occur. These are due to causes external to the radium, possibly extra-terrestrial, since a second apparatus, under the same conditions, gave the same minima at the same time.

W. E. G.

**Apparatus for Measuring the Heat Liberated by Radio-active Substances.** M. D. YOVANOVITCH (*Compt. rend.*, 1924, 179, 163—165).

**Photochemical Threshold and Energies of Linking.** A. JOB and G. EMSCHWILLER (*Compt. rend.*, 1924, 179, 168—171).—On the basis of the value previously obtained from photochemical considerations (cf. this vol., i, 929) for the energy of linking of iodine with carbon in ethyl iodide, and the heats of combustion of iodides and hydrocarbons found by other investigators, the authors have shown how the distribution of the energy of combination throughout the molecule can be calculated. This method leads to a value for the heat of combustion of an atom of carbon :  $337 \pm 18$  Cal. On assuming the values for this oxidation, obtained by Wertenstein and Jedrzejewski and by de Forcrand, it is found that the introduction of iodine into the molecule increases the energy of association of two carbon atoms and decreases that between carbon and hydrogen.

M. S. B.

**Relation between Chemical Affinity and the Infra-red Spectra of [Condensed] Compounds.** A. BALANDIN (*Z. Physik*, 1924, 26, 145—160).—Assuming the Kossel molecular model, together with certain simplifying assumptions, the mutual affinity of the atoms in a condensed molecule,  $u$ , is given by  $K - c(\nu_1 - \nu_2)$ , where  $K$  and  $c$  are constants, and  $\nu_1, \nu_2$  are the frequencies of the two residual rays observed for binary compounds. The formula holds for many salts, e.g., certain halides, chlorates, sulphates, carbonates; it also holds for some gaseous carbon compounds, although the assumptions on which it is based are not wholly valid in this case.

S. K. T.

**Localisation and Specific Action of Subsidiary Valencies.** P. PFEIFFER (*Z. anorg. Chem.*, 1924, 137, 275—290).—The formation of all the known additive products of hydrogen chloride, water, ammonia, and unsaturated hydrocarbons may be explained by assuming that these compounds contain localised subsidiary valencies having a certain definite and specific action and that ammonia and the unsaturated hydrocarbons each have one additive centre, and hydrogen chloride and water each two separate and distinct additive centres for all the characteristic reactions of these compounds. The substitution of halogen, hydroxyl, or amino groups for hydrogen in organic compounds confers on these compounds in many cases the power of forming additive molecular compounds, and it is shown that the subsidiary valencies of the substituted

groups play an important part in defining the nature and properties of these compounds. A. R. P.

**Polarity of Valencies.** W. A. NOYES (*Ber.*, 1924, 57, [B], 1233—1242).—A lecture delivered before the German Chemical Society. H. W.

**Colour and Molecular Geometry. II. Explanation of the Results of Chattaway and Clemo.** J. MOIR.—(See i, 1076.)

**Derivation of the Principal Types [of Space Lattice] from the Basic Types,  $\alpha_1$  and  $\beta_1$ .** J. BECKENKAMP (*Z. anorg. Chem.*, 1924, 137, 418—420).—The basic type  $\alpha_1$  has, as the elementary parallelepiped, a rhombohedron built up by superimposing a tetrahedron on each of two opposite faces of an octahedron, and the derived types are formed by the space-centring either of the tetrahedron or of the octahedron. Type  $\alpha_2$  (diamond type) is formed by the interpenetration of two lattices such that one of the tetrahedra of each lattice is space-centred. In type  $\alpha_3$  (calcium fluoride), both tetrahedra of the basic type are space-centred with reference to two different elements; type  $\alpha_4$  (lithium) is formed by the interpenetration of four lattices so that the tetrahedral centres of gravity of two other  $\alpha_1$  lattices coincide with each point of the  $\alpha_4$  lattice, giving it the appearance of a space-centred cubic lattice. Type  $\alpha_1^{OC}$  is formed by the interpenetration of two  $\alpha_1$  lattices so that the points of one lattice lie on the octahedral centres of gravity of the other. The corresponding  $\beta$  types of lattice are formed by displacing the lattice in the direction  $xy$ . There are two types of  $\beta_1$  lattice, the normal or wurtzite type having  $c=\sqrt{2}$  or  $\frac{3}{2}\sqrt{6}$  and the  $\beta_1'$  (zinc type) having a principal axis  $4/3$  that of the normal type. A. R. P.

**Tabulated Data for the Examination of the 230 Space-groups by Homogeneous X-Rays.** W. T. ASTBURY and K. YARDLEY (*Phil. Trans.*, 1924, A, 224, 221—257).—A set of diagrams of each of the 230 space-groups is given showing the distribution of symmetry elements and the relative positions and orientations of the molecules in the unit cell. These are accompanied by tables giving the fundamental Bravais lattice, the number of asymmetric molecules per cell, the abnormal spacings to be expected, and the possible molecular symmetry for each space-group. L. J. H.

**Reflection of Characteristic Bromine X-Radiation by a Crystal of Potassium Bromide.** S. K. ALLISON and W. DUANE (*Proc. Nat. Acad. Sci.*, 1924, 10, 298—302).—X-Rays from a high-voltage tube with a molybdenum target were reflected from the (100) face of a crystal of potassium bromide and the spectrum was examined with an ionisation spectrometer. In the first order spectra, a weak indication was found of the  $K_\alpha$  line of bromine, and in the second order a definite peak for  $K_\alpha$  was obtained, but the bromine  $K_\beta$  and  $K_\gamma$  lines were masked by a strong molybdenum peak. In the third order spectra,  $K_\alpha$  for bromine was obscured by molybdenum lines, but  $K_\beta$  and  $K_\gamma$  were separated and clearly

indicated. The peaks for the characteristic bromine radiations which are found only in the second and third order spectra are superimposed on a scattered radiation of considerable intensity and hence would be difficult to detect by a photographic method (cf. Clarke and Duane, A., 1923, ii, 468, 469; Walter, *Z. Physik*, 1923, 20, 257). S. S.

**Scattered X-Rays.** P. A. ROSS (*Proc. Nat. Acad. Sci.*, 1924, 10, 304—306).—Spectrograms of molybdenum *K*-radiation, scattered at  $90^\circ$  from blocks of paraffin, aluminium, copper, silver, and lead, have been obtained, and all show, in addition to the undeviated molybdenum line, a shifted line, the displacement of which is the same in all the photographs and is of the order required by Compton's quantum theory of scattering (*Physical Rev.*, 1923, 21, 483). The intensity of the shifted line falls off very rapidly with increasing atomic weight of the scattering element. These results show that the phenomenon cannot be ascribed to the tertiary radiations studied by Clarke and Duane (this vol., ii, 368, 369). Rays scattered by paraffin at  $60^\circ$  and  $30^\circ$  show the predicted Compton shift and, in the latter case, the shifted line has moved past the short wave limit for the tertiary rays calculated from the *K* absorption limit for carbon and hence cannot be due to a strongly filtered tertiary radiation. A spectrogram on a larger scale of molybdenum rays scattered by graphite at  $90^\circ$  shows each component shifted to the same extent. S. S.

**Fine Structure of X-Ray Absorption Edges.** K. CHAMBERLAIN (*Nature*, 1924, 114, 500—501).—Experimental evidence is adduced to show that the white line on the long wave-length side of the absorption edge, observed by Coster (this vol., ii, 581) in the case of iodic acid and of potassium permanganate, is due to reduction of the compound by the X-rays; the plates thus show, not only the absorption edge of the original compound, but also that of the reduction product. A. A. E.

**Crystal Structure of Graphite.** O. HASSEL and H. MARK (*Z. Physik*, 1924, 25, 317—337).—The elementary crystal unit of graphite shows hexagonal symmetry and contains eight carbon atoms. The axes are:  $a=2.47$ ,  $b=4.25$ ,  $c=6.79$  Å. The results agree with Hull's determinations (*Physical Rev.*, 1917, 10, 661). S. K. T.

**Relation between Crystal Structure and Constitution of Carbon Compounds of Methane. II. Crystallography of further Simple Substitution Products.** I. E. KNAGGS.—(See i, 1050.)

**Preparation of Single Crystals of Metals.** I. OBREIMOW and L. SCHUBNIKOW (*Z. Physik*, 1924, 25, 31—36).—If a molten metal be kept in a vessel with a capillary exit below, the whole evacuated to remove trapped or occluded gas, and the metal in the capillary cooled until solidification sets in, a single centre of crystallisation is formed. Solidification may then be allowed to extend

throughout the vessel, thus producing a single crystal. The maximum cross-section of the capillary, for the formation of a monocrystalline block, varies with the metal. [Cf. *B.*, 1924, 874.]  
M. S. B.

**Quantum Theory of Monatomic Ideal Gases.** G. SCHAY (*Z. Physik*, 1924, 25, 37—41; cf. this vol., ii, 232).—A theoretical paper in which it is shown by statistical methods that the region of degradation of energy for ideal gases lies below temperatures accessible to measurement, and therefore is practically non-existent. New limiting values for the thermodynamic functions at the absolute zero are given. The mathematical deductions recorded only apply to very dilute gases in which the volume of the atoms is negligible.  
M. S. B.

**Specific Heats of Magnesium, Calcium, Zinc, Aluminium, and Silver at High Temperatures.** E. D. EASTMAN, A. M. WILLIAMS, and T. F. YOUNG.—(See ii, 681.)

**Induced Alternate Polarities in a Carbon Chain on the Basis of Bohr's Theory.** K. HøjENDAHL (*J. Chem. Soc.*, 1924, 125, 1381—1388).—It is assumed that shared electrons pursue looped or figure-of-eight orbits around the nuclei of the two atoms joined by a non-polar valency as suggested by Sidgwick (*Trans. Faraday Soc.*, 1923, 19, 459). When dissimilar atoms are joined the loops of the orbits differ in size, and in order to maintain the same period of revolution for the electron it is necessary that one or both loops become smaller than in the uncombined atom. When chlorine is combined with carbon, the carbon loop of the orbit becomes smaller and the electron is for a shorter period in the neighbourhood of the carbon atom, which may therefore be said to be positive. Considerations of symmetry indicate that this contraction of the orbit in the first carbon atom will produce an enlargement of the loop of the electrons passing around the second carbon atom and forming the covalency. Hence an alternating polarity is produced along the chain. The magnitude of the effect is estimated to be  $+1, -\frac{1}{3}, +\frac{1}{9}, -\frac{1}{27}, +\frac{1}{81}$ , in successive carbon atoms in a saturated chain,  $+1, -\frac{2}{3}, +\frac{1}{3}, -\frac{2}{9}, +\frac{1}{9}$  in a chain of alternate single and double bonds, and, in the benzene ring, ortho,  $-0.565$ , meta,  $+0.408$ , para,  $-0.360$ , the polarity of the substituted carbon atom being taken as unity. A modification of G. N. Lewis' electronic formulæ is suggested which indicates the postulated distribution of electrons.  
S. S.

**Relationship between Melting Points and Boiling Points.**

G. G. LONGINESCU (*Bul. Soc. Romăna Stiin.*, 1923, 26, 51—52).—The relationship between the absolute melting points and boiling points of elements and compounds given by Lorenz and Herz (cf. *A.*, 1922, ii, 739) can be derived from the author's formula,  $T/d\sqrt{n}=k$ , where  $T$ =absolute m. p. or b. p.,  $d$ =density of the solid or liquid,  $n$ =the number of atoms in the molecule, and  $k$ =50 for the solid state and 100 for the liquid state respectively. For the same element or compound, m. p./b. p.=0.50 ( $d$  solid/ $d$

liquid), and as  $d$  solid/ $d$  liquid lies between 1 and 1.2, the ratio m. p./b. p. should lie between 0.50 and 0.60. This agrees with the average values of the ratio as calculated by Lorenz and Herz for organic compounds and elements, i.e., 0.5839 and 0.5583, respectively, but the average for inorganic compounds lies somewhat higher, viz., 0.7183.

L. A. C.

**Vapour Pressure of Liquid Nitrosyl Chloride.** M. TRAUTZ and W. GERWIG.—(See ii, 673.)

**Vapour Pressure of Liquid Chlorine.** M. TRAUTZ and W. GERWIG.—(See ii, 671.)

**Internal Pressure of Solids.** T. W. RICHARDS (*J. Amer. Chem. Soc.*, 1924, **46**, 1419—1436).—The equation of state,  $p + \pi_0(v_0/v)^n = (\pi_p)_0(v_0/v_1)^n + (T \cdot \alpha/\beta)_0$ , in which  $\pi_0$  is the internal cohesive pressure,  $\pi_p$  the internal distending pressure,  $\alpha$  the cubic coefficient of expansion, and  $\beta$  the compressibility, all of which quantities have a definite physical meaning, is correlated with an equation  $(p + \rho)(v - \beta_1) = k_1 + CT$  previously put forward (cf. A., 1923, ii, 233). For simple solids at the absolute zero  $\pi_0 = 1/\beta(n - m)$ . If this is combined with the derived equation  $\pi = R/V_A \alpha$  ( $V_A$  = atomic volume) the value of  $(n - m) = V_A \alpha / R \beta$  can be determined. The exponents  $n$  and  $m$  are probably not constant, but depend to some extent on volume. The internal pressures of solids calculated from the above considerations agree in the case of mercury with the pressure calculated from the heat of evaporation.

H. T.

**Critical Temperature for the Condensation of Metal Vapours.** J. CHARITON and N. SEMINOFF (*Z. Physik*, 1924, **25**, 287—291).—The critical temperatures of condensation of metal vapours on different surfaces depend on the nature of the surface; thus for cadmium on paraffin,  $-67^\circ$  to  $-70^\circ$ , and for cadmium on mica,  $-77^\circ$  to  $-80^\circ$ . The results are in agreement with Langmuir's theories of evaporation of adsorbed films from surfaces.

W. E. G.

**Diffusion in Solid Metals.** W. GEISS and J. A. M. VAN LIEMPT (*Z. Metallk.*, 1924, **16**, 317—318).—When a single crystal made up of successive layers of molybdenum and tungsten is heated at  $2400^\circ$  in hydrogen for 3 hours, practically no diffusion of the two metals takes place. On the other hand, a pressed ingot made from an intimate mixture of very small crystals of the two metals consists almost entirely of solid solution after heating for 15 mins. at  $2400^\circ$ , diffusion of the metals commencing at  $1300^\circ$ . Powdered iron does not diffuse into a sintered and swaged bar of tungsten at  $1400^\circ$ , but diffusion is rapid when a pressed mixture of the two metal powders is heated. Carbon commences to diffuse into a prepared tungsten bar at  $1550^\circ$ , but has no action on a single crystal of tungsten, or on a rod prepared from it, even at  $1900^\circ$ . [Cf. B., 1924, 835.]

A. R. P.

**Electrolytic Conductivity in Fused Metallic Alloys. I. Electrolysis of Antimony-Zinc Alloys.** R. KREMANN, H. ORTNER, and R. MARKL (*Monatsh.*, 1924, **44**, 401—415).—In view

of the work of Moers on the electrical conductivity of lithium hydride (A., 1921, ii, 200), and of Lewis, Adams, and Lanman (A., 1916, ii, 76) on sodium and potassium amalgams, the conductivity of various alloys has been studied, the problem having a bearing on the theory of the metallic state. Experiments with antimony-zinc alloys containing 20—30% of antimony show that the passage of a current through the molten alloy is accompanied by electrolytic action, the antimony moving towards the anode and the zinc towards the cathode. At the ordinary temperature the effect is not observed with the solid alloy. Further experiments at 620° with an alloy containing 53—61% of antimony show that the electrolytic effect increases with the current density, but finally approaches a limit which depends on the temperature and on the composition. The maximal electrolytic effect represents a balance between the effect produced directly by the current and the tendency of the metals to mix again by diffusion. Rise of temperature shortens the time for the attainment of equilibrium, but does not disturb the maximum. Similar effects have been found with sodium and cadmium amalgams.

R. B.

**Electrolytic Conductivity of Fused Metallic Alloys. II. Electrolysis of Lead-Bismuth Alloys.** R. KREMANN and A. BRODAR (*Monatsh.*, 1924, 44, 383—399).—Experiments on the electrical conductivity of the eutectic alloy (42% Pb) afford evidence of electrolysis, the lead moving towards the cathode and the bismuth towards the anode. The electrolysis increases with the current density up to a maximum at about 10 amp. per sq. mm., as was observed with zinc-antimony alloys. The length of the tube has no apparent influence, but the effect is more pronounced with tubes of wide cross-section. It appears to be independent of temperature. The changes in composition produced by the current tend to be neutralised by diffusion. These appear to be equally influenced by temperature up to 440°, but it is probable that, above 1000°, the influence of diffusion will preponderate and no electrolytic effect will be observed.

R. B.

**Condition of Hydrogen Dissolved in Platinum.** K. BENNEWITZ and P. GÜNTHER (*Z. physikal. Chem.*, 1924, 111, 257—268).—Various facts suggest that hydrogen in contact with heated platinum is ionised. The resistance of a platinum wire heated in hydrogen at 750—850° decreases during the absorption of the gas, and increases when the gas is extracted. The change in resistance depends on the temperature and somewhat below 1200° the change is very slight. At higher temperatures, the resistance increases during the absorption of hydrogen; this is accompanied by the formation of larger metal crystals, a loosening of the texture of the metal, and a diminution in contact between the individual crystal surfaces. Hence other investigators working only at these higher temperatures have only observed an increase in the resistance of the metal due to the solution of the hydrogen. It is inferred that the catalytic activity of platinum in hydrogenation reactions is due to the accumulation of hydrogen ions at the surface of the metal



and that the seat of catalytic activity is in the neighbourhood of the surface and not in the metal itself.

J. B. F.

**Thermo-electric Researches on Nickel Alloys.** W. ROHN (*Z. Metallk.*, 1924, 16, 297—300).—The thermo-electric power of nickel alloys with 5 and 10% of various other metals against platinum is recorded graphically, together with results of experiments designed to discover a thermocouple that will give a large *E.M.F.* at 1000°. A couple consisting of 84% Ni–16% Mo and 70% Ni–30% Cu gave a reading of 85 millivolts at 1000°, but could only be used without deterioration up to 800°, whereas a 9.5% Cr–90.5% Ni and 100% Ni couple gave a reading of 50 millivolts at 1000° and withstood that temperature for long periods. [Cf. *B.*, 1924, 835.]

A. R. P.

**Variation with Composition of the Dielectric Constant of Mixtures of Alcohols with Water.** G. G. SALAZAR (*Anal. Fis. Quím.*, 1924, 22, 275—338).—Measurements of the dielectric constants of methyl, ethyl, and propyl alcohols confirm the rule of Tereschin and Schlundt, according to which the dielectric constant increases with molecular weight in homologous series. The values obtained show that water and the alcohols have a high internal ionisation. Mixtures of the alcohols with water do not agree in their dielectric constants with the formulæ of Silberstein, or of Philip and Haynes. The curves showing the connexion between the dielectric constant and the composition of mixtures exhibit singular points corresponding with definite hydrates. All three alcohols appear to form hydrates, with 1, 3, and 6 mols. of water, respectively. Propyl alcohol also forms a hydrate with 16 mols. of water. Between these singular points the curves are strictly linear.

G. W. R.

**Criticism of Distillation Method of Measuring Vapour Pressure.** L. J. HUDLESTON (*J. Chem. Soc.*, 1924, 125, 1558—1559).—It is suggested that, in the experiments of Dunn and Rideal (this vol., ii, 306), in which hydrochloric acid at 25° was distilled into a receiver at 0°, the composition of the distillate was not that of the vapour above the acid on account of the independent diffusion of the components at the low total pressure prevailing. The suggestion may be tested by changing the temperature of the condenser.

L. J. H.

**Indirect Measurement of the Aqueous Vapour Pressure of Capillary Systems by the Freezing-point Depression of Benzene.** E. M. CROWTHER and A. N. PURI (*Proc. Roy. Soc.*, 1924, A, 106, 232—242).—The vapour pressures of soils, as measured by the freezing-point depression of benzene with which the soils are in equilibrium (cf. Sidgwick, T., 1920, 117, 1340), show a systematic deviation from the values obtained by measurement in air or in a vacuum. This can be accounted for by the assumption that part of the water is held in fine capillaries (micropores).

S. K. T.

**Supersaturation of Gases in Water and certain Organic Liquids.** J. METSCHL (*J. Physical Chem.*, 1924, **28**, 417—437).—The solubilities of gases in different solvents have been determined by saturating at pressures up to 5 atm., reducing the pressure, and determining the amount of gas which can then be shaken out. The supersaturated solutions are comparatively stable, no gas escaping until the surface of the liquid is broken. The results for solutions of carbon dioxide in water and in ethyl alcohol are very irregular, but in general the graph obtained by plotting the volume of gas shaken out of a supersaturated solution against the excess pressure at which saturation took place is in agreement with Henry's law.

The following gases and liquids have been examined: oxygen in water, ethyl alcohol, acetone, and carbon tetrachloride; nitrogen in water, aniline, nitrobenzene, ethyl alcohol, and benzene; hydrogen and air in water; carbon dioxide in water and ethyl alcohol.

M. S. B.

**Solubility of Gasoline (Hexane and Heptane) in Water at 25°.** L. H. MILLIGAN (*J. Physical Chem.*, 1924, **28**, 494—497).—The solubility of a sparingly soluble liquid, which has an appreciable vapour pressure, is conveniently determined by measuring the solubility of the substance, in the form of vapour, at a pressure which is less than that of the vapour pressure of the pure liquid at the same temperature. Regarding the vapour as a perfect gas, the amount dissolved when the vapour pressure equals that of the pure liquid may be calculated. The solubility coefficients at 25° for hexane, heptane, and benzene in water are 0.012, 0.017, and 1.5, respectively, and the volumes of these in the liquid form which dissolve in 100 vols. of water at 25°, are approximately 0.0014, 0.0007, and 0.07, respectively.

M. S. B.

**Measurement of Activity by the Partition Method. I.** B. CAVANAGH (*Proc. Roy. Soc.*, 1924, **A**, 106, 243—250).—A knowledge of the partition ratio of a substance between two liquids, and of the activity of the substance in one of the liquids, enables the activity in the other liquid to be calculated. This principle may be used to determine accurately activity coefficients in very dilute solutions, and an experimental method is devised for measuring the partition coefficients in such cases. The activity coefficients of lithium chloride in dilute amyl alcohol solutions at 25° are tabulated.

S. K. T.

**Viscosities of some Univalent Salts of Higher Fatty Acids in Organic Solvents.** M. PRASAD (*J. Physical Chem.*, 1924, **28**, 636—643).—These determinations have been made in order to correct for viscosity the conductivity measurements of Bhatnagar and Prasad (*Kolloid-Z.*, 1923, **33**, 279), because, on plotting equivalent conductivity against dilution, straight lines were obtained. Incidentally, the viscosity measurements have also been employed to test the viscosity formulæ given by different investigators. The corrected values for the conductivities still give straight-line graphs.

**Electrical Conductance of Mixtures of Aniline, Acetic Acid, and Water.** J. R. POUND (*J. Chem. Soc.*, 1924, 125, 1560—1564).—The conductivities at 30° of mixtures of aniline, acetic acid, and water over the whole range of ternary composition were measured. Mixtures having good conductivity are, in general, those showing the greatest contraction and having the greatest viscosity, *i.e.*, those in which complex formation is prominent (cf. this vol., ii, 389), but the mixtures of greatest conductivity contain large proportions of water. Dilute solutions of acetic acid, or of acetic acid and water, in aniline have molecular conductivities which decrease continually with dilution. L. J. H.

**Moving Boundary Method for Determining Transference Numbers.** E. R. SMITH and D. A. MACINNES (*J. Amer. Chem. Soc.*, 1924, 46, 1398—1403).—A simplified form of the moving boundary method (cf. A., 1923, ii, 828) for determining transport numbers has been tested. Owing to heating effects and the change of the transport number with the concentration of the indicator, the method is not considered satisfactory. H. T.

**Ion Migration in Solid Electrolytes.** G. C. SCHMIDT (*Z. Elektrochem.*, 1924, 30, 440—443).—Many metallic salts, especially halides (cf. this vol., ii, 13), emit positive ions at temperatures above 200°. Solids behaving thus are electrolytic conductors; those which emit electrons at higher temperatures (*e.g.*, oxides) conduct metallically. Lead chloride is exceptional in emitting negative ions. It is suggested that solid cadmium iodide, for instance, ionises into  $\text{Cd}^+$  and  $\text{Cd}_{n-1}\text{I}_{2n}^-$ ; solid lead chloride into  $\text{Pb}_n\text{Cl}_{2n-1}^+$  and  $\text{Cl}^-$ . The fact that in electrolytically conducting solids one ion only appears to migrate would be accounted for by the difference in the mobility of such ions. W. A. C.

**State of Equilibrium in Mixed Salt Solutions.** N. SASAKI (*Z. anorg. Chem.*, 1924, 137, 215—220).—A mathematical paper in which expressions are deduced for the concentration of all the ions and ionic groups in a solution containing hydrogen, sodium, and ferric chlorides and sodium bromide. A. R. P.

**Heterogeneous Equilibria. IV. Solubility of Strong Electrolytes.** J. A. V. BUTLER (*J. Physical Chem.*, 1924, 28, 438—448; cf. this vol., ii, 530).—Regarding the process of separation of a solid from solution as the adsorption of positive and negative ions alternately by the undissolved solid, the author has developed an equation,  $\log_{10} P = (U/2.303RT) + K$ , showing the relationship between the ionic solubility product  $P$  and the heat of solution  $U$ , where  $K$  is a constant of which the factors are given. By assuming that  $K$  is independent of temperature  $U$  may be determined from the above equation. Values for  $U$  and  $K$  have been calculated from observations on the effect of added salts, with or without a common ion, on the solubility of certain electrolytes. The general parallelism between the values of  $U$  and the solubility, and also the approximate constancy of  $K$ , appear to confirm the equation. Since only "total ion concentration" has been used in calculating

solubility products the results afford some support for the theory of complete electrolytic dissociation. The relation between the equations given and the conception of activities is indicated.

M. S. B.

**Solubility of Tyrosine in Acid and Alkali.** D. I. HITCHCOCK (*J. Gen. Physiol.*, 1924, 6, 747—757).—The solubility of tyrosine in water and in hydrochloric acid and sodium hydroxide solutions (0.001 to 0.05*M*) has been determined; the  $p_H$  values of the saturated solutions are recorded. The calculated ionisation constants of tyrosine are:  $K_b = 1.57 \times 10^{-12}$ ,  $K_{a_1} = 7.8 \times 10^{-10}$ ,  $K_{a_2} = 8.5 \times 10^{-11}$ , and the changes in solubility with  $p_H$  can be satisfactorily explained in terms of these constants.

D. R. N.

**Solid Phases of Invariable Composition.** T. W. J. TAYLOR (*J. Chem. Soc.*, 1924, 125, 1969).—Polemical against Clendinning and Rivett (T., 1921, 119, 1329; 1922, 121, 801; 1923, 123, 1634).

M. B. D.

**Electrical Resistance of Protein-Water Systems.** M. H. FISCHER (*Kolloid-Z.*, 1924, 35, 138—143).—The electrical resistance of gelatin-water systems shows a sharp increase with falling temperature which is comparable with, but not so pronounced as, that found for soap-water systems (this vol., ii, 312). At a given temperature, the addition of acid or alkali lowers the resistance, but as the temperature falls, the increase in resistance is still observed. The influence of acids and alkalis is not determined merely by the concentration of hydrogen or hydroxyl ions, but is specific. The results indicate that at lower temperatures the low-resistance system of gelatin in water is converted into the system of water in gelatin, which is a poorer conductor.

S. S.

**Physical Chemistry of Globulin. IV. Migration Velocity of Globulin Ions.** M. ADOLF (*Koll.-Chem. Beihefte*, 1924, 19, 363—380).—Measurement of the mobility of negative globulin ions in neutral solution by the method of Landsteiner and Pauli (*Verhandlung. d. Kongresses f. Innere Medizin*, Wien, 1908, XXXV) gives 0.00048 cm./sec. Dilution has little effect on the mobility, but the addition of alkali gives a considerable increase. Experiments with solutions of the phosphate and sulphate give for the positive globulin ion  $U_\infty = 0.00052$  cm./sec. Dilution or the addition of sulphuric acid does not change this value, but the addition of phosphoric or hydrochloric acid causes a marked decrease.

S. S.

**Amphoteric Character of Gelatin and its Bearing on certain Electrochemical Phenomena.** P. K. FROHLICH (*Trans. Amer. Electrochem. Soc.*, 1924, 46, 153—169).—The electrolytic properties of gelatin explain its influence in the electrolysis of inorganic salt solutions. Owing to the presence of both acidic and basic groups, it may behave as an acid or as a base, according as the  $p_H$  value of the solution is above or below 4.7, the  $p_H$  value at the isoelectric point. In acid solution, therefore, it migrates

to the cathode and accumulates there as a film. This offers a certain resistance to the discharge of metallic ions, and thus increases the polarisation. Also, by hindering the diffusion of the liquid, the gelatin keeps down the concentration of metallic ions in the neighbourhood of the cathode, and thus favours the conditions which produce a smooth, even deposit rather than a crystalline one. The experimental results of a number of investigators are discussed in the light of this theory, and the "co-precipitation" theory is critically considered.

M. S. B.

**Dielectric Constant of Vanadium Pentoxide Sol.** R. FÜRTH and O. BLÜH (*Kolloid-Z.*, 1924, **34**, 259—262).—For a wave-length of 70 cm. a vanadium pentoxide sol three years old showed an increase in dielectric constant with increase in concentration, but the converse was found in the case of a freshly-made sol. These results are in general agreement with those of Errera (A., 1922, ii, 694) for much longer wave-lengths. Errera (A., 1923, ii, 225) is wrong, however, in supposing that the dielectric constant increases with the field strength. It is the polarisation which increases.

M. S. B.

**Action of Penetrating Radium Rays on Gels.** A. FERNAU (*Kolloid-Z.*, 1924, **34**, 308—312; cf. Fernau and Pauli, A., 1917, ii, 189).—Variations in electrical conductivity with time have been observed for ceric and ferric hydroxide gels and the corresponding salt solutions, both under the action of penetrating  $\beta$ - and  $\gamma$ -radiations and when left to age naturally. For ceric hydroxide, there is an increase of conductivity in both cases, but it is much greater for the irradiated gel. Similar results, but less pronounced, are obtained for ferric chloride and ferric nitrate gels. An irradiated ceric ammonium nitrate solution decreases in conductivity, although in the absence of radium rays the conductivity remains practically constant. The behaviour of ferric nitrate solution is similar to that of the gel. In order to determine the cause of the behaviour of the cerium salt solution, a similar experiment was carried out with ammonium nitrate solution, but the conductivity with and without radiation was practically the same. The influence of the platinum electrodes was also insufficient to explain the behaviour.

M. S. B.

**Experiments in Diffusions. Periodic Precipitations and Markings.** R. GRANT (*J. Sydney Tech. Coll. Chem. Soc.*, 1924, **1**, 64—83).—Experiments on Liesegang ring formation in gels are described.

E. M. C.

**Diffusion of Potassium Sulphate in Jellies containing Barium Chloride.** C. L. WAGNER and C. HAUFFEN (*Kolloid-Z.*, 1924, **35**, 164—166).—The authors have attempted, without success, to repeat the experiment of Dreaper (*ibid.*, 1914, **14**, 170). In every case the diffusion of potassium sulphate into jellies containing barium chloride led to the precipitation of barium sulphate in a continuous manner, and the disappearance of this precipitate described by Dreaper (and explained by him by assuming the

formation of a soluble double sulphate) was never observed. Since the postulated double salt cannot be prepared by fusing together the anhydrous salts (Grahmann, A., 1913, ii, 586) and the corresponding calcium compound is decomposed by water, it is improbable that such a compound could be formed in aqueous solution even in the presence of gelatin. S. S.

**Behaviour of Silver Chromate in Gelatin and a New Explanation of Liesegang's Rings.** K. C. SEN and N. R. DHAR (*Kolloid-Z.*, 1924, **34**, 270—279).—Contrary to the conclusions of Williams and Mackenzie (T., 1920, **117**, 844), silver chromate in the presence of gelatin diffuses much more slowly than a crystalloid. Since a peptising medium is always necessary for the production of rings, these are apparently due to the periodic coagulation of a peptised colloid. The space between the rings may be either free from the colloid on account of the adsorption of the latter by the precipitate or, if the adsorptive power of the coagulum is not very large, it may simply consist of peptised colloid which has not been precipitated because of its lower concentration. M. S. B.

**Diffusion Processes in Gelatin. II. Liesegang's Phenomenon.** C. A. SCHLEUSSNER (*Kolloid-Z.*, 1924, **34**, 338—341; cf. A., 1923, ii, 59).—The distances from the origin of a succession of Liesegang's rings form a geometrical series; that is, if  $x_n$  be the interval for the  $n$ th ring  $x_n/x_{n-1}=K$ , or  $\log x_n - \log x_{n-1}=k_1$ . It may also be seen that  $n=\log x_n/k_1$ . This has been shown to be true for silver dichromate. By Fick's law,  $k_2=x^2/t$ , where  $t$  is the time of formation of the ring at distance  $x$ , from which it can be shown that  $k_1=(\log k_2 + \log t)/2n$ , and this formula is verified by the results of Köhler's measurements of the time of formation (A., 1916, ii, 554).

The substructure of the gelatin, that is, the distance apart of the rings which fill the space between the visible rings and can only be seen under the microscope, has also been examined. It is found to be governed by the same constant  $k_1$ , so that  $k_1=\log(1+d/x)/z$ , where  $z$  is the number of microscopic rings in the interval  $d$  adjacent to the visible ring at distance  $x$  from the starting point. The constant  $k_1$  is independent of the concentration of the salt present in the gelatin, but increases with diminishing concentration of silver nitrate. M. S. B.

**Oriented Wedge Theory of Emulsions and the Inversion of Emulsions.** W. D. HARKINS and E. B. KEITH (*Science*, 1924, **59**, 463—467).—The evidence in support of the theory that the shape of the molecule of soap is of importance in determining the size of the drop is discussed. The size of the drops depends very much on the nature of the oil which is emulsified, and the diameter of the drops decreases as the metallic atom of the emulsifying oleate soap becomes larger. The addition of oleic acid or the corresponding base (up to 0.1M), or of sodium chloride or potassium iodide, also decreases the size of the drops. The addition of 0.1M

oleic acid inverts a sodium oleate emulsion of heptane to the water-in-oil type. The effect of high-speed mixing in decreasing the size of the drops in emulsions is described, and a more comprehensive theory of emulsions is envisaged. A. A. E.

**Surface Tension and Fine Particles.** E. F. BURTON (*Nature*, 1924, **114**, 502).—The attractive forces between two equal small spheres of matter induce an acceleration which varies inversely as the square of the radius of the particles. This quantity, although not measurable in individual cases, may be regarded as a measure of the effect of surface tension on small particles. A. A. E.

**Capillary Phenomena Appearing at the Surface of Separation of Water and Benzene in Presence of Fatty Acids and Alkalis.** R. DUBRISAY (*Compt. rend.*, 1924, **178**, 1976—1977).—The change in surface tension produced at the surface of separation between water and a benzene solution of a fatty acid by the addition of sodium hydroxide (cf. Donnan, A., 1900, ii, 201) has been examined by a method previously described (this vol., ii, 154) for a series of acids extending from butyric to melissic acid. The effect of the addition of sodium chloride on the activity of the hydroxide has also been determined (cf. Dubrisay and Picard, A., 1923, ii, 741). Both solutions differ little from water in their action on acids of lower molecular weight than capric acid. From lauric to arachidic acid, the sodium hydroxide produces a considerable lowering of surface tension, which is still more pronounced in the presence of sodium chloride. For acids of still higher molecular weight, the behaviour is similar to that of the earlier members of the series. Among other organic acids examined, only abietic acid has been found to exhibit similar behaviour. M. S. B.

**Surface Tension of Oil-in-Water and Water-in-Oil Emulsions. II.** S. S. JOSHI (*Kolloid-Z.*, 1924, **34**, 280—283).—Water-in-oil emulsions prepared by using sodium oleate solutions as emulsifying agent, and olive oil and castor oil, respectively, as dispersion media, have the same surface tension as the oil itself. Determinations of the surface tension of an emulsion may therefore be used to show whether it is of the oil-in-water or water-in-oil type, since, in either case, the observed surface tension will be that of the dispersive medium (cf. Sanyal and Joshi, *J. Physical Chem.*, 1922, **26**, 481). M. S. B.

**Surface Tension of Colloidal Solutions and Dimensions of certain Organic Molecules.** P. L. DU NOÛY (*Phil. Mag.*, 1924, **48**, 264—277).—According to measurements made at intervals of 15 to 30 secs., the surface tension of all colloidal solutions shows an initial fall at the rate of about 1 dyne per minute. This fall increases with dilution and attains a maximum at a certain concentration. For colloids with little influence on the surface tension of water, such as blood-serum and albumin, the fall may reach 20 dynes. Certain solutions, e.g., saponin at high concentrations, do not show any fall, but a slight increase. The surface tension rises when such

solutions are stirred. From the results, it is calculated that the length of a molecule of sodium oleate is  $12.3 \times 10^{-8}$  cm. and its width  $6.8 \times 10^{-8}$  cm. The lengths for serum-albumin and egg-albumin are respectively  $43.3 \times 10^{-8}$  and  $52.8 \times 10^{-8}$ . The presence of one-millionth part of most colloids prevents the crystallisation of sodium chloride solution or other salts in large crystals. At a dilution of  $10^{-4}$ , serum solutions evaporate much more slowly than at any other concentration; this is attributed to the formation of an orientated unimolecular layer at this concentration. The addition of sodium oleate or any active colloid to a more inert colloidal solution, such as pure serum, produces a considerable drop in surface tension, which then rises immediately and after 7 mins. may attain its initial value. J. B. F.

**Adsorption. II. Adsorption and Heterogeneous Distribution.** P. N. PAVLOV (*Kolloid-Z.*, 1924, **35**, 87—88; cf. this vol., ii, 594).—The distribution of a substance between two immiscible solvents is considered for the case in which the molecular condition of the solvents and of the solute depends on the concentration, and it is shown that distribution can be represented by an exponential equation. E. M. C.

**Adsorption. III. Surface Tension of Liquid Mixtures and Adsorption.** P. N. PAVLOV (*Kolloid-Z.*, 1924, **35**, 89—97).—The Gibbs adsorption equation holds only for adsorption from a phase consisting of a single component and its application to adsorption from solutions is unwarranted. The number of moles of each component adsorbed by the surface of a liquid mixture is proportional to the molar fraction of the component in the liquid. A binary mixture of normal liquids satisfies the relation  $\gamma_2 v_2^{2/3}(1-x) + \gamma_1 v_1^{2/3} \cdot x - \gamma v^{2/3} = 0$ , where  $\gamma$ ,  $\gamma_1$ ,  $\gamma_2$  and  $v$ ,  $v_1$ ,  $v_2$  are the surface tensions and specific volumes of the mixture, and the two components, respectively, and  $x$  is the molar fraction. This equation is in agreement with the experimental data for mixtures of carbon tetrachloride and ethyl acetate, carbon tetrachloride and propyl formate, and for benzene and ethyl acetate. The equation does not hold when abnormal liquids such as water and acetic acid are components of the mixtures. The conception of a gradual change at the liquid-vapour interface involves the occurrence of negative adsorption. E. M. C.

**Adsorption. IV. Interfacial Tension between a Liquid Mixture and another Non-gaseous Phase.** P. N. PAVLOV (*Kolloid-Z.*, 1924, **35**, 156—159).—The theory of adsorption at liquid interfaces is discussed and it is shown that  $\gamma_{21}(1-x) + \gamma_{23}x - \gamma = 0$ , where  $\gamma$  is the interfacial tension between an insoluble liquid (2) and a mixture of  $(1-x)$  parts of a liquid (1) with  $x$  parts of a liquid (3);  $\gamma_{21}$  and  $\gamma_{23}$  are the interfacial tensions between the insoluble liquid (2) and pure (1) and (3), respectively. Measurements by a drop-weight method of the interfacial tension between mercury and carbon tetrachloride, ethyl acetate, and a mixture of the latter give values which are in agreement with the above formula. S. S.



**Adsorption. V. Capillary Adsorption.** P. N. PAVLOV (*Kolloid-Z.*, 1924, **35**, 159—162).—A mathematical discussion of adsorption formulæ. S. S.

**Adsorption. VII. Coagulation of Negatively Charged Chromium Hydroxide and the Influence of Ions carrying the same Charge as the Colloid.** K. C. SEN and N. R. DHAR (*Kolloid-Z.*, 1924, **34**, 262—269).—Negatively charged chromium hydroxide sol has been prepared by adding sodium hydroxide to chromium nitrate solution in the presence of arsenious acid, and then dialysing. Coagulation of the sol by positive ions appears to follow the Schulze-Hardy law except in the case of the thorium ion. The influence of various anions in preventing coagulation runs parallel with their coagulating power for the positive chromium hydroxide sol as determined by Weiser (A., 1922, ii, 575). With diminishing concentration of colloid, the concentration of all electrolytes, necessary for coagulation, also diminishes. This is contrary to the observations made by other investigators on the precipitation of arsenic and antimony trisulphide sols by salts of univalent cations. This is explained by the difference in the adsorbing powers of the two types of sol for the anion, which exerts a peptising action, the anion being adsorbed by arsenic trisulphide much more readily than by chromium hydroxide.

M. S. B.

**Adsorption. VIII. Adsorption by Freshly-precipitated Barium Sulphate During and After its Preparation.** S. GHOSH and N. R. DHAR (*Kolloid-Z.*, 1924, **35**, 144—156).—Freshly-precipitated barium sulphate is a poor adsorbent for cupric ions, but readily adsorbs colloidal dyes and other colloids. The amount of adsorption increases with increase in the size of the colloid particles. The protective influence of gum arabic, agar-agar, and starch on the precipitation by barium sulphate of sols of the sulphides of arsenic and antimony is in the ratio 13.5 : 4.85 : 1, which agrees with Zsigmondy's gold numbers for these substances. At the moment of precipitation barium sulphate is a good adsorbent for anions; the precipitate is positively charged and the filtrate is alkaline. Thus 19.1% of the dichromate ion in 20 c.c. of a 0.0333*M* solution is adsorbed in the precipitation of 0.5609 g. of barium sulphate. Quantitative measurements of the adsorption of anions has given the following series:  $\text{Cr}_2\text{O}_7^{--} > \text{S}_2\text{O}_3^{--} > \text{BrO}_3^- > \text{AsO}_3^{--} > \text{C}_2\text{O}_4^{--} > \text{IO}_3^- > \text{IO}_4^- > \text{MnO}_4^- > \text{NO}_2^- > \text{FeCy}_6^{--} > \text{FeCy}_6^{--} > \text{Cl}^- > \text{CNS}^- > \text{Br}^- > \text{I}^-$ . Only small amounts of positive ions are adsorbed. The entrainment of copper, iron, and chromium salts in the precipitate is explained by the strong adsorption of the anion which leads to the precipitation of the metals as hydroxides.

S. S.

**Electrical Nature of Adsorption Forces. I. Adsorption Heats and Dielectric Constants.** W. TARASSOFF (*Physikal. Z.*, 1924, **25**, 369—374).—A theoretical paper in which it is shown

the heat of adsorption should be proportional to  $(\epsilon-1)/\epsilon$ , where  $\epsilon$  is the dielectric constant of the adsorbed gas. The data of Homfray (A., 1910, ii, 771, 1041) and of Titoff (A., 1910, ii, 1041) on adsorption by charcoal are in close agreement with this relation. The data of Gurwitsch (*Kolloid-Z.*, 1923, 32, 13) show that the order of the heats of adsorption when different liquids are adsorbed by a given solid is approximately the same as that of the dielectric constants.

S. S.

**Adsorption as a Preliminary Stage in Chemical Combination Investigated by Adsorption Measurements on Zirconium Oxide Gel. II.** E. WEDEKIND and H. WILKE (*Kolloid-Z.*, 1924, 34, 283—289).—The amounts of phosphoric acid which can be removed by washing, from zirconium oxide gel which has been left in contact with phosphoric acid solutions of varying concentration for different lengths of time, indicate that adsorption takes place first, and is then followed by salt formation. Since arsenic acid behaves similarly (cf. this vol., ii, 238), although salt formation in the latter case follows adsorption less rapidly, it was thought that this behaviour might be a function of the chemical affinity of the acid. To test this, similar experiments have been carried out with monochloroacetic acid, but with this acid adsorption only occurs, the process being reversible and the desorption curve normal. Zirconium monochloroacetate may be prepared by precipitation of zirconium oxychloride solution by sodium monochloroacetate. The resulting compound behaves differently from the adsorption product obtained above.

M. S. B.

**Adsorption by Activated Sugar Charcoal. III. Mechanism of Adsorption.** F. E. BARTELL and E. MILLER (*J. Physical Chem.*, 1924, 28, 992—1000).—Langmuir's theory is developed to account for the authors' results on adsorption by charcoal (cf. A., 1922, ii, 741; 1923, ii, 464). In water, hydrogen and hydroxyl ions are adsorbed in equivalent quantities, but neutral water molecules are adsorbed to a much greater extent. Adsorption from solution consists of the displacement of these ions and thus depends on the relative attraction of carbon for the ions and on the ease with which the solute dissociates. Hydroxyl ions are displaced by almost any anion, most readily by organic anions; the order of the anions differs markedly from the Hofmeister series. Hydrogen ions are only displaced by more noble cations, except in a few cases where chemical interaction occurs. The origin of the electrical double layer is discussed in terms of this hypothesis. The influence of chemical constitution on the adsorption of anions is explained in terms of the orientation of the surface molecules.

S. S.

**Adsorption from Salt Solutions by Colloidal Copper Ferrocyanide.** M. FRANKERT and J. A. WILKINSON (*J. Physical Chem.*, 1924, 28, 651—658).—The nature of the adsorption process has been studied with colloidal copper ferrocyanide as adsorbent suspended in solutions of a large number of electrolytes of different types. The solutions were afterwards examined for acidity or alkal-

inity, and for the amount of copper dissolved. Copper ferrocyanide is negatively charged in aqueous solution, probably due to adsorption of the  $\text{OH}'$  ion. On the addition of potassium chloride, both ions are adsorbed, but the adsorbed  $\text{K}'$  ion is sufficient to neutralise both the  $\text{Cl}'$  and  $\text{OH}'$  ions, since the ferrocyanide is precipitated. As a result of this preferential adsorption a certain amount of acid is thus formed in solution. The order of adsorption of anions as shown by the acidity developed is  $\text{Cl}' < \text{NO}_3' < \text{SO}_4'' < \text{Fe}(\text{CN})_6''' < \text{OH}'$  and  $\text{CH}_3\text{COO}' < \text{HPO}_4'' < \text{Fe}(\text{CN})_6''''$ . The  $\text{Fe}(\text{CN})_6''''$  ion is more freely adsorbed than the  $\text{K}'$  ion and since  $\text{H}'$  ions are adsorbed to counterbalance the difference, the solution becomes alkaline. Potassium ferricyanide is interesting in that, at low concentrations, the solution becomes alkaline, owing to the greater adsorption of the anion. At high concentrations, however, it becomes acid because of the greater adsorption of  $\text{K}'$  ions.

The solutions which develop most acidity show least dissolved copper, with the exception of the acetate. At low concentrations hydrochloric acid is completely adsorbed and gives no copper; as the concentration of the acid increases, the amount of copper increases, but is never equivalent to the amount of acid adsorbed; from this it appears that adsorption precedes chemical action. Aluminium salts all develop alkalinity, but there is no definite relationship between the quantities of copper dissolved and the alkalinity developed. The results obtained can be explained more readily by the selective adsorption theory outlined above than by the theory of base exchange.

M. S. B.

**Adsorption Experiments with very dilute Copper and Lead Solutions and their Significance in the Study of Mineral Deposits.** C. W. CORRENS (*Kolloid-Z.*, 1924, **34**, 341—349).—Experiments have been made to determine the amount of copper sulphate and lead nitrate taken up by sand, kaolin, and chalk from dilute solutions, and the nature of this process. The copper in solution was determined by its catalytic effect on the reaction between potassium persulphate and potassium iodide, in weak acid solution, in presence of an iron salt (cf. Freundlich and Schucht, A., 1914, ii, 39), and the lead colorimetrically as the sulphide. Only in the case of copper sulphate and sand is a true adsorption curve obtained, probably on account of the ferric hydroxide present in the sand. With kaolin and copper sulphate, a maximum is obtained, and it is probable that both adsorption and, ultimately, chemical reaction take place. With chalk, chemical decomposition occurs with both lead and copper salts. The adsorption of lead nitrate by sand and kaolin is less than that of copper, and the curves are difficult to interpret. Copper and lead sulphide sols do not appear to be adsorbed. These experiments seem to show that, although during sedimentation rocks may adsorb small quantities of copper and lead (up to 0.8 and 0.25%, respectively), deposits containing larger quantities cannot be formed in this way.

M. S. B.

**Adsorption of Polonium by Colloids.** J. H. BRENNEN (*Compt. rend.*, 1924, **179**, 161—163).—Different colloids, namely,

silver, ferric hydroxide, silica, and aluminium hydroxide, have been precipitated by electrolytes in the presence of polonium, and the amount of adsorbed polonium determined, after the separation of the precipitated colloid from solution by filtration. The fraction of polonium removed from the solution increases with the time the polonium is left in contact with the colloid before precipitation, reaching a maximum, which varies for different colloids, after 20 to 30 minutes. If, on the other hand, precipitation is made to take place immediately after bringing together the polonium and colloidal solutions, the same maximum is reached when the precipitated colloid remains in contact with the solution, and also when the colloid is first precipitated and the polonium then added. It is suggested that the results are due to the combined effect of adsorption of polonium at the surface of the colloidal particles and its diffusion into the interior, whilst the particles are gradually increasing in size as the result of the coagulating action of the electrolytes. M. S. B.

**Absorption of Potassium Hydroxide by Humic Acid.**

A. CHARRIQU (Compt. rend., 1924, 179, 206—209).—When humic acid adsorbs potassium hydroxide from solution, a portion of the base becomes insoluble and cannot be removed by washing. Since, however, the amount thus fixed decreases exponentially with the concentration of the solution, the phenomenon is one of adsorption and not of compound-formation. Similar adsorption, but to a somewhat less extent, occurs in solutions of potassium carbonate, and still less in the hydrogen carbonate. In potassium chloride solutions, the fixation of potassium is very much reduced, the hydrochloric acid set free checking further adsorption. In a solution containing potassium and calcium hydrogen carbonates in equivalent concentrations, the calcium is preferentially adsorbed. Further, when humic acid containing adsorbed potassium is washed with a solution of calcium hydrogen carbonate, the potassium passes into solution and calcium is fixed in its place. These results are to be expected on account of the higher valency of calcium (cf. A., 1923, ii, 540). The fact that transference of potassium may take place in soils, in the presence of calcium carbonate, is thus explained. Similarly, potassium may be removed from the humic acid by washing with solutions of salts of barium, magnesium, or iron. M. S. B.

**Adsorption of Polonium by Silver Chloride.** J. ESCHER-DESRIVIÈRES (Compt. rend., 1924, 179, 158—160).—In the preparation of polonium, the latter is deposited on a silver plate, which is then dissolved in nitric acid and precipitated as silver chloride by hydrochloric acid, the polonium remaining in solution. If the precipitate is fairly large, for example, 100 mg. in 3 c.c., and the solution only contains a small excess of hydrochloric acid, the polonium is adsorbed to a considerable extent by the precipitate, even in the presence of a large excess of nitric acid. The retention of the polonium in solution appears to be connected, not

with the concentration of hydrogen ions, but with the concentration and nature of the cations, because, provided the solution is at the same time acid, chlorides of the alkali metals, and also ferric chloride, are effective in preventing adsorption, but not, however, the chlorides of divalent metals. A careful study has been made of the action of hydrochloric acid in excess, with or without sodium or potassium chloride. If  $N = n_1 + (n_2 \cdot M_2/M_1)$ , where  $n_1$  and  $n_2$  are the numbers of c.c. of  $N/10$  hydrochloric acid and salt, respectively, and  $M_1$  and  $M_2$  the molecular weights, it is found that a straight line is obtained when values of  $N$  are plotted against  $\log X$ , where  $X$  is the ratio of dissolved to precipitated polonium.

M. S. B.

**Wetting of Barium Sulphate.** V. LENHER and H. G. TAYLOR (*J. Physical Chem.*, 1924, **28**, 962—964).—When shaken with a mixture of selenium oxychloride and heptane, barium sulphate passes into the oxychloride layer; with a mixture of selenium oxychloride and 70% sulphuric acid, it goes into the acid layer, whilst with heptane and water it remains at the interface and emulsions are readily formed. Hence barium sulphate is wetted more easily by selenium oxychloride than by heptane, and still more easily by 70% sulphuric acid. Selenium oxychloride has no action on barium sulphate, and the gelatinous product obtained when barium sulphate is precipitated in this solvent can therefore contain nothing but adsorbed oxychloride.

S. S.

**Retention of Organic Dyes by Silicic Acid.** E. BERL and W. PFANMÜLLER (*Kolloid-Z.*, 1924, **35**, 166—169).—Finely powdered quartz adsorbs basic dyes; the reaction is reversible and the colour can be removed by washing. With ignited quartz powder and with commercial specimens of precipitated silica irreversible adsorption occurs.

S. S.

**Adsorption. VI. New Interpretation of the Schulze-Hardy Law and the Importance of Adsorption in the Charge Reversal of Colloids.** N. R. DHAR, K. C. SEN, and S. GHOSH (*J. Physical Chem.*, 1924, **28**, 457—474; cf. Ganguly and Dhar, A., 1922, ii, 829; 1923, ii, 58; Dhar and Sen, A., 1923, ii, 391; Chatterji and Dhar, A., 1923, ii, 615).—A review of the literature on coagulation and adsorption affords evidence of two distinct stages in the adsorption process. To the first stage, the electrical neutralisation of the charge on the colloidal particle by adsorption of an ion of opposite charge, the Schulze-Hardy law is applicable. Apparent deviations from this law are due to the second stage, namely, the further adsorption of electrolyte or separate ions by the coagulum. Minimum concentration of electrolyte for coagulation, charge reversal, and the dependence of the latter on the chemical affinity between the adsorbent and the substance adsorbed, are also discussed. Soil acidity is explained as probably due to the adsorption of the basic portion from salts by colloidal silica, humic acid, etc. present in the soil.

M. S. B.

**Behaviour of Silver Halides towards Acid and Basic Dyes.** O. HASSEL (*Kolloid-Z.*, 1924, **34**, 304—307; cf. Fajans and Hassel, this vol., ii, 60).—An examination of the sensitiveness to light has been made of the three silver salts which are obtained by the addition of eosin to solutions in which silver bromide is precipitated with (1) excess silver nitrate, (2) excess potassium bromide, (3) exactly equivalent quantities of silver nitrate and potassium bromide. The first is sensitive to red light, but not the second and third. The third is sensitive to green light but the second only slightly so.

The behaviour of basic dyes, such as *isoquinoline*-red and rhodamine-6G, towards silver nitrate and excess of potassium bromide solutions, is similar to that of fluorescein and its derivatives towards these two solutions, when silver nitrate is in excess. In both cases, the colour is intensified because of adsorption at the surface of the silver halide sol, and this colour is removed by the addition of an excess of potassium bromide or silver nitrate, according to whether acid or basic dyes are in question. M. S. B.

**Cataphoresis of Mastic Sol.** L. MICHAELIS and A. DOMBOVICEANU (*Kolloid-Z.*, 1924, **34**, 322—327).—The negatively charged micellar ion of a mastic sol is surrounded by a movable layer of oppositely charged ions attracted from the dispersion medium, thus forming an electrical double layer. In order to study the relation between the rate of cataphoresis and variations in the electrical properties of the double layer, it is desirable that the cations should be all of one kind. This has been effected by using the hydrogen ion as the adsorbed cation. Since a hydrogen-ion concentration above  $10^{-3}$  to  $10^{-4}$  *N* coagulates the sol, buffer solutions, consisting of sodium acetate and acetic acid were used, so as to bring the electrical conductivity of the non-colloid side liquids in the cataphoresis apparatus up to that of the mastic sol, and so prevent irregularities in the field strength, and coagulation. The sodium ion is not much adsorbed, especially in presence of the hydrogen ion. Experiments were also made at  $p_H$  values higher than 7 by replacing acetic acid by sodium hydroxide. The potential difference of the double layer may be calculated from the rate of movement of the colloid under a given field strength. This potential difference increases with diminishing hydrogen-ion concentration, but not by any means to the same degree as for a hydrogen electrode. The difference of potential associated with electrokinetic phenomena in a colloidal solution is not, therefore, to be compared with the difference of potential which is set up at one pole of a galvanic chain, and to which Nernst's thermodynamic formula is applicable. M. S. B.

**Reversal of the Hofmeister Ion Series in the Swelling of Powdered Colloid Mixtures.** K. VON NEERGAARD (*Kolloid-Z.*, 1924, **35**, 111—120).—The swelling velocity of powdered mixtures of hydrophilic colloids in the presence of glycerol shows a reversal of the Hofmeister series when the salts are added to the powdered colloid instead of to the dispersive medium. The swelling

increases in the order: potassium iodide, silver nitrate, sodium sulphate, sodium citrate. Cations have relatively little effect on the rate of swelling. E. M. C.

**Dependence of Reciprocal Precipitation of Gelatin and Colloidal Chromic Oxide Hydrosols on the Equivalent Aggregation of the Chromic Oxide Micelle. Contribution to the Theory of Chrome Tanning.** R. WINTGEN and H. LÖWENTHAL (*Kolloid-Z.*, 1924, **34**, 289—295; cf. A., 1923, ii, 78; this vol., ii, 156, 534, 535).—At the point of maximum precipitation, in the mixing of chromium oxide and gelatin sols, the number of equivalent aggregates of chromium oxide for a given quantity of gelatin is always the same for the same kind of gelatin, no matter what the degree of dispersion of the chromium oxide sol. A value of about 30,000 is thus found for the molecular or equivalent aggregate weight of gelatin, which is in agreement with values found by osmotic measurements (cf. Biltz, A., 1917, ii, 17). Temperature rise, or the addition of dilute acid or alkali, appears to cause a disintegration of these large aggregates. In technical chrome tanning liquors, ultrafiltration shows the presence of both colloidal and crystalloidal components. By experiments with chromic oxide sols on gelatin leaves, and on solidified gelatin solutions, it has been shown that a high degree of dispersity of the chrome sol is necessary for satisfactory tanning. M. S. B.

**Precipitation of Colloidal Gold by Colloidal Chromic Oxide.** R. WINTGEN and H. LÖWENTHAL (*Kolloid-Z.*, 1924, **34**, 296).—By means of an immersion ultramicroscope, observations have been made on the movements of the particles during coagulation, when a gold sol and chromic oxide sol are mixed together. M. S. B.

**Pyrrole-red Sols.** H. FREUNDLICH and F. ISHIWARA (*Kolloid-Z.*, 1924, **34**, 257—259).—Pyrrole-red sols may be obtained by warming a small quantity of pyrrole with dilute acid and then dialysing. Brown solutions with a green tint are obtained and their behaviour on cataphoresis and coagulation shows that the particles carry a positive charge. Hydrophilic sols, such as gelatin and saponin, have a strong protective action on the pyrrole-red sols. They are sensitised by serum-albumin at low concentrations, but if large concentrations are used the sol is partly precipitated by small quantities of electrolyte, whilst larger quantities of the latter exert a peptising action. M. S. B.

**Physico-chemical Properties of Plant Nutrient Solutions.** S. PRÁT (*Kolloid-Z.*, 1924, **35**, 97—105).—In the coagulation of Congo-red hydrosols the addition of a second cation affords no evidence of increased flocculating power or of ionic antagonism; the action of the cations is additive. Many nutrient solutions cause rapid flocculation of Congo-red and Nile-blue hydrosols and also of plant saps and extracts. E. M. C.

**Protective Colloids. XIII. Semen ceratoniae siliquæ as a Protective Colloid. II. Colloidal Selenium.** A. GUTBIER (*Kolloid-Z.*, 1924, **34**, 336—338).—A dialysed extract of carob

beans, made with chloroform as a stabiliser (cf. A., 1923, ii, 619), is saturated with selenium oxide, which may then be slowly reduced by hydrazine hydrate at temperatures up to  $40^{\circ}$ , but low temperatures are best. The colour of the resulting colloidal selenium solution may vary from yellow to dark red, according to the degree of reduction or the concentration. It is advisable to leave a little selenious acid in solution rather than to have an excess of hydrazine hydrate. The solution is dialysed, and any precipitate formed in the dialysis removed by filtration. The optimum concentration of the protective agent is 0.2 to 0.3% and the corresponding concentration of selenium 0.05 to 0.07%, giving a bright red solution. This does not compare favourably with the stability acquired using *Semen psylli* as protective colloid (cf. A., 1923, ii, 393), and is too low a concentration for medical purposes. Many such bright red preparations begin to precipitate after 10 days. Light has no influence on coagulation. Electrolytes coagulate the solution rapidly. Sodium hydroxide, which, in concentrations 0.02 to 0.04*M* acts as a retarder, is an exception to this rule. Under the action of an electric current, the colloid collects at the anode and coagulates. Colloidal selenium may be obtained in the solid state by slow evaporation in a vacuum, and again brought into colloidal solution by treatment with luke-warm water, but the resulting product is not very stable. M. S. B.

**General Colloid Chemistry. XII. Constitution and Stability of Iron Oxide Sols. III.** W. PAULI and F. ROGAN (*Kolloid-Z.*, 1924, 35, 131—138).—When ferric hydroxide sols obtained by dialysis of ferric chloride are precipitated by potassium chromate or sodium oxalate, the number of equivalents of precipitating anion carried down by the coagulum is always greater than the number of equivalents of chlorine ion liberated from the sol. With potassium sulphate exact equivalence is found. The anomaly becomes smaller with increasing dilution, and is ascribed to the replacement of  $\text{Cl}'$  by  $\text{KCrO}_4'$  or  $\text{Na}_2\text{C}_2\text{O}_4'$  in the stronger solutions. The liberated chlorine is always less than the total chlorine in the sol, which is given the general formula  $[x\text{Fe}(\text{OH})_3, y\text{FeOCl}, \text{FeO} \cdot ]\text{Cl}'$ . By prolonged dialysis,  $x$  is increased and the sol becomes less stable. During the precipitation all the ionised chlorine is replaced, but only part of the chlorine in the oxychloride, since a portion of the latter is situated so deeply within the particle that it cannot come into contact with the precipitating anion. In accordance with this view, it is found that as  $x$  increases from 35 to 60.5 the percentage of total chlorine replaced diminishes from 84.1 to 72.8. S. S.

**Physico-chemical Hypothesis on "Ageing."** A. DE G. ROCASOLANO (*Koll.-Chem. Beihefte*, 1924, 19, 441—476).—The author reviews the hypotheses advanced to account for senescence and cell-decay, and suggests that these deal in general with effects rather than causes. Attention is directed to a correlation of cell-vitality with the movement of colloidal particles within the cells. The catalytic activity of metallic sols in the decomposition of



hydrogen peroxide is shown to exhibit considerable random fluctuations and a slow decay as the sol "ages." It is possible that the "ageing" of an organism arises from the reduced efficiency of its catalysts owing to their dehydration and coagulation.

E. M. C.

**Ageing Phenomena in Vanadium Pentoxide Sols.** H. GESSNER (*Koll.-Chem. Beihefte*, 1924, **19**, 213—297).—Vanadium pentoxide sols, prepared by the method of Biltz from hydrochloric acid and ammonium vanadate, always contain ammonia and chlorine. All the chlorine is ionised and passes through an ultra-filter, which retains part of the ammonia and vanadic acid; in the non-filtrable portion, the ratio  $\text{NH}_4 : \text{V}_2\text{O}_5$  is nearly constant and equal to 1:3. The constitution  $[\text{V}_2\text{O}_5, \frac{1}{3}\text{NH}_4, \text{H}_2\text{O}] \begin{smallmatrix} \text{VO}_3\text{H}^+ \\ \text{VO}_3\text{NH}_4 \end{smallmatrix}$  is therefore assigned to the sol. The concentration of molecularly dispersed vanadium pentoxide is always less than the solubility of crystalline vanadic acid and furthermore decreases with increasing age of the sol; at the same time, changes occur in the viscosity and conductivity. An equilibrium value is finally attained, and in a series of sols the equilibrium concentration of molecularly dispersed vanadium pentoxide decreases rapidly with increasing concentration of colloid. These phenomena are ascribed to the growth of rod-like particles in the original sol, which contains an unstable form of condensed vanadic acid in particles of irregular size. The larger particles adsorb dissolved vanadic acid and build it into their crystal structure, thus growing at the expense of the smaller particles. The coagulation experiments show that ageing increases the sensitivity of a sol towards electrolytes. Sols prepared by Muller's method of pouring fused vanadium pentoxide into water have the constitution  $[\text{V}_2\text{O}_5, \text{H}_2\text{O}]\text{VO}_3\text{H}^+$ ; they behave in a very similar manner to the Biltz sols.

S. S.

**Kinetics of Gelatinisation and its General Significance.** R. REIGER (*Koll.-Chem. Beihefte*, 1924, **19**, 381—440).—The changes in the optical rotatory power of gelatin solutions have been followed when the solutions are rapidly cooled from 45° to lower temperatures. The change in rotation increases with the degree of cooling, and the rotation-time curves show differences of shape which are most marked for cooling temperatures between 15° and 30°. The curves show no essential difference in type over a wide range of concentration and no disturbance is found corresponding with the change from liquid to solid. Many curves show evidence of discontinuities, and can be divided into three distinct portions. It is suggested that a succession of unimolecular reactions is involved in the change of rotatory power. Solutions which have been cooled and then warmed show distinct differences in behaviour according to the duration of the cooling. Viscosity-time curves for cooled gelatin solutions are sigmoid in type, and afford evidence for the superposition of two or more distinct unimolecular changes. Elasticity measurements extending over several days indicate three further changes, so that six distinct stages

appear to be involved in the gelatinisation process. The evidence for the existence of similar discontinuities in other colloidal systems is discussed.

E. M. C.

**Influence of Emulsoids on the Rate of Solution of Iron.** J. N. FRIEND, D. W. HAMMOND, and G. W. TROBRIDGE (*Trans. Amer. Electrochem. Soc.*, 1924, **46**, 197—208; cf. Friend, T., 1921, **119**, 932; Friend and Dennett, T., 1922, **121**, 41; Friend, A., 1922, ii, 267; Friend and Vallance, T., 1922, **121**, 466).—The protective action of various colloids on the corrosion of iron by lead acetate, copper sulphate, and sulphuric acid has been examined. The relation between the retarding effect of agar and its concentration indicates that the effect is due to the adsorption of the emulsoid at the surface of the metal. With rise in temperature from 1° there is at first an increase in the retarding effect, and then a decrease. Rapid revolution of the metal in the solution apparently prevents the formation of an adsorbed protective layer of colloid. The colloids in food probably exercise a protective effect on iron cooking utensils. [Cf. B., 1924, 946.] M. S. B.

**Electrolytic Potential of Calcium.** M. TAMELE (*J. Physical Chem.*, 1924, **28**, 502—505).—The normal potential of calcium has been determined indirectly by measuring the potential of a dilute calcium amalgam in calcium chloride solution against a calomel electrode, and also the potential of pure calcium against the same amalgam in a solution of calcium iodide in pyridine or diethylamine. The calcium becomes passive in this solution and so must be scraped with an automatic glass scraper throughout the experiment. The value found for  $E$  is  $-2.758 \pm 0.004$  volts. Calculation by means of Nernst's heat theorem, taking the heat of oxidation of calcium as 145,000 cals., gives the value  $-2.77$  volts. M. S. B.

**Effect of Hydrogen Pressure on the Electromotive Force of a Hydrogen-Calomel Cell.** II. Fugacity of Hydrogen and Hydrogen Ion at Pressures to 1000 Atmospheres. W. R. HAINSWORTH, H. J. ROWLEY, and D. A. MACINNES (*J. Amer. Chem. Soc.*, 1924, **46**, 1437—1443).—Measurements of the  $E.M.F.$  of the cell  $H_2|0.1N HCl HgCl|Hg$  have been extended to 1000 atm. (cf. A., 1922, ii, 467). The empirical equation given in the previous paper is modified to  $\Delta E = 0.02958 \log R + 6.12 \times 10^{-6}(p-1) + 6.6 \times 10^{-10}(p^2-1)$ . At the highest pressure, the fugacity is 100% greater than that calculated on the assumption of proportionality between fugacity and pressure. Approximately 75% of this deviation is due to the departure of hydrogen from the perfect gas laws and the remainder to the decrease in the activity of the hydrogen ion consequent on solubility of the hydrogen. H. T.

**Temperature Coefficient of the Quinhydrone Electrode.** E. BILLMANN and I. KRARUP (*J. Chem. Soc.*, 1924, **125**, 1954—1956).—The potential of the quinhydrone electrode has been measured at 18° and 25° (A., 1922, ii, 111; this vol., ii, 596; and T., 1923, **123**, 2203). By determining the value for similar cells at 0° and 37°, the potential-temperature curve of the quinhydrone

electrode is shown to be a straight line represented by the equation  $\pi_t = 0.7175 - 0.00074t$ , where  $\pi_t$  is the potential of the electrode at  $t^\circ$ .

M. B. D.

**Passivity.** W. J. MÜLLER (*Z. Elektrochem.*, 1924, **30**, 401—416).—The behaviour of a horizontal iron anode, guarded against convection currents, in *N*-sulphuric acid saturated with ferrous sulphate has been studied in detail. A visible film of insoluble salt is formed on the anode and the resistance rises, at first slowly, then very rapidly, to a maximum. After a definite time  $t$ , a critical current density is attained at which the electrode becomes passive. The *P.D.* does not exceed 0.68 volt, being much less than that required for evolution of oxygen. The mean current intensity employed for passivation is directly proportional to  $\log t$ . On short-circuiting the cell, the anode loses its coating and becomes bright, but retains its passivity for some time after. Passivation is attributed to shifting of the equilibrium between metals, ions, and electrons within the surface layer of the anode in the direction of ions of higher valency, and is brought about by high current density. A non-conducting film is essential to the formation of passive surfaces but not to their preservation. In hydrochloric acid saturated with ferrous chloride there is evidence of similar phenomena, but when a sufficient voltage is applied the resistance suddenly breaks down and iron goes into solution as ferric ion. In dilute nitric acid, a film of oxide is formed, but the time  $t$  is much the same as in dilute sulphuric acid. To explain passivation without the use of the current, it is supposed that both activating and passivating local currents set in at the metal surface, but that in presence of strong cathodic polarisers (oxidising solutions) the former are suppressed and the latter enabled to render the whole surface passive.

W. A. C.

**Influence of Temperature on the Galvanic Polarisation of Nickel.** S. TRIANDAFIL (*Compt. rend.*, 1924, **178**, 1973—1975).—The commutator method has been employed to determine the polarisation at a nickel electrode in *N*-solutions of nickel chloride and nickel sulphate, for different current densities and temperatures. The curves obtained by plotting maximum polarisation against temperature for the two salts between  $0^\circ$  and  $100^\circ$  are practically parallel, the maximum polarisation in the sulphate solution being approximately 1.38 volt higher than that in the chloride throughout the whole temperature range. M. S. B.

**Slight Variations in the Heat Given Out by Different Samples of Radium Bromide.** J. H. LE BEL (*Compt. rend.*, 1924, **179**, 160—161).—A centigram of radium bromide was put into a Dewar vessel packed in down, and left in a cellar at constant temperature. The difference in temperature between the radium and its surroundings was measured by a thermo-couple. After equilibrium had been established, the galvanometer deviation remained constant, except once or twice each month when it definitely diminished, and then rose again to the original value. In a second

simultaneous experiment under the same conditions, the same minima were observed at exactly the same time. The desirability of carrying out the same experiment at widely separated places on the earth's surface is suggested. M. S. B.

**Oxidation Potentials of Ferrous and Ferric Salts in Concentrated Hydrochloric Acid and Phosphoric Acid.** S. R. CARTER and F. H. CLEWS (*J. Chem. Soc.*, 1924, 125, 1880—1888).—Measurements were made of the oxidation potentials of various mixtures of ferric and ferrous salts at 17° under various conditions to ascertain why sulphur dioxide behaves as a reducing agent in dilute acid solution and as an oxidising agent in strongly acid solutions (cf. T., 1920, 117, 1093, 1241). The relation  $E_{oc} = E_c - 0.058 \log [\text{Fe}^{\text{III}}]/[\text{Fe}^{\text{II}}]$ , where  $E_c$  is the potential measured against a normal calomel electrode and  $E_{oc}$  the potential when the concentrations of ferric and ferrous iron are equal was found to hold good in concentrated acid solution. Increase in acid concentration causes a decrease in the oxidation potential whatever the proportion of ferric to ferrous iron. This is attributed to the formation of complexes, since the diffusion potential is insufficient to account for the change in potential. The connexion between the action of sulphur dioxide and the oxidation potential is shown by a diagram. M. B. D.

**Application of the Diffusion Hypothesis to Membrane Potentials.** C. D. MURRAY (*J. Gen. Physiol.*, 1924, 6, 759—768).—When two aqueous solutions containing equal concentrations of lactic acid but different concentrations of sodium lactate are separated by a layer of amyl alcohol, the system exhibits electrical properties ranging (as the concentration of sodium lactate is increased) from those characteristic of a simple Donnan equilibrium to those characteristic of simple diffusion. D. R. N.

**Diffusion Potentials.** P. F. BÜCHI (*Z. Elektrochem.*, 1924, 30, 443—449).—The influence of the activity coefficient on the diffusion potential in concentration cells is discussed. Measurements of diffusion potentials when an intermediate electrolyte is used give results in good agreement with Henderson's formula (A., 1907, ii, 426), provided the system be first allowed to come to rest. W. A. C.

**Free Energy and Heat Content of Arsenic Trioxide and the Reduction Potential of Arsenic.** R. SCHUHMAN (*J. Amer. Chem. Soc.*, 1924, 46, 1444—1449).—Measurements of the *E.M.F.* of the cell  $\text{As(s)} + \text{As}_2\text{O}_3(\text{s})\text{HClO}_4(0.22-0.94N)\text{H}_2(\text{g})$  gave  $-0.2340$  and  $-0.2250$  volt at 25° and 45°, respectively. The calculated free energy of formation of octahedral arsenic trioxide from metallic arsenic and oxygen at 25° is  $-137,300$  cals. and the heat content  $-153,800$  cals. From the relation between the electrode potential  $E$  of arsenic and the reduction potential  $E_0$  it follows that  $E_0 = -0.2375$  volt. H. T.

**Action of Metals on Nitric Acid.** W. D. BANCROFT (*J. Physical Chem.*, 1924, **28**, 475—493).—The literature on the subject is reviewed, and methods of attacking the problem, assuming the reaction to be electrolytic in character, are suggested. It seems probable that the direct reduction products of nitric acid are nitrous acid, hyponitrous acid, hydroxylamine, and ammonia, whilst nitrogen peroxide, nitric oxide, nitrous oxide, and nitrogen are due to secondary reactions.

M. S. B.

**Rate of Dissociation of Bromine Molecules.** M. BODENSTEIN (*Z. Elektrochem.*, 1924, **30**, 416—417).—In the reaction between hydrogen and bromine with sufficient iodine present as catalyst, the observed reaction velocity is that of the dissociation  $\text{Br}_2 = 2\text{Br}$ . At  $300^\circ$  and 1 atm. velocity measurements indicate that about 1/120th of the molecular impacts are chemically effective. Under the action of light as catalyst, at  $218^\circ$  and 0.3—0.8 atm. total pressure, 1/500th of the impacts are effective.

W. A. C.

**Decomposition of Hydrogen Iodide.** H. A. TAYLOR (*J. Physical Chem.*, 1924, **28**, 984—991).—A dynamical study of the rate of decomposition of hydrogen iodide at temperatures between  $400^\circ$  and  $520^\circ$ . The reaction is complex and consists of simultaneous volume and surface reactions, the latter predominating when powdered glass is placed in the reaction vessel. The temperature coefficient of the surface reaction is 1.10 and that of the volume reaction approximately 2 over the temperature range studied.

S. S.

**Ionisation Produced in certain Gaseous Reactions.** A. K. BREWER (*J. Amer. Chem. Soc.*, 1924, **46**, 1403—1419).—Evidence of the liberation of ions has been obtained in the reactions: nitric oxide+oxygen ( $385^\circ$  and  $50^\circ$ ), nitric oxide+ozone ( $50^\circ$ ), nitrogen pentoxide decomposition ( $385^\circ$ ), ozone decomposition ( $200^\circ$ ), nitrogen dioxide decomposition ( $385^\circ$ ). The ionisation currents, which are proportional to the number of reacting molecules and to the applied voltage, indicate that 1 pair of ions is produced by the interaction of about  $10^{13}$  molecules.

H. T.

**Relation between the Rate of Stirring and the Reaction Velocity in Heterogeneous Systems.** A. KLEIN (*Z. anorg. Chem.*, 1924, **137**, 56—65).—It is shown that the velocity of a reaction in a heterogeneous system is equal to the sum of the reaction velocity in the unstirred mixture and a factor which is proportional to the rate of stirring and is dependent on the nature of the stirring apparatus.

A. R. P.

**Kinetic Salt Effect.** J. N. BRÖNSTED and C. E. TEETER, jun. (*J. Physical Chem.*, 1924, **28**, 579—587; cf. Brönsted, A., 1922, ii, 699).—The velocity of reaction between two molecules A and B in dilute solution is given by  $v = kc_Ac_B$ , only when  $f_A f_B / f_{AB} = 1$ ,  $f$  being the activity coefficient which depends on the electric charge of each of the substances concerned. Otherwise the "activity" theory,  $v = ka_Aa_B$  (cf. Harned, A., 1916, ii, 8; Jones and Lewis, T., 1920, **117**,

1120; Åkerlöf, A., 1922, ii, 134), must be applied. If the term  $f_A f_B / f_{AB}$  be altered, whilst the concentrations  $c_A$  and  $c_B$  remain the same, the resulting alteration in  $v$  is a primary kinetic salt effect. A change in  $v$  brought about by a change in the concentration of  $c_A$  or  $c_B$ , by the addition of a neutral salt, whilst  $f_A f_B / f_{AB}$  remains unchanged, is a secondary kinetic salt effect. In the reaction between the two positive ions of mercuric nitrate and chloropentammine cobaltic nitrate, giving the aquopentammine ion and undissociated mercuric chloride, the primary salt effect, produced by the addition of nitric acid, potassium nitrate, and strontium nitrate, has been examined, and is found to be in agreement with theory. The decomposition of ethyl diazoacetate, catalysed by acetic acid, in the presence of varying amounts of potassium nitrate, has been investigated, and a positive secondary kinetic salt effect has been found. This is due to the increased ionisation of the acetic acid brought about by the addition of the neutral salt. In the catalysis of the same reaction by chromic nitrate, the secondary kinetic salt effect produced by potassium nitrate is negative, since potassium nitrate reduces the concentration of the hydrated chromic ion, and hence that of the hydrogen ion as produced by the following reaction:  $\text{Cr}(\text{H}_2\text{O})_6^{+++} \rightarrow \text{Cr}(\text{H}_2\text{O})_5^{\text{OH}^{++}} + \text{H}^+$ . These results also are in agreement with the theory. M. S. B.

**Negative and Positive Catalysis and the Activation of Molecules.** N. R. DHAR (*J. Physical Chem.*, 1924, 28, 948—961).—A survey of more recent work on catalysis and allied phenomena. The intermediate compound theory is held to account for negative catalysis and for many cases of positive catalysis. It is suggested that active nitrogen and hydrogen and the activated oxygen which takes part in autoxidation contain activated molecules which are not dissociated into atoms but contain electrons raised to a higher energy level. The luminosity observed in the decay of active nitrogen and in many slow oxidations is therefore due to the return of the electron to the normal level. The interchange of energy quanta between electrons, ions, and normal molecules is thought to play an important part in the production of activated molecules. S. S.

**Catalytic Action of Nitrous Acid.** W. D. BANCROFT (*J. Physical Chem.*, 1924, 28, 973—983).—A review of published work on the influence of nitrous acid on the oxidising action of nitric acid. Nitrous acid is not so strong an oxidising agent as nitric acid and its catalytic action depends on the activation of the nitric acid molecule at some stage in the reactions involved in the dynamic equilibrium  $\text{HNO}_3 + \text{HNO}_2 \rightleftharpoons 2\text{NO}_2 + \text{H}_2\text{O}$ . S. S.

**Influence of Nitrogen Dilution on the Speed of Flame.** I. C. CAMPBELL and O. C. DE C. ELLIS (*J. Chem. Soc.*, 1924, 125, 1957—1960).—The retarding effect of nitrogen on the propagation of flame (cf. Dixon, *Phil. Trans.*, 1893, A, 184, 165; Mason and Wheeler, T., 1917, 111, 1048) has been examined for the case when

inflammation proceeds from the closed end of a tube. The speeds given are the average speeds over the first 5 cm. of the path of the flame under conditions which were kept as uniform as possible. When the speeds are plotted against calorific values of gas mixtures containing sufficient oxygen for complete combustion, the graph obtained is a straight line. Dixon's figures for hydrogen satisfy this relation, but for methane, ethylene, and acetylene they give a curve owing to incomplete combustion in the head of the flame.

M. B. D.

**Influence of Nitrogen Dilution on the Speed of Flame. II.** O. C. DE C. ELLIS and S. R. STUBBS (*J. Chem. Soc.*, 1924, **125**, 1960—1963).—The other variables which influence the speed of the flame (cf. preceding abstract) such as the density, viscosity, and specific heat are grouped together under the style of "thermal conductivity." When the calorific values for a set of mixtures of carbon disulphide and air are equal, the speeds are directly proportional to their thermal conductivities.

M. B. D.

**Ignition of Gases. III. Ignition by the Impulsive Electrical Discharge. Mixtures of Paraffins with Air.** R. V. WHEELER (*J. Chem. Soc.*, 1924, **125**, 1858—1869).—Further investigations on the mechanism of ignition of gases by means of a high-tension spark (cf. T., 1920, **117**, 903) are recorded. The most readily ignitable mixture of methane and air contains a greater percentage of air than is required for complete combustion or for maximum speed of flame propagation, whilst for mixtures of all the higher paraffins and air the reverse is true. Any difference in the insulating powers of these gas mixtures does not appreciably affect the igniting power of the secondary discharge. For the propagation of flame, a minimum volume of the mixture must be burnt. An addendum by S. C. Lind states that the rate of reaction between a combustible gas and oxygen increases with the concentration of whichever gas has the greatest stopping power for radiant energy which will activate it, and that its stopping power depends on the density of the gas in a similar manner to its stopping power for  $\alpha$ -rays.

M. B. D.

**Ignition of Gases. IV. Ignition by a Heated Surface. Mixtures of the Paraffins with Air.** W. MASON and R. V. WHEELER (*J. Chem. Soc.*, 1924, **125**, 1869—1875).—The researches on methane and air (T., 1922, **121**, 2079) have been extended to ethane, butane, propane, and pentane. Measured by their relative ignition temperatures in an 85 c.c. quartz cylinder, the mixtures of methane and air are appreciably the most difficult to ignite, whilst the others become easier to ignite as the series is ascended. Methane shows the same anomaly as in the case of ignition by secondary discharge (cf. preceding abstract). The relative ignitibilities of these gaseous mixtures have also been determined by the duration of the pre-flame period when the reaction vessel is maintained at a constant temperature, appreciably higher than the "ignition temperature" of any of the mixtures.

M. B. D.

**Chemical Effect of the Emanations of Radioactive Metals.**

A. SLOSSE (*Compt. rend. Soc. Biol.*, 1923, **89**, 812—814; from *Chem. Zentr.*, 1924, i, 1507; cf. this vol., i, 497).—Radium emanation produces optical and chemical changes when allowed to act on a solution of dextrose. Formaldehyde is produced, as is the case when dextrose is subjected to  $\gamma$ -rays. The effect of the emanations is, however, weaker than that of  $\gamma$ -rays from radium. Optical changes are also produced by thorium emanation; these are due to the formation of  $\beta$ -glucose.

G. W. R.

**Photochemical Studies. II. Activation of a Mercury Surface by Light. Possible Relation between Photoelectric Effect and Photochemical Action.** H. R. MOORE and W. A. NOYES, jun. (*J. Amer. Chem. Soc.*, 1924, **46**, 1367—1376).—Measurements of the threshold value of the photoelectric effect of mercury gave values between 2750 and 2537 Å. When the mercury surface is activated the reaction between mercury and oxygen or nitrogen peroxide is accelerated. A maximum effect is obtained when a potential of about one volt is applied to the mercury surface. Higher voltages, even when these tend to drive the "electrons" away from the surface, reduce the magnitude of the effect. The duration of the state of activation after turning off the light is always less than one second.

H. T.

**Apparatus for Collecting a Gas at a Constant Pressure.**

H. J. E. DOBSON (*J. Chem. Soc.*, 1924, **125**, 1968).—The apparatus consists of an aspirator fitted with an automatic pressure regulator capable of collecting 15 litres of gas during five hours, the greatest deviation from atmospheric pressure not exceeding 0.1 mm. of mercury. The regulating device depends on the provision of an external supply of water which automatically overflows into the aspirator as soon as the pressure in it falls below atmospheric and ensures that the net outflow of water is always equal to the inflow of gas.

M. B. D.

**Simple Pressure-measuring Device for Use with Corrosive**

**Gases.** D. F. SMITH and N. W. TAYLOR (*J. Amer. Chem. Soc.*, 1924, **46**, 1393—1396).—A diaphragm of glass prepared by flattening a thin bulb so that a wrinkled or uneven surface is obtained, has been used for measurements of changes of pressure. A "clicking" noise is heard as the diaphragm passes through a critical position. Diaphragms are easily made which are sensitive to 0.2—0.3 mm. and capable of withstanding a pressure difference of 60 cm.

H. T.

**Combustion Micro-calorimeter.** W. A. ROTH, H. GINSBERG, and R. LASSÉ (*Z. Elektrochem.*, 1924, **30**, 417—420).—A combustion bomb of the usual pattern, but of only 21.5 c.c. capacity, and requiring only 500 c.c. of water in the calorimeter, is described. Working with correspondingly small quantities of substance, heats of combustion are determined with an error of less than 0.1%.

W. A. C.



## Inorganic Chemistry.

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**Thermal Decomposition of Chlorine Monoxide. II. Relation to the General Theory of Bimolecular Reactions.** C. N. HINSHELWOOD and J. HUGHES (*J. Chem. Soc.*, 1924, **125**, 1841—1847).—The application of Lewis' theory (T., 1918, **113**, 471) to the thermal decomposition of chlorine monoxide has been tested experimentally. An intermediate product is formed (T., 1923, **123**, 2730), but no information could be obtained as to its nature. The results, which merely offer chemical confirmation of the results obtained previously, render it almost certain that bimolecular reactions can be interpreted in terms of simple thermal collisions. The presence of air, carbon monoxide or dioxide has no influence on the course of the reaction. S. K. T.

**Electrolysis of Hypochlorite Solutions.** F. FOERSTER [in part with O. JENSEN and A. TENNE] (*Trans. Amer. Electrochem. Soc.*, 1924, **46**, 101—128).—The electrolysis of pure solutions of hypochlorous acid containing an indifferent electrolyte such as phosphoric acid results in the formation of chloric acid and the liberation of chlorine and oxygen at the anode, the free oxygen being almost exactly one-third and the free chlorine two-thirds of that in the chloric acid formed. This is in agreement with the theory expressed in the schemes  $6\text{ClO}' + 6\oplus \rightarrow 6\text{ClO}$ ;  $6\text{ClO} + 3\text{H}_2\text{O} \rightarrow 2\text{ClO}_3' + 4\text{Cl}' + 6\text{H}' + 3\text{O}$ , and  $4\text{Cl}' + 4\oplus \rightarrow 2\text{Cl}_2$ . In the electrolysis of concentrated alkali chloride solutions, chlorine ions are first discharged at the anode; the chlorine then reacts with hydroxyl ions to give hypochlorite and chloride ions, and the hypochlorite is then either converted into chlorate, as stated above, or undergoes a purely secondary chemical reaction,  $2\text{HClO} + \text{ClO}' \rightarrow \text{ClO}_3' + 2\text{HCl}$ . The current efficiency of chlorate formation is greater the larger the amount of chlorate formed by the secondary reaction, and this condition holds when the solution is slightly acid, hot, and concentrated; in alkaline solutions, no secondary formation of chlorate occurs. Agitation of both acid and alkaline solutions of sodium chloride during electrolysis diminishes the amount of hypochlorite and consequently of chlorate formed, and both solutions behave similarly. In the electrolysis of bromide solutions, the secondary bromate formation proceeds at a much greater rate than the secondary chlorate formation from chloride solutions, and the formation of bromate during electrolysis takes place almost wholly as the result of this purely chemical reaction. This phenomenon is even more marked in iodide solution.

A. R. P.

**Absorption Spectrum of Liquid Bromine.** P. BOVIS.—(See ii, 712.)

**Hydrocarbons and Carbon Chlorides. III. Solubility of Iodine in Chlorinated Hydrocarbons of the Aliphatic Group.** B. M. MARGOSCHES, W. HINNER, and L. FRIEDMANN (*Z. anorg. Chem.*, 1924, **137**, 81—90).—The solubility of iodine has been

determined in chlorinated derivatives of methane, ethane, and ethylene between 11° and 25°. In all the cases examined, the solubility was found to increase linearly with the temperature and decrease with the degree of chlorination of the hydrocarbon. The ratio of the solubility in any compound to that in the compound of the same series containing one more chlorine atom (*e.g.*, methylene chloride/chloroform) is, under the same conditions, approximately a constant (1.31). Where there are two isomerides, iodine is more soluble in the symmetrical compound than in the asymmetrical. The solubility of iodine in chloroform is approximately the same as in dichloroethylene and in carbon tetrachloride the same as in tetrachloroethylene.

A. R. P.

**Theory of the Landolt Reaction.** A. THIEL and E. MEYER (*Z. anorg. Chem.*, 1924, **137**, 125—140).—The interaction of iodate and sulphite takes place in three stages: (i)  $\text{IO}_3' + 3\text{SO}_3'' = \text{I}' + 3\text{SO}_4''$ ; (ii)  $\text{IO}_3' + 5\text{I}' + 6\text{H}' = 3\text{I}_2 + 3\text{H}_2\text{O}$ ; (iii)  $\text{I}_2 + \text{SO}_3'' + \text{H}_2\text{O} = 2\text{I}' + \text{SO}_4'' + 2\text{H}'$ . The kinetics of the first stage have been studied by conducting the reaction in the presence of freshly-precipitated, finely-divided silver chloride, which removes the iodine ion as soon as it is formed and entirely suppresses the second reaction. The reaction constant of (i) is only six times as great in a solution of  $p_{\text{H}}$  2 as in a solution of  $p_{\text{H}}$  5, showing that the reaction is not directly influenced by the hydrogen-ion concentration, but is dependent on the degree of dissociation of the sulphurous acid; the reaction is unimolecular with respect to iodate and to sulphite, and between 40° and 99° has the high temperature coefficient of 2.38. The reaction constant of (iii) is so greatly affected by the hydrogen-ion concentration that it may reasonably be assumed that hydroxyl ions play a direct part: thus  $\text{SO}_3'' + \text{OH}' + \text{I}_2 = \text{SO}_4'' + \text{H}' + 2\text{I}'$ . (Cf. Skrabal, this vol., ii, 543.)

A. R. P.

**Diffusion of Oxygen through Silver.** F. M. G. JOHNSON and P. LAROSE (*J. Amer. Chem. Soc.*, 1924, **46**, 1377—1389).—Measurements were made of the rate of diffusion of oxygen through silver (of different thicknesses) at temperatures between 400° and 630°, and oxygen pressures of 159, 392, and 760 mm. The rate of diffusion,  $X$ , in c.c. per m.<sup>2</sup> per hour, is given by the expression  $X = p^{\frac{1}{2}} T^{14.62} (1.71 \times 10^{-43}) / h$ , where  $p$  is the oxygen pressure in mm.,  $h$  the thickness of the silver in mm., and  $T$  the absolute temperature.

H. T.

**Reactions Occurring during the Discharge of the Oxygen-Hydrogen Cell.** M. TRAUTZ (*Z. anorg. Chem.*, 1924, **137**, 79—80).—A reply to the criticism of the author's earlier work by Fischer and Krönig (cf. this vol., ii, 542).

A. R. P.

**Molecular Lowering of the Freezing Point of Liquid Ammonia.** L. D. ELLIOTT (*J. Physical Chem.*, 1924, **28**, 611—635).—Measurements of the lowering of the freezing point of ammonia, for a number of organic and inorganic solutes, have been made at concentrations not less than 0.006 g.-mol. of solute per 100

g. of ammonia. Only for acetamide and *o*-nitrophenol have approximately constant values been obtained, giving an average value of 9.7 for *K*, the molecular lowering per 100 g. of solvent. A decreasing value of *K* with increasing concentration, for carbamide, ethyl alcohol, *n*-propyl alcohol, and aniline, indicates a tendency to association. In the case of electrolytes, an initial fall from a value higher than 9.7, followed by a rise as the concentration increases, indicates first a decrease in ionisation at higher concentrations is over-balanced by solvation. Exceptions to this form of curve have been found. In general, the data for electrolytes, organic and inorganic, support the view that ammonia exerts a much smaller dissociating power than water, the high conductivity of ammonia solutions being no doubt due to the relatively greater mobility of the ions. The freezing point of liquid ammonia is  $-77.73 \pm 0.03^\circ$ .  
M. S. B.

**Preparation of Hydrazine, its Salts and Hydrate.** N. PUTOCHIN (*Trans. Inst. Chem. Reagents, Moscow*, 1923, No. 2, 50—56).—Raschig's method for preparing hydrazine is described in detail; the preparation of the hydrochloride, the hydrate, and the free base from the sulphate is also given, as well as the method for determining hydrazine.  
G. A. R. K.

**Homogeneous Thermal Decomposition of Nitrous Oxide.** C. N. HINSHELWOOD and R. E. BURK (*Proc. Roy. Soc.*, 1924, A, 106, 284—291).—The thermal decomposition of nitrous oxide, studied by the method previously described (this vol., ii, 251), was found to be homogeneous over the range 565—852°, neither platinum, rhodium, nor silica having any catalytic effect. Variation of the initial pressure showed the reaction to be bimolecular, although the velocity constant increased as the reaction proceeded. This was probably due to the catalytic influence of by-products. The observed heat of activation agreed well with that calculated on the basis of Lewis' theory (T., 1918, 113, 471).  
S. K. T.

**Kinetics of the Interaction of Nitrous Oxide and Hydrogen.** C. N. HINSHELWOOD (*Proc. Roy. Soc.*, 1924, A, 106, 292—298).—The rate of reduction of nitrous oxide by hydrogen, at about 700°, is practically that which would be expected from the rate of thermal decomposition of nitrous oxide (preceding abstract). Glass surfaces catalyse the reaction slightly. In the presence of a heated platinum wire, the reaction takes place solely on the surface of the latter. The wire appears to be coated with a film of hydrogen, in the gaps of which the nitrous oxide reacts. The "latent heat of evaporation of the film of adsorbed hydrogen" is approximately 25,000 cal. per g.-mol. (cf. Langmuir, A., 1922, ii, 629).  
S. K. T.

**Substances Dissolved in Rain and Snow.** H. S. FRIES and N. KNIGHT (*Proc. Iowa Acad. Sci.*, 1923, 30, 375—378).—From Sept. 19, 1921, to June 2, 1922, rain and snow contained (in kg. per acre): nitrogen as nitrate, 0.490; nitrogen as nitrite, 0.083; free

ammonia, 0.838; albuminoid ammonia, 0.603;  $\text{SO}_3$ , 0.089; chlorine, 3.61.

CHEMICAL ABSTRACTS.

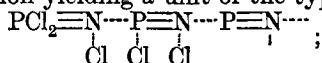
**Formation of Phosphorus Pentachloride from Phosphorus Trichloride and Chlorine.** H. A. TAYLOR (*J. Physical Chem.*, 1924, **28**, 510—513).—An attempt has been made to show that the formation of phosphorus pentachloride from the trichloride and chlorine is an uncatalysed reaction. Precautions were taken to ensure the complete drying of the gases. It was then found that they reacted as readily in wax vessels, *i.e.*, in contact with a non-polar surface, as in glass, a polar surface. This probably indicates that the reaction takes place in the gaseous phase. To test this supposition, the two vapours, in dry nitrogen, were made to impinge on one another in a 3-litre flask. A thin film of phosphorus pentachloride immediately formed on the surface of the glass, and 20 or 30 secs. later the whole flask was filled with a white cloud. The phenomenon suggested the precipitation of a super-saturated vapour of phosphorus pentachloride, since cloud formation began in the region where the first film of pentachloride had formed and then travelled, in a direction opposed to the normal direction of flow of the gases, to the point at which they first impinged on one another. The conclusion is drawn that the reaction is a true gaseous reaction unaffected by surface catalysts and by water.

M. S. B.

**Phosphonitrilic Chlorides and their Transformations. I.** R. SCHENCK and G. RÖMER (*Ber.*, 1924, **57**, [B], 1343—1355).—The preparation of the phosphonitrilic chlorides by the action of phosphorus pentachloride on ammonium chloride under pressure (cf. Couldridge, T., 1888, **53**, 399; Stokes, A., 1897, ii, 94; 1898, ii, 70) is very troublesome and is conveniently replaced by heating the reactants in boiling *s*-tetrachloroethane until hydrogen chloride ceases to be evolved. After removal of the solvent under diminished pressure, the liquid chlorides (which cause polymerisation during distillation) are separated by filtration and treatment of the product with cold benzene. The residual solid is separated by cautious distillation under diminished pressure into triphosphonitrilic chloride  $(\text{PNCl}_2)_3$ , b. p.  $124^\circ/10$  mm., m. p.  $114^\circ$ , and tetraphosphonitrilic chloride  $(\text{PNCl}_2)_4$ , b. p.  $185^\circ/10$  mm., m. p.  $123.5^\circ$ . At temperatures above  $255^\circ$ , the chlorides become polymerised to a colourless, transparent mass resembling caoutchouc which, contrary to the observations of Stokes (*loc. cit.*), does not become depolymerised when heated at a higher temperature. Tri- and tetra-phosphonitrilic chlorides dissolved in benzene are transformed by aniline and piperidine into the same monomeric anilide,  $\text{N:P}(\text{NHPh})_2$ , m. p.  $261^\circ$ , and piperidide, m. p.  $231^\circ$ . They are converted by the requisite amount of water in the presence of pyridine into pyridine hydrochloride and *pyridinium metaphosphimate*,  $\text{N:P}(\text{OH})_2\text{C}_5\text{H}_5\text{N}$ ; the metaphosphimates derived from the two chlorides are very closely similar, but, since the molecular weights cannot be determined, their identity with one another is not regarded as established. Either salt, when heated at  $200^\circ/11$  mm., loses the whole of the pyridine and leaves a

residue of a metaphosphimic acid which is characterised as its silver salt  $(\text{N}:\text{PO}_2\text{Ag})_n$ , and by titration with ferric alum solution, with which it reacts to yield the salt,  $\text{H}_3[\text{Fe}_2(\text{NPO}\cdot\text{OH})_3]$ . The identity of these metaphosphimic acids with one another and with the similar compound described by Stokes is not placed beyond doubt. The enhanced activity of the phosphonitrilic chlorides in the presence of pyridine as compared with other solvents points to the existence of additive compounds which, however, have not been isolated.

The constitutions,  $\text{Cl}_2\text{P}\cdot\text{N}\begin{smallmatrix} \text{N}\cdot\text{PCl}_2 \\ \text{N}\cdot\text{PCl}_2 \end{smallmatrix}$  or  $\text{Cl}_2\text{P}\begin{smallmatrix} \text{N}-\text{PCl}_2 \\ \text{N}=\text{PCl}_2 \end{smallmatrix}\text{N}$ , assigned previously to triphosphonitrilic chloride do not appear to be adequate, and it is suggested that main and subsidiary valences are brought into action yielding a unit of the type,



single groups can then be added indefinitely at the terminal nitrogen atom. The oily phosphonitrilic chlorides are regarded as open-chain compounds, whereas in the more stable tri- and tetraphosphonitrilic chlorides the groups are united to closed rings.

H. W.

**Internally Complex Borates.** A. ROSENHEIM and H. VERMEHREN.—(See i, 1194.)

**Silicic Acids.** I. R. SCHWARZ and E. MENNER (*Ber.*, 1924, 57, [B], 1477—1481).—Sodium meta-, di-, and tri-silicates are prepared by heating quartz powder with the calculated quantity of sodium carbonate at  $1150^\circ$ ; the metasilicate is immediately crystalline, whereas the other salts required to be maintained at  $700^\circ$  during many hours to cause them to crystallise. They are converted by sulphuric acid (80%) at  $10^\circ$  into the corresponding silicic acids, which are thus obtained as white, finely granular powders containing about 5% more than the theoretical amount of water, which can be almost completely removed by alcohol and ether. The desiccation curve for metasilicic acid at the atmospheric temperature shows definite breaks, indicating the existence of silicic acids,  $\text{H}_4\text{Si}_3\text{O}_8$  and  $\text{H}_6\text{Si}_2\text{O}_5$ , which have been described previously by Tschermak under the names granatic and datolithic acids; the acid,  $\text{H}_4\text{Si}_3\text{O}_8$ , does not appear to be capable of existence at  $32^\circ$ . If it be assumed that the water is lost from a single molecule of metasilicic acid, the latter must be at least hexameric. Di- and tri-silicic acids rapidly lose their adsorbed water in the presence of phosphoric oxide, but desiccation is subsequently so slow that conclusions with regard to the state of hydration cannot be reached.

H. W.

**Crystal Structure of Graphite.** O. HASSEL and H. MARK.—(See ii, 721.)

**Structure of "Black Diamonds" [Carbonado].** W. GERLACH (*Z. anorg. Chem.*, 1924, 137, 331—332).—The Debye-Scherrer

röntgenogram of carbonado shows the usual interference lines of ordinary diamond, but the lines are much more intensely black and the background is also deep black. This appears to show that carbonado consists of a confused mass of small crystals of diamond, each crystal being coated with a thin layer of amorphous carbon or graphite.

A. R. P.

### Internal Structure of Crystallised Carbon and of Benzene.

J. BECKENKAMP (*Z. anorg. Chem.*, 1924, **137**, 249—274).—In continuation of earlier work (this vol., ii, 32), it is shown how the most important types of atomic arrangement in crystalline elements are built up. Assuming three layers, each of twelve spheres in the closest packing, two arrangements are possible:  $\alpha$ , the spheres of the upper layer are so arranged on the second layer that they cover the hollow spaces between the spheres of that layer;  $\beta$ , the spheres of the upper layer are arranged so that hollow spaces go right through the three layers in straight lines. Several layers of type  $\alpha$  give rise to the regular tetrakis-trigonal symmetry and several layers of type  $\beta$  to the hexagonal hexakis-octahedral symmetry. The centres of gravity of the first type form a face-centred lattice; the primary elementary body is a rhombohedron with vertical angles of  $60^\circ$  and the secondary a cube at the corners and face centres of which are situated points of mass. Each half of type  $\beta$  forms a space-centred, triangular prismatic lattice  $a:c=1:\frac{2}{3}\sqrt{6}$ ; the elementary body is a six-sided prism having an axial ratio of  $a:c=1:\sqrt{2}$ . From the elementary types the derivation of the octahedron is described; from this, the chain and ring type of structure is developed, and the formation of the lattices of magnesium, zinc, beryllium, and aluminium explained.

The atomic centres of gravity of the diamond crystal form two interpenetrating face-centred lattices of type  $\alpha$ , the centres of gravity of one lattice lying on the centres of gravity of the tetrahedron of the other lattice, and each centre of gravity belonging to four rings the axes of which are perpendicular to the octahedral faces. The author considers that each valency electron rotates round the points of contact of each electrically neutral sphere of each of two atoms, that inside this surface in each atom the influence of the negative inner electrons, and outside it, that of the positive atomic nucleus predominates, and that, therefore, the valency electrons lie along these neutral surfaces, especially at the points of contact between two of them. Because of this arrangement, the atoms of the diamond crystal are all exactly parallel and the diamond forms hexakis-octahedra which are assumed to be tetartohedral; owing, however, to quasi-homogeneous twinning along the (110) planes, further growth on the (111) planes, and subsequent twinning along the (100) plane, the crystals appear to be holohedral. Evidence in support of this theory is given and in a similar way it is shown that the form of graphite is in accordance with a hexagonal structure of the type  $\beta'_2$ . According to Groth, benzene crystallises in the rhombic system; for this to be true, the hydrogen nuclei must rotate in a vertical direction so that the magnetic axes of the three

upper and the three lower hydrogen nuclei are parallel to the *b* axis of the crystal. The author considers that the benzene molecule is built up from graphite, and not from diamond, but points out that if this is so there should be two optically active isomerides of benzene. Further work is needed to determine with greater certainty the molecular structure of benzene. A. R. P.

**Preparation of Carbon Monoxide by Means of the Electric Arc.** H. G. KREUL (*Z. phys.-chem. Unterr.*, 1924, 37, 43—45; from *Chem. Zentr.*, 1924, i, 2405).—An apparatus is described whereby carbon monoxide is prepared by maintaining an electric arc between carbon electrodes in an atmosphere of carbon dioxide.

G. W. R.

**Critical Densities of Salts.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, 138, 330—332).—The critical densities of a number of alkali salts have been calculated from the data of Jaeger (A., 1918, ii, 33) by means of the formula of Saslawsky (this vol., ii, 452), and the results are compared with those calculated from the densities at the m. p. by the formula of Lorenz ("Raumerfüllung und Ionenbeweglichkeit," Leipzig, 1922, p. 30). The general agreement between the two sets of figures is satisfactory.

W. H.-R.

**Influence of Nitric Acid on the Solubility of Nitrates in Water.** A. A. KASANCEV (*Trans. Inst. Chem. Reagents, Moscow*, 1923, No. 2, 10—27).—The solubilities of silver, copper, potassium, sodium, and ammonium nitrates in aqueous solutions of nitric acid of varying concentrations and temperatures were determined and expressed in the form of curves. All these curves show a minimum in the region between 0° and 30°; copper, potassium, and sodium nitrates also show a minimum at 75°; the minimum is most pronounced in salts capable of forming acid salts. The lowering of solubility by nitric acid closely follows the exponential law. The solubility curves for silver nitrate and copper nitrate can be expressed by  $y = Ae^{-Kx} \pm Be^{-K'x}$  or  $y = A - Bx + De^{Kx}$ , in which *y* and *x* are the weights of salt and nitric acid in 100 g. of solution. The solubilities of silver, copper, and ammonium nitrates in pure water at temperatures from 0° to 100° were also determined and the curves obtained can be expressed as follows: for silver nitrate,  $y = 55.65 + 0.86123t - 0.0096165t^2 + 0.00004439t^3$ ; for copper nitrate hexahydrate,  $y = 46.49 + 0.45397t - 0.012305t^2 + 0.0006331t^3$ ; for copper nitrate trihydrate,  $y = 57.78 + 0.09228t + 0.0004515t^2$ , where *y* is the weight of salt in 1 g. of solution. The transition temperature of copper nitrate hexahydrate to the trihydrate is 25.4°; the addition of nitric acid lowers this temperature in accordance with the linear law. It is possible to obtain values for the solubility of the trihydrate below the transition temperature.

G. A. R. K.

**Vacuum-arc Spectrum of Sodium.** I. H. BARTELS.—(See ii, 709.)

**Decomposition of Liquid Sodium Amalgam in Aqueous Solutions.** A. KLEIN (*Z. anorg. Chem.*, 1924, **137**, 39—55).—The rate of solution of the sodium in a 0.5% sodium amalgam in water decreases rapidly with increase in the concentration of sodium hydroxide and is independent of the rate of stirring. Addition of sodium chloride reduces the rate of solution, but renders it constant, showing that it depends more on the concentration of the sodium ions than on that of the hydroxyl ions. The temperature coefficient of the reaction is 1.45 in neutral or alkaline solutions, but only 1.07 in acid solutions. The rate of solution of the sodium in acid solutions depends on two factors, one of which is the same as that governing the rate in neutral solutions and the other is proportional to the acid concentration at any instant, is reproducible under the same conditions of temperature, acidity, and rate of stirring, and is independent of the concentration of the sodium in the amalgam. (Cf. Fraenkel and Heinz, this vol., ii, 475.)  
A. R. P.

**Lithium. I. Hydrates of Lithium Chloride and Bromide.** G. F. HÜTTIG and F. RENSCHER (*Z. anorg. Chem.*, 1924, **137**, 155—180).—Lithium chloride and bromide each give hydrates with 1, 2, and 3 mols. of water, and the systems lithium chloride–water and lithium bromide–water each have three quadruple points. In the chloride system these are (a)  $\text{LiCl}\cdot 3\text{H}_2\text{O}$ – $\text{LiCl}\cdot 2\text{H}_2\text{O}$ –saturated solution–water vapour,  $t = -16.5^\circ$ ,  $p = 0.8$  mm., (b)  $\text{LiCl}\cdot 2\text{H}_2\text{O}$ – $\text{LiCl}\cdot \text{H}_2\text{O}$ –saturated solution (68 g. of  $\text{LiCl}$  per 100 g. of water)–water vapour,  $t = 12.5^\circ$ ,  $p = 2$  mm., (c)  $\text{LiCl}\cdot \text{H}_2\text{O}$ – $\text{LiCl}$ –saturated solution (130 g.  $\text{LiCl}$  in 100 g. of water)–water vapour,  $t = 100.5^\circ$ ,  $p = 90$  mm. The heats of formation of the hydrates from Nernst's equation are:  $\text{LiCl}(\text{solid}) + \text{H}_2\text{O}(\text{gas}) = \text{LiCl}\cdot \text{H}_2\text{O} + 15,400$  cal.,  $\text{LiCl}\cdot \text{H}_2\text{O}(\text{solid}) + \text{H}_2\text{O}(\text{gas}) = \text{LiCl}\cdot 2\text{H}_2\text{O} + 13,900$  cal., and  $\text{LiCl}\cdot 2\text{H}_2\text{O}(\text{solid}) + \text{H}_2\text{O}(\text{gas}) = \text{LiCl}\cdot 3\text{H}_2\text{O} + 13,600$  cal.

For lithium bromide, the corresponding quadruple points and compositions of the saturated solutions are respectively (a)  $t = 4^\circ$ ,  $p = > 0.14$ ,  $< 0.8$  mm., 145 g.  $\text{LiBr}$  in 100 g. of water, (b)  $t = 32^\circ$ ,  $p = 2.8$  mm., 192 g.  $\text{LiBr}$  in 100 g. of water, (c)  $t = 159^\circ$ ,  $p = 228$  mm., solubility not determined; the heats of formation of the hydrates are 17,250, 14,730, and between 13,740 and 14,730 cal., respectively.  
A. R. P.

**Spectrum of Cæsium.** A. L. HUGHES and C. F. HAGENOW.  
—(See ii, 709.)

**Ammonium Nitrate. IX. Reciprocal Salt Pair Ammonium Nitrate and Lithium Chloride.** E. P. PERMAN and W. R. HARRISON (*J. Chem. Soc.*, 1924, **125**, 1709—1713).—The system is very similar to the ammonium nitrate–sodium chloride system (cf. T., 1922, **121**, 2473), there being three ternary and seven binary systems. A ternary eutectic occurs at  $84^\circ$  for  $\gamma$ -ammonium nitrate, lithium nitrate, and ammonium chloride; subsidiary ternary eutectics occur at  $95^\circ$  (lithium nitrate, lithium and ammonium



chlorides) and at 119° (ammonium chloride,  $\delta$ - and  $\gamma$ -ammonium nitrates). No double salts or mixed crystals are formed.

S. K. T.

**Solubility of Silver Chloride and Gay-Lussac's Silver Titration.** R. LORENZ and E. BERGHEIMER (*Z. anorg. Chem.*, 1924, 137, 141—154).—The solubility of silver chloride has been determined by adding alternate drops of 0.005*N*-silver nitrate and 0.005*N*-sodium chloride to a large volume of water and observing nephelometrically the formation of (a) a temporary cloud round the drop, and (b) a permanent cloud throughout the solution. The results obtained agreed closely with those obtained conductometrically by Kohlrausch and Rose for all temperatures up to 70°, and the effect of sodium chloride and silver nitrate on the solubility of silver chloride agreed with the values calculated from Nernst's equation. Sodium nitrate and nitric acid increase the solubility of silver chloride, whilst sodium acetate and sodium hydroxide decrease it; acetic acid first increases then, in larger quantity, decreases the solubility. Under certain conditions, a modification of silver chloride may be obtained the solubility of which is of the order of  $2 \times 10^{-7}$  mol. per litre.

A. R. P.

**Non-existence of Silver Suboxide.** G. R. LEVI and A. QUILICO (*Gazzetta*, 1924, 54, 598—604).—Application of the method of X-ray analysis to silver oxide and peroxide and to preparations hitherto assumed to consist of the suboxide gives results showing that no such suboxide of the formula  $\text{Ag}_4\text{O}$  exists, that the compound  $\text{Ag}_2\text{O}_2$  is a well-defined chemical individual having a low degree of crystalline symmetry, and that the presence of silver when mixed with its oxide may be detected more sensitively by the use of X-rays than by gravimetric analysis.

T. H. P.

**Partition of Silver Nitrate between Water and Aniline.** A. FRUMKIN and R. KULVARSKAJA (*Z. anorg. Chem.*, 1924, 138, 278—280).—At 15° the partition coefficient of silver nitrate between water and aniline varies with the concentration, but in all cases the silver nitrate is attracted chiefly to the aniline, in agreement with previously determined *E.M.F.* measurements (cf. Müller and Duschek, A., 1922, ii, 612). This result, which is contrary to the general rule for the distribution of salts between water and an organic solvent, is due to the formation of a complex compound,  $\text{AgNO}_3 \cdot 3\text{PhNH}_2$ , which has been prepared by shaking aniline with a concentrated aqueous solution of silver nitrate.

W. H.-R.

**Cathodoluminescence of Fluorite.** F. G. WICK.—(See ii, 714.)

**Crystal Structure of Calcium Hydroxide.** G. R. LEVI (*Giorn. Chim. Ind. Appl.*, 1924, 6, 333—334).—X-Ray analysis shows that calcium hydroxide possesses a hexagonal structure analogous to that of magnesium hydroxide;  $a = 3.52 \text{ \AA.}$  and  $c = 4.93 \text{ \AA.}$ , the calculated value of  $d$  being 2.30.

T. H. P.

**Mechanism and Thermochemistry of the Reaction between Calcium Carbide and Nitrogen.** H. J. KRASE and J. Y. YEE (*J. Amer. Chem. Soc.*, 1924, **46**, 1358—1366).—Calcium carbide, when heated at temperatures above 1100°, decomposes into calcium and carbon. In the formation of calcium cyanamide, this elemental decomposition represents the first stage. The nitrogen then forms nitride with the calcium and subsequently unites with the carbon to give calcium cyanamide: (i)  $3\text{CaC}_2 = 3\text{Ca} + 6\text{C}$ ; (ii)  $3\text{Ca} + \text{N}_2 = \text{Ca}_3\text{N}_2$ ; and (iii)  $\text{Ca}_3\text{N}_2 + 3\text{C} + 2\text{N}_2 = 3\text{CaCN}_2$ . Calcium chloride accelerates the decomposition of calcium carbide, its influence in the cyanamide process being thereby explained. The following mean values were obtained for the heats of reaction at 25°: (a)  $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C} + 98,430$  cal.; (b)  $\text{Ca}_3\text{N}_2 + 3\text{C} + 2\text{N}_2 = 3\text{CaCN}_2 + 198,240$  cal.; whence  $\text{Ca} + 2\text{C} = \text{CaC}_2 + 5050$  cal.

H. T.

**Dehydration and Rehydration of Gypsum.** G. LINCK and H. JUNG (*Z. anorg. Chem.*, 1924, **137**, 407—417).—Calcium sulphate dihydrate (gypsum) is stable in the air up to 99°, at which temperature it loses  $1.5\text{H}_2\text{O}$  and is converted into the hemihydrate. Further heating converts this gradually into anhydrous salt without altering the crystal structure, dehydration being complete at 190°. On keeping in the air, this "soluble anhydrite" rehydrates to the hemihydrate again, showing it to be of a zeolitic nature. At a red heat, the soluble anhydrite is converted into small crystals optically identical with native anhydrite. These crystals become turbid at 1100—1200°, owing to the formation of calcium oxide.

A. R. P.

**Reactivity in the Solid State of Boric Anhydride with Metallic Oxides.** C. MAZZETTI and F. DE CARLI (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 512—515).—The borates of various metals are obtainable by the interaction of boric anhydride and the corresponding oxides at temperatures below those at which the mixtures fuse. When calcium oxide (1 mol.) and boric anhydride (1 mol.) are heated together in an electric furnace, the reaction commences when the temperature reaches 625°, the heat developed raising the temperature in a few seconds to 1020° and almost fusing the mass; a hard, porous borate is obtained on cooling. With barium oxide similar results are obtained, and also with magnesium oxide (3 mols.). With zinc oxide, two temperature arrests are observed, each being preceded by a rapid rise. The results obtained with oxides of copper, nickel, cadmium, lead, tin, cobalt, aluminium, tin, and chromium, and with ferric oxide and manganese dioxide are also given.

T. H. P.

**Solubility of Strontium, Barium, and Heavy-metal Carbonates in Water under High Pressure of Carbon Dioxide, and the Properties of such Solutions.** O. HAEHNEL (*J. pr. Chem.*, 1924, [ii], **108**, 187—193; cf. this vol., ii, 551).—The solubility of strontium carbonate in water containing carbon

dioxide increases from 0.12% at 1 atm. carbon dioxide pressure to 0.38% at 35 atm., thereafter remaining constant. Barium carbonate, solubility 0.27% at 1 atm., reaches similarly a solubility limit of 0.59% at 25 atm. Solid carbonates in contact with these solutions appear to be converted into solid hydrogen carbonates under pressure. The solubilities of carbonates of the heavy metals, under 1 atm. and 56 atm. carbon dioxide pressure respectively, are as follows: silver, 0.105%, 0.170%; iron, 0.072%, 0.077%; zinc, 0.07%, 0.084%; manganese, 0.04%, 0.08%; copper, 0.03%, 0.041%; lead, 0.014%, 0.015%. Solutions of the alkaline-earth carbonates prepared under high pressure of carbon dioxide deposit the dissolved salts, at the ordinary pressure, much more slowly than corresponding solutions of the heavy-metal carbonates. Measurements of the electrical conductivities of the solutions prepared under high pressure are appended. F. G. W.

**Basic Magnesium Hypochlorite and its Electrolytic Preparation.** A. LISSNER (*Bull. Acad. Sci. Roumaine*, 1924, 8, 262—266).—The electrolysis of a thoroughly agitated solution of magnesium chloride containing excess of magnesium hydroxide at 18—20° gives, in 90% of the theoretical yield, a stable insoluble basic magnesium hypochlorite, containing 5.8% of magnesium peroxide and 0.4% of chlorate, and having an active chlorine content of 43.05%, as compared with the 38% of Merck's product. Owing to deposition of the insoluble product on the cathode, thereby increasing the electrolytic resistance, the direction of the current is reversed at intervals. An abnormal cathodic reduction (due to irreversible polarisation) also tends to reduce the yield, and this reduction is prevented by the addition of neutral sodium or potassium chromate. A similar reduction is observed to the extent of 8—14% in the electrolysis of magnesium chloride alone, and this reduction is not diminished by the addition of chromate. Equimolecular quantities of the alkali chlorides decrease the reduction to 0.5—2% and a further addition of chromate renders it negligible. The minimum decomposition potential of magnesium chloride is 2.01 volts. Basic magnesium hypochlorite so obtained loses water at 155—160°; decomposition with liberation of chlorine and oxygen begins at 260—270° and is complete at 300°, yielding peroxide and basic chlorides. On agitation with boiling water, the hypochlorite shows a slow decrease in its active chlorine content and an increase in the chlorate content. R. B.

**Solubility of Magnesium Carbonate in Water containing Carbon Dioxide under High Pressure, and the Properties of such Magnesium Carbonate Solutions.** O. HAEHNEL (*J. pr. Chem.*, 1924, [ii], 108, 61—74).—Using the apparatus previously described (this vol., ii, 551), the solubility of magnesium carbonate was determined at 18° in water under pressures up to 56 atm. of carbon dioxide. With increasing pressure up to 18 atm., the solubility increases rapidly to a maximum of 7.49% of magnesium carbonate, or 13% of magnesium hydrogen carbonate (per 100 g. of water); above 18 atm. there is no further increase. The saturated solu-

tions of magnesium hydrogen carbonate so obtained decompose but slowly at the ordinary temperature when the pressure is released; the solid hydrogen carbonate decomposes rapidly, but can be kept for some time at  $-5^{\circ}$ . The 13% solution of magnesium hydrogen carbonate has a high electrical conductivity,  $\lambda \cdot 10^6 = 24948$ , about equal to that of a 10% cadmium chloride solution; the salt is highly dissociated.

When the magnesium hydrogen carbonate solution decomposes slowly at  $0^{\circ}$ , it deposits magnesium carbonate pentahydrate. The transition temperature from the penta- to the tri-hydrate is between  $16^{\circ}$  and  $22^{\circ}$ . The change from trihydrate to the anhydrous form only occurs in the presence of carbon dioxide under pressure and starts slightly above  $100^{\circ}$ . The salt obtained between  $100^{\circ}$  and  $150^{\circ}$  tends to change back to the trihydrate. Magnesite is only formed above  $150^{\circ}$ . The existence of mono-, di-, and tetra-hydrates of magnesium carbonate could not be confirmed. E. H. R.

**Crystalline Lattices of the Rhombohedral Carbonates of Bivalent Metals.** G. R. LEVI and A. FERRARI (*Atti R. Accad. Lincei*, 1924, [v], 33, i, 516—521; cf. this vol., ii, 611).—The values of  $\alpha$  for smithsonite, magnesite, dolomite, and calcite are, respectively, 5.870, 5.840, 6.143, and 6.362, the calculated specific gravities being 4.51, 3.08, 2.86, and 2.76, which are in good agreement with the experimental numbers. The results for dolomite accord well with the supposition of a deformation of the lattices of the components, the volume of the basic rhombohedron being intermediate between those of magnesite and calcite. For smithsonite and magnesite, the isomorphism is perfect as regards, not only the angle  $\alpha$ , which has the respective values,  $103^{\circ} 28'$  and  $103^{\circ} 21.5'$ , but also the length  $a$ . It is probable that the true value of  $\alpha$  for smithsonite is somewhat smaller than that given by crystallographic measurements, the disparity being explainable by the difficulty of procuring well-formed crystals of this mineral.

T. H. P.

**Temperature Coefficients of the *E.M.F.* of Silver-Cadmium and Copper-Cadmium Alloys.** E. SCHREINER and K. SELJESAETER (*Z. anorg. Chem.*, 1924, 137, 389—400).—Measurements of the *E.M.F.* of cells containing silver-cadmium or copper-cadmium alloys in combination with pure cadmium in 0.5*N*-cadmium sulphate were made at  $0^{\circ}$  and  $25^{\circ}$ . The temperature coefficient of the silver-cadmium series shows a very marked maximum value with the alloy corresponding with AgCd and a minimum at the composition AgCd<sub>4</sub>. In the copper-cadmium series, the maximum temperature coefficient is obtained with the alloy Cu<sub>2</sub>Cd<sub>3</sub>. By employing the two compounds AgCd and Cu<sub>2</sub>Cd<sub>3</sub> as cathodes and metallic cadmium as anode and measuring the heat of the reactions involved, the value of the temperature coefficient of the *E.M.F.* of the first-named cell as calculated from Helmholtz's equation was found to be of the same order of magnitude as that experimentally obtained.

A. R. P.

**Equilibrium between Fused Metals and Salts. IV. Theoretical. II.** R. LORENZ (*Z. anorg. Chem.*, 1924, **138**, 285—290).—The equation previously derived by the authors for the equilibrium between fused metals and salts (this vol., ii, 484) is applicable only to the simplest cases. An alternative method is adopted and an equilibrium equation derived on the basis of the law of mass-action, the vapour-pressure theory of van Laar (A., 1910, ii, 583), and the conception of thermodynamic potentials. The equation is then applied to the equilibria  $\text{Pb} + \text{CdCl}_2 \rightleftharpoons \text{Cd} + \text{PbCl}_2$ , and  $2\text{Tl} + \text{CdCl}_2 \rightleftharpoons \text{Cd} + \text{Tl}_2\text{Cl}_2$ , and the reaction constants are satisfactorily constant. W. H. R.

**Equilibrium between Metals and Salts in the Molten State. III. The System Thallium-Cadmium-Thalious Chloride-Cadmium Chloride.** R. LORENZ, W. FRAENKEL, and J. SILBERSTEIN (*Z. anorg. Chem.*, 1924, **137**, 204—214; cf. this vol., ii, 258, 484).—When cadmium and thallium are fused under a layer of thalious and cadmium chlorides between 460° and 700°, two phases only are present, a homogeneous salt layer and a homogeneous metal layer. Metallic cadmium is in equilibrium with a salt layer containing about 40 mol.-% of cadmium chloride. When 1 g.-atom of cadmium is fused with 1 g.-mol. of thalious chloride or 2 g.-atoms of thallium with 1 g.-mol. of cadmium chloride, equilibrium is reached when the metal layer contains about 69 at.-% Cd and the salt layer 10 mol.-% of cadmium chloride; addition of an equimolecular mixture of potassium and sodium chlorides to the salt layer causes a gradual displacement (which soon terminates) of the equilibrium from right to left in the equation  $2\text{Tl} + \text{CdCl}_2 \rightleftharpoons \text{Cd} + \text{Tl}_2\text{Cl}_2$ , final equilibrium with the above mixtures being obtained when the salt layer contains about 15 mol.-% of cadmium chloride and the metal layer 60 at.-% Cd. Addition of bismuth to the metal layer causes a considerable displacement of the equilibrium towards the left, showing that thallium is monatomic; antimony causes a much more marked displacement in the same direction, but this is probably due to the formation of a definite cadmium-antimony compound. The effect of alkali chloride on the equilibrium is explained by assuming that thalious chloride has the formula  $\text{Tl}_2\text{Cl}_2$  in the molten salt layer.

A. R. P.

**Low-voltage Arc Spectra of Copper and Silver.** A. G. SHENSTONE.—(See ii, 709.)

**Copper Oxide and the Atomic Weight of Copper.** R. RUER and K. BODE (*Z. anorg. Chem.*, 1924, **137**, 101—114).—Carefully purified cupric oxide can be heated only up to 800° in an atmosphere of oxygen at the ordinary pressure without decomposition. Above this temperature, it becomes gradually converted into cuprous oxide and this change is complete at 1105°. Previous to its use for the determination of the atomic weight of copper by reduction in hydrogen, the oxide was heated at 1000° in purified air, then below 800° in pure oxygen. Prolonged heating

of this material in pure hydrogen at 700—750° gave, as the mean of eight determinations, 63.546 as the atomic weight of copper with a possible error of  $\pm 0.003$ .

A. R. P.

**Double Salts of Potassium Chloride with Cuprous Chloride.**

J. J. P. VALETON and W. FRÖMEL (*Z. anorg. Chem.*, 1924, **137**, 91—100).—A study of the system potassium chloride-cuprous chloride-water at 25° has led to the isolation of the double salts,  $2\text{KCl}, \text{CuCl}$  and  $\text{KCl}, \text{CuCl}, \text{H}_2\text{O}$ , which dissolve congruently in water.

A. R. P.

**Discontinuity in Dehydration of Salt Hydrates.**

E. M. CROWTHER and J. R. H. COUTTS (*Proc. Roy. Soc.*, 1924, **A**, 106, 215—222).—The changes in weight of certain salt hydrates during rapid dehydration have been followed continuously by means of the Odén-Keen automatic recording balance (*ibid.*, 1924, **A**, 106, 33). When thin layers of small crystals were used, to ensure unimpeded drying, the rates of evaporation from copper sulphate pentahydrate and barium chloride dihydrate showed very marked minima at points corresponding with the composition of definite lower hydrates. A parallel is drawn with Faraday's observations on the metastability and efflorescence of hydrated sodium carbonate. An explanation of the phenomena may be based on Langmuir's view that such heterogeneous reactions only proceed at the common boundary of the two solid phases. When one solid phase is present in very small quantity only, the reaction should be correspondingly slow.

S. B.

**Direct Formation of Mercuric Oxychlorides, Oxybromides, and Oxyiodides.**

H. PÉLABON (*Compt. rend.*, 1924, **178**, 1971—1973).—The material of the containing vessel has an important influence on the velocity with which equilibrium between mercuric oxide and mercuric halides, in the presence of water, is reached, and on the nature of that equilibrium. If mercuric oxide, either red or yellow, with water and an amount of mercuric chloride corresponding with that necessary for the formation of the black oxychloride,  $2\text{HgO}, \text{HgCl}_2$  (cf. Toda, A., 1922, ii, 768), be shaken in a glass vessel at 15°, the product blackens in a few hours in fusible soda glass, which is readily attacked by water, whilst in Jena glass it is distinctly yellow after 10 days. The addition of a drop of 0.01*N*-alkali or alkali chloride, however, blackens it rapidly. Blackening takes place in silica, but extremely slowly. Alkali is not essential to the reaction, because the oxide and chloride will react even in the dry state, but it acts as an accelerator. Similar results are obtained with the bromide and iodide, which, however, being less soluble and volatile than the chloride, react more slowly.

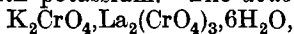
M. S. B.

**Mechanism of the Precipitation of Metals by Hydrogen Sulphide. Sulphur Complexes of Mercury.**

G. McP. SMITH and W. L. SEMON (*J. Amer. Chem. Soc.*, 1924, **46**, 1325—1343).—In the precipitation of sulphides with hydrogen sulphide it is contended that unstable soluble intermediate hydrosulphide com-

plexes are formed and that the excess of hydrogen sulphide present in freshly-precipitated sulphides is partly in combination as a complex hydrosulphide. The preparation of diethylthiolmercurous perchlorate,  $[\text{Hg}(\text{SC}_2\text{H}_5)_2\text{Hg}](\text{ClO}_4)_2$ , is described, and it is shown that the formulæ ascribed to diethylthiolmercurous acetate (cf. Sachs, A., 1921, i, 762) and to diethylthiolmercurous chloride, bromide, and iodide (cf. Hofmann and Rabe, A., 1897, i, 310) should be doubled. Evidence was obtained for the existence of thiomercurous perchlorate. H. T.

**Chromates of Thorium and the Rare Earths. II. Lanthanum, Praseodymium, Neodymium, and Samarium.** H. T. S. BRITTON (*J. Chem. Soc.*, 1924, 125, 1875—1880).—The chromates of lanthanum, praseodymium, neodymium, and samarium, prepared by Böhm's method (cf. A., 1902, ii, 455), form isomorphous, yellow, monoclinic crystals, having the general formula  $\text{M}_2(\text{CrO}_4)_3 \cdot 8\text{H}_2\text{O}$ . The solubilities at 25° are 0.020, 0.021, 0.027, and 0.043, respectively, expressed as g. of anhydrous salt per 100 g. of water; these numbers decrease with rise in temperature. A slight excess of potassium chromate solution precipitates the simple chromates from aqueous solutions of the salts of lanthanum and praseodymium; with neodymium salts a mixture of simple and basic chromates is formed, and with samarium salts, a basic chromate of indefinite composition. Lanthanum, praseodymium, and samarium show a strong tendency to form sparingly soluble double chromates with potassium. The double chromate,



was obtained as a microcrystalline powder by keeping mixed solutions of lanthanum chromate and (excess) potassium chromate. Cleve's potassium samarium chromate (cf. *Chem. News*, 1886, 53, 100) is probably a mixture of a double and a basic chromate.

S. K. T.

**Revision of the Atomic Weight of Aluminium. II. Analysis of Aluminium Chloride.** H. KREPELKA (*J. Amer. Chem. Soc.*, 1924, 46, 1343—1351).—The atomic weight of aluminium was determined from the analysis of carefully synthesised aluminium chloride. The mean of eleven determinations gave a value of  $26.972 \pm 0.001$  ( $\text{Ag} = 107.88$ ;  $\text{Cl} = 35.458$ ). H. T.

**Composition and Properties of Clay.** A. F. JOSEPH and J. S. HANCOCK (*J. Chem. Soc.*, 1924, 125, 1888—1895).—The analysis of homogeneous preparations of clays shows that the most important chemical constant of such substances is the ratio of silica to alumina. This ratio is related to the chemical reactivity shown by clays towards sodium hydroxide and neutral electrolytes. It increases with increase in plasticity, and it is proposed to measure the latter by means of some property which is modified by ignition and by electrolytes, e.g., the moisture equivalent. [Cf. B., 1924, 910.] S. K. T.

**Absorption of Near Infra-red Radiation by Alums.** S. HIGUCHI.—(See ii, 712.)

**Reaction between Hydrogen Chloride and Nitrides. I.** C. MONTEMARTINI and L. LOSANA (*Giorn. Chim. Ind. Appl.*, 1924, **6**, 323—325).—Aluminium, magnesium, calcium, titanium, and boron nitrides are converted almost quantitatively into the corresponding chlorides and ammonia when subjected to the action of hydrogen chloride at temperatures varying from about 600° to 1000°. T. H. P.

**Electrolytic Formation of Alloys and Amalgams of Manganese.** A. N. CAMPBELL (*J. Chem. Soc.*, 1924, **125**, 1713—1719).—Alloys of nickel and of iron with small quantities of manganese are formed by electrolysis of the appropriate mixed electrolytes (sulphates); there is no "Foerster effect," i.e., the manganese content of the alloy (the constituent with the more electronegative equilibrium potential) decreases with decreasing current density. Stable semi-solid amalgams are formed by the electrolysis of a manganese sulphate solution with a well-stirred mercury cathode; no alloy is formed when a lead cathode is used. Attempts to depolarise aluminium discharge by means of manganese were unsuccessful. S. K. T.

**Specific and Latent Heats of Iron and Steel.** A. MALLOCK (*Nature*, 1924, **114**, 429—430).—Curves were obtained showing the variation of expansion of iron containing 0.04% C when heat is supplied continuously, and of the same sample after being heated with graphite for various periods. Heating with graphite for even 30 minutes causes a slight fall in the critical temperature and some change in the character of that part of the curve which indicates the extension while change of state is in progress. With more prolonged heating in graphite, two arrests in the heating and cooling curves are observed. The time necessary for the diffusion of carbon into a thin iron wire is therefore surprisingly long.

A. A. E.

**Relation between Tarnishing and Corrosion.** U. R. EVANS (*Trans. Amer. Electrochem. Soc.*, 1924, **46**, 75—100).—It is shown that the presence of moisture is essential for corrosion of iron or zinc to take place in an atmosphere containing sulphur dioxide and for any action to take place between copper and hydrogen sulphide, and that the course of all these reactions in the presence of sufficient moisture is in accord with the electrochemical theory of corrosion. In an atmosphere of hydrogen sulphide not saturated with water vapour, however, copper becomes slowly covered with an iridescent coloured film which is only partly permeable to gases and becomes more protective as it increases in thickness until colours of the fourth order are reached, when further action ceases. The condensation of liquid water on this film immediately sets up corrosion proper and the film soon breaks up into flocculent copper sulphide. [Cf. *B.*, 1924, 913.] A. R. P.

**Free and Pearlitic Cementite.** E. MAURER and F. STÄBLEIN (*Z. anorg. Chem.*, 1924, **137**, 115—124).—The specific resistance of iron-carbon alloys (steel) increases linearly with the carbon



content to 0.9% C when a sharp bend occurs in the curve and the resistance then increases at a slower rate with increase in the carbon content. This break corresponds with a change in the character of the pearlite from lamellar to granular. The specific resistance of iron carbide varies between 0.8 and 0.9. [Cf. B., 1924, 871.] A. R. P.

**Kinetics of the Ionic Reaction between Ferric and Iodide Ions.** N. SASAKI (*Z. anorg. Chem.*, 1924, **137**, 181—203; 291—327).—The reaction between ferric chloride and a soluble iodide in the presence of sodium chloride consists essentially of the decomposition of those ionic groups which can be formed from the ferric chloride molecule and its dissociation products by the replacement of one, two, and three atoms of chlorine by iodine, and the concentration of these groups has been calculated on the assumption that the chlorine and iodine ions behave electrolytically in the same manner. With a large excess of sodium chloride the ionic reaction takes place in a simple manner and the speeds of the different reactions can then be calculated without the above assumption. The calculated velocity constant of the reaction between varying quantities of ferric and ferrous salts and a soluble iodide agrees closely with the results obtained in numerous experiments. The reaction is not affected by light provided that the liberated iodine is removed, as fast as it is formed, by addition of thiosulphate; the resulting tetrathionate and the starch used as indicator have no effect on the velocity of the reaction, but the starch-iodine complex accelerates, and the accumulation of ferrous salt retards it. The latter action is entirely due to ferrous ions and is exerted only during the double decomposition between ferric and iodide ions. In the presence of sodium chloride, the reaction is of the first order with respect to ferric ions in strongly acid solutions and of the second order in feebly acid solutions, the difference being due entirely to the action of the acid in repressing hydrolysis of the ferric salt. The order of the reaction with respect to iodide ions lies between the first and second, but under certain conditions the reaction can be of an even higher order. The velocity of the reaction between tri-iodide and ferric salt is approximately one-tenth that between the normal iodide and a ferric salt. A new "precision burette" is described and illustrated; it allows a liquid to run into a solution at any desired rate and permits of readings being taken with an accuracy of 0.002 to 0.003 c.c. A. R. P.

**Complex Ferrous Sulphate-Ammonia Compounds.** J. A. VERHOEFF (*Chem. Weekblad*, 1924, **21**, 471).—By treatment of ferrous ammonium sulphate with ammonia in a reducing atmosphere and precipitation with alcohol saturated with ammonia, a white precipitate,  $\text{FeSO}_4 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ , very sensitive to traces of oxygen, was obtained (cf. Peters, A., 1913, ii, 42). S. I. L.

**Catalytic Oxidation of Ferrous Sulphate by Air in presence of Copper Salts.** J. A. VERHOEFF (*Chem. Weekblad*, 1924, **21**, 469—470).—Oxidation of a ferrous salt on passage of a stream of

air proceeds very slowly in acid solution. Addition of zinc oxide causes fairly rapid oxidation; if zinc sulphate also be present in such proportions that the concentration of zinc ions is greater than that of ferrous ions, the reaction velocity calculated for the second order  $[2\text{FeSO}_4 + \text{O} + 3\text{H}_2\text{O} + 2\text{ZnO} \rightarrow 2\text{Fe}(\text{OH})_3 + 2\text{ZnSO}_4]$  is fairly constant ( $K=0.000555$ ). Addition of copper sulphate increases the velocity considerably, but not in proportion to the amount added. In presence of ammonia and an ammonium salt, and a copper salt, ferrous salts take up oxygen so rapidly that the solution may be employed as an absorbent in analysis. S. I. L.

**Conversion of Nickel Carbonyl into Carbonate in Toluene Solution.** P. C. L. THORNE (*J. Chem. Soc.*, 1924, 125, 1967—1968).—Solutions of nickel carbonyl in toluene deposit a basic nickel carbonate on exposure to air, and not a compound of the carbonyl and hydroxide (cf. A., 1900, ii, 349). S. K. T.

**Thermoelectrical and Actinoelectrical Properties of Molybdenite.** W. W. COBLENTZ.—(See ii, 716.)

**Compounds of Tervalent Molybdenum. I.** W. WARDLAW, F. H. NICHOLLS, and N. D. SYLVESTER (*J. Chem. Soc.*, 1924, 125, 1910—1913).—A new *molybdenum oxysulphate*,  $\text{Mo}_2\text{O}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$  ( $x=5$  or  $6$ ), is obtained as a green, hygroscopic precipitate when an electrolytically reduced solution of molybdenum trioxide in sulphuric acid is poured into air-free acetone. It precipitates the metals from copper sulphate and silver nitrate solutions and reduces mercuric and ferric salts to the mercurous and ferrous condition respectively; it decomposes on heating:  $\text{Mo}_2\text{O}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O} = \text{Mo}_2\text{O}_5 + 2\text{SO}_2 + x\text{H}_2\text{O}$ . The sulphate radical is precipitated by barium chloride only on warming. When dried over phosphorus pentoxide, the salt turns grey and the sulphate content decreases. S. K. T.

**Preparation of Metallic Tungsten and Some of its Alloys.** L. and H. H. KAHLBERG (*Trans. Amer. Electrochem. Soc.*, 1924, 46, 51—61).—Tungsten trioxide dissolves in fused alkali chloride with the evolution of chlorine and the formation of a compound,  $\text{M}_2\text{O} \cdot \text{W}_2\text{O}_5$ ; under similar conditions, tungstic acid,  $\text{H}_2\text{WO}_4$ , causes the evolution of hydrogen chloride and the formation of the tungstate,  $\text{M}_2\text{O} \cdot 5\text{WO}_3$ , but prolonged heating is necessary for complete removal of the hydrogen chloride. Electrolysis of tungstic acid dissolved in a fused mixture of sodium and potassium chlorides yielded good deposits of very pure tungsten when the ratio of tungstic acid to fused chloride was less than 1:2; a blue crystalline tungsten bronze,  $\text{Na}_2\text{O} \cdot \text{W}_5\text{O}_{14}$ , when the ratio was 1:1; a red bronze,  $2\text{Na}_2\text{O} \cdot \text{W}_5\text{O}_{13}$ , when the ratio was 3:5; and a violet bronze when the ratio was 4:5. From solutions of tungstic acid in fused chlorides, zinc and aluminium liberated very finely-divided metallic tungsten, whereas iron had no action; excess of zinc or aluminium yielded alloys of these metals with tungsten. Nickel-tungsten alloys were obtained by electrolysis of mixtures of nickel chloride, alkali chloride, and tungstic acid. [Cf. B., 1924, 913.] A. R. P.

**Preparation of Pure Uranium.** W. JANDER (*Z. anorg. Chem.*, 1924, 138, 321—329).—Uranium dioxide is reduced by heating with metallic calcium, in a welded iron crucible embedded in charcoal, for 40 minutes at 950—1250°. The resulting mass is then treated with ammonium chloride solution to remove the unchanged calcium, and the residual powder is levigated, when a light black powder is separated which consists of highly oxidised uranium. The remaining powder contains particles of iron which can be separated by a magnet, and the residue is then passed through a sieve which retains coarse impure powder, and gives a fine black powder containing about 97.2% U, 2.5% Fe, and 0.3% O, the yield being about 66% of the theoretical. If the crucible is prepared with a thick lining of lime, a product is obtained containing 99.9% U, and not more than 0.09% O, but the yield is only 27% of the theoretical. W. H. R.

**Hydrates and Hydrogels. VI. The Simplest Stannic Acids.** R. WILLSTÄTER, H. KRAUT, and W. FREMERY (*Ber.*, 1924, 57, [B], 1491—1501; cf. this vol., ii, 266).—Stannic hydroxide gels, when prepared by the action of ammonium hydroxide and ammonium chloride on stannic chloride under conditions which ensure a low hydroxyl-ion concentration and great rapidity of experiment, and subsequently dried by the authors' acetone method at -35° to -10°, have the composition  $\text{Sn}(\text{OH})_4 \cdot \text{H}_2\text{O}$ , whereas after similar treatment at the atmospheric temperature they have the composition of the ortho compound,  $\text{Sn}(\text{OH})_4$ . Monostannic acid becomes transformed in an aqueous medium into a more feebly basic acid which appears to be the first member of a series of  $\alpha$ -stannic acids [termed previously (*loc. cit.*)  $\alpha'$ -acids]. When dried by the acetone process at 0—10°, the compound has approximately the composition of an orthodistannic acid,  $(\text{OH})_3\text{Sn} \cdot \text{O} \cdot \text{Sn}(\text{OH})_3$ , whereas after treatment at 30—56° or on prolonged heating with acetone it has exactly the composition of an orthotetrestannic acid,  $(\text{OH})_3\text{Sn} \cdot \text{O} \cdot \text{Sn}(\text{OH})_2 \cdot \text{O} \cdot \text{Sn}(\text{OH})_2 \cdot \text{O} \cdot \text{Sn}(\text{OH})_3$ . It therefore appears probable that the union of several molecules of stannic hydroxide with loss of water yields a series of polyorthostannic acids with diminishing basic properties.

Ferric hydroxide gels prepared from ferric ammonium alum, ammonia, and ammonium sulphate in weakly alkaline solution and dried by the acetone process are intermediate in stability between aluminium hydroxide and stannic hydroxide. The water content of the product, treated at +10° to +20°, is somewhat less than that required by the formula  $\text{Fe}(\text{OH})_3$ , and decreases slowly when the substance is preserved for a protracted period in contact with water. A preparation dried with acetone at -15°, on the other hand, had approximately the composition required by the formula,  $\text{Fe}(\text{OH})_3 \cdot \text{H}_2\text{O}$ .

The nature of the dehydration curves of gels in comparison with those of hydrates is discussed in detail. H. W.

**Vanadium in Petroleum.** E. S. PORTER (*Mining and Met.*, 1924, 5, 133).—A review. CHEMICAL ABSTRACTS.

**Chlorides of Bivalent Molybdenum, Tungsten, and Tantalum. III. Derivatives of Tri-tantalum Hexachloride** ["Tantalum Dichloride"]. K. LINDNER and H. FEIT (*Z. anorg. Chem.*, 1924, 137, 66—78).—The "dichloride,"  $Ta_3Cl_6$ , is formed by heating tantalum pentachloride with metallic lead at  $600^\circ$  in an atmosphere of nitrogen. The residue is extracted with dilute hydrochloric acid in a reflux apparatus, and after removal of the lead with hydrogen sulphide the solution is evaporated in a vacuum, whereby a green precipitate of  $Ta_3Cl_6$  is obtained. Saturation of the solution with hydrogen chloride yields dark green, six-sided crystals of  $H[Ta_3Cl_7 \cdot H_2O] \cdot 3H_2O$  analogous to the corresponding molybdenum compound (this vol., ii, 192). The chloro-acid dissolves in alcohol and the solution yields, on evaporation in a vacuum, the compound  $H[Ta_3Cl_7 \cdot EtOH] \cdot EtOH$  as a brown, resinous mass. With pyridine and hydrochloric acid in aqueous and in alcoholic solutions, deep green crystalline compounds are formed similar to the corresponding molybdenum compounds; the following are described:  $(C_5H_5N)_2H_2[Ta_3Cl_8] \cdot 3H_2O$ ,  $(C_5H_5N)H[Ta_3Cl_7 \cdot C_5H_5N]$ , and  $(C_5H_5N)H_3Ta_3Cl_9$ .

Extraction of the lead reduction product of tantalum pentachloride with hydrobromic acid yields a solution from which green crystals of  $H[Ta_3Cl_6Br \cdot H_2O] \cdot 3H_2O$  are obtained by evaporation in a vacuum. With pyridine and ether, this acid yields the salt  $(C_5H_5N)H[Ta_3Cl_6Br \cdot C_5H_5N]$ , and with pyridinium bromide and saturation of the solution with hydrogen bromide, dark red cubic crystals of  $(C_5H_5N)H_3[Ta_3Cl_6Br_3]$ .

Extraction of the lead reduction product with dilute sulphuric acid and evaporation of the solution yields the sulphato-acid,  $H_2[Ta_3Cl_6SO_4]$ . Treatment of the chloro-acid with dilute potassium hydroxide followed by acidification with acetic acid gives a dark brown, amorphous precipitate of  $[Ta_3Cl_5(H_2O)_5]OH \cdot aq$ . In all the above compounds tantalum is shown to be bivalent. A. R. P.

**Micro-determination of the Oxide Content of Colloidal Gold.** P. A. THIESSEN (*Mikrochemie*, 1924, 2, 1—13).—The substance was heated at  $400^\circ$  in a current of pure carbon dioxide and the resulting gases were measured and analysed; the loss in weight of the substance was also determined. Red colloidal gold, prepared by means of formaldehyde, coagulated with sodium chloride and washed free from chloride, did not contain any oxide; colloidal gold prepared with hydrazine hydrate, however, contained from 12.8 to 36.4% of gold oxide. W. P. S.

**Oxide Content of Colloidal Gold.** W. PAULI (*Mikrochemie*, 1924, 2, 47—50).—A claim for priority (cf. A., 1923, ii, 329) against Thiessen (preceding abstract). W. P. S.

**Isomorphism between certain Cubic Compounds of Platinum, Lead, Selenium, and Tin.** E. CAROZZI (*Gazzetta*, 1924, 54, 556—567).—The following compounds form crystals belonging to the cubic system:  $(NH_4)_2PbCl_6$ , lemon-yellow

octahedra,  $d$  2.925;  $(\text{NH}_4)_2\text{SnCl}_6$ , colourless octahedra with vertices truncated by cube faces,  $d$  2.39,  $n_D$  1.677 at  $18^\circ$ ;  $(\text{NH}_4)_2\text{PtCl}_6$ , orange-yellow octahedra,  $d$  3.009;  $(\text{NH}_4)_2\text{SeBr}_6$ , deep red octahedra,  $d$  3.328;  $(\text{NH}_4)_2\text{SnBr}_6$ , pale yellow octahedra often showing cube faces,  $d$  3.51;  $(\text{NH}_4)_2\text{PtBr}_6$ , scarlet octahedra often combined with cube faces,  $d$  4.20.  $(\text{NH}_4)_2\text{PbCl}_6$  and  $(\text{NH}_4)_2\text{SnCl}_6$  form isomorphous mixtures for which the specific volumes and refractive indices lie on a straight line between those of the components. Similar behaviour is shown by isomorphous mixtures of  $(\text{NH}_4)_2\text{SeBr}_6$  and  $(\text{NH}_4)_2\text{SnBr}_6$ ,  $(\text{NH}_4)_2\text{SeBr}_6$  and  $(\text{NH}_4)_2\text{PtBr}_6$ , and  $(\text{NH}_4)_2\text{SnCl}_6$  and  $(\text{NH}_4)_2\text{PtCl}_6$ , excepting that in the last case a miscibility gap exists between 22% and 74.5% of  $(\text{NH}_4)_2\text{SnCl}_6$ . T. H. P.

**Pentammine Compounds of Quadrivalent Platinum.** L. TSCHUGAEV (*Z. anorg. Chem.*, 1924, **137**, 1—31).—Ammonium chloroplatinate is converted by the prolonged action of liquid ammonia at the ordinary temperature in a sealed tube into a mixture of hexammineplatinic chloride, dichlorotetrammineplatinic chloride, and amidochlorotetrammineplatinic chloride,  $[\text{Pt}(\text{NH}_3)_4\text{NH}_2\text{Cl}]\text{Cl}_2$ . The latter is converted by the action of hot, dilute hydrochloric acid into chloropentammineplatinic chloride,  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$ , which, together with the hexammine salt, dissolves, leaving a residue of the tetrammine salt. The solution yields a yellow, crystalline precipitate of the amidotetrammine compound with ammonia, whilst the hexammine salt can be recovered from the solution by precipitation with strong hydrochloric acid. A better yield of the chloropentammine salt may be obtained by the action of 20% ammonia solution and ammonium carbonate or phosphate on the chloroplatinate. In the presence of carbonate, chloropentammineplatinic carbonate,  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]_2(\text{CO}_3)_3$ , is formed as a white, amorphous precipitate in 12 to 14 days at the ordinary temperature, whilst in the presence of phosphate the corresponding phosphate crystallises from a hot solution as white needles after heating for 10 minutes; in either case, chloropentammineplatinic chloride is obtained by dissolving the precipitate in dilute hydrochloric acid and, after filtration, adding a large excess of strong hydrochloric acid.

*Chloropentammineplatinic chloride* crystallises in needles or prisms which are readily soluble in water and decompose on keeping into dichlorotetrammineplatinic chloride and amidochlorotetrammineplatinic chloride, both of which are white, sparingly soluble compounds. With potassium iodide, the pentammine salt gives black crystals of *di-iodotetrammineplatinic iodide*,  $[\text{Pt}(\text{NH}_3)_4\text{I}_2]\text{I}_2$ , and with chloroplatinic acid, thin, orange-yellow, sparingly soluble rhombohedra of the *chloro-chloroplatinate*,  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl} \cdot \text{PtCl}_6 \cdot 2\text{H}_2\text{O}$ . The following salts of the pentammine series are described: *chloropentammineplatinic bromide*,  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Br}_3$ , pale yellow, sparingly soluble needles; *chloropentammineplatinic nitrate*,  $[\text{Pt}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_3$ , colourless prisms; *bromopentammineplatinic bromide*,  $[\text{Pt}(\text{NH}_3)_5\text{Br}]\text{Br}_3$ ;

yellow prisms.

[In part with W. CHLOPIN.]—Hot dilute sodium hydroxide

solution converts the chloropentammine salts into hydroxypentammine compounds. The following are described: *hydroxypentammineplatinic chloride*,  $[\text{Pt}(\text{NH}_3)_5\text{OH}]\text{Cl}_2$ , colourless, rhombic tablets or needles; *hydroxypentammineplatinic nitrate*,  $[\text{Pt}(\text{NH}_3)_5\text{OH}](\text{NO}_3)_3$ , colourless, glistening scales. The former compound is converted into the tetrammine compound on heating with hydrochloric acid in a sealed tube at  $150^\circ$  and ammonium chloride and water are liberated.

The reactions of the hexammine- and chloropentammine-platinic salts recall those of barium and lead, as they give characteristic precipitates with sulphuric acid, potassium chromate, potassium oxalate, ammonium carbonate, and ammonium chloride.

A. R. P.

**New Series of Acidoamidotetrammine Derivatives of Quadrivalent Platinum. II.** L. TSCHUGAEV (*Z. anorg. Chem.*, 1924, **137**, 401—406).—Acidoamidotetrammineplatinic salts are obtained by treating the corresponding acidopentammineplatinic salt with ammonia or a neutral ammonium salt. They are all characterised by a pale yellow colour and are usually slightly soluble in water, giving strongly alkaline solutions; treatment with acid regenerates the acidopentammine salt, whilst alkali hydroxides transform further ammino groups into amido groups. The following compounds of this series are described: *amidochlorotetrammineplatinic chloride*,  $[\text{Pt}(\text{NH}_3)_4\text{NH}_2\text{Cl}]\text{Cl}_2$ , *bromide*,  $[\text{Pt}(\text{NH}_3)_4\text{NH}_2\text{Cl}]\text{Br}_2$ , and *nitrate*,  $[\text{Pt}(\text{NH}_3)_4\text{NH}_2\text{Cl}](\text{NO}_3)_2$ ; *amidobromotetrammineplatinic bromide*,  $[\text{Pt}(\text{NH}_3)_4\text{NH}_2\text{Br}]\text{Br}_2$ , all yellow, crystalline substances.

A. R. P.

**Ruthenium Halides.** F. KRAUSS and H. KÜENTHAL (*Z. anorg. Chem.*, 1924, **137**, 32—38).—Chlorination of ruthenium at  $360^\circ$  in the presence of carbon monoxide results in the formation of a mixture of chlorides in which the dichloride predominates (cf. Howe, Howe, and Ogburn, this vol., ii, 344). Prolonged action of the chlorine gave a product containing 46% Cl corresponding almost exactly with  $\text{Ru}_2\text{Cl}_5$ . The solution of these compounds in dilute alcohol is blue or violet and reacts only very slowly with silver nitrate, hydrogen sulphide, and potassium hydroxide, so that it would appear that the liquid contains the ruthenium as complex compounds possibly with the co-ordination number 4.

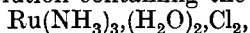
Ruthenium trichloride and tribromide may be made by heating the trihydroxide in the corresponding hydrogen halide at  $100$ — $110^\circ$  and the iodide by addition of potassium iodide to an aqueous solution of the chloride. Ruthenium trifluoride could not be made by any similar process.

A. R. P.

**Platinum Metals. V. Thermal Decomposition of Ruthenium Trichloride and Ruthenium Dioxide.** H. REMY [with M. KÖHN] (*Z. anorg. Chem.*, 1924, **137**, 365—388; cf. A., 1923, ii, 329).—Measurements of the decomposition tension of ruthenium trichloride between  $689^\circ$  and  $841^\circ$  indicate that the

substance decomposes directly into its elements on heating without the intermediate formation of lower chlorides of ruthenium. The pressure of oxygen in equilibrium with ruthenium dioxide at  $930^{\circ}$  and  $950^{\circ}$  is reduced considerably by admixture of finely-divided ruthenium with the dioxide, but the reduction of pressure is independent of the proportions of the two substances within wide limits, showing that a definite lower oxide of ruthenium is incapable of existence at these temperatures, but that a continuous series of solid solutions exists between the metal and its dioxide. The heats of formation of ruthenium trichloride and dioxide are, respectively,  $\text{Ru} + 1.5\text{Cl}_2 = \text{RuCl}_3 + 63 \text{ Cal.}$  and  $\text{Ru} + \text{O}_2 = \text{RuO}_2 + 52.5 \text{ Cal.}$   
A. R. P.

**Reaction Products of Ruthenium Tetroxide and Hydrochloric Acid.** S. AOYAMA (*Z. anorg. Chem.*, 1924, **138**, 249—270).—Ruthenium tetroxide and hydrogen chloride react to form tetrachloro-oxyruthenic acid,  $\text{H}_2\text{RuO}_4\text{Cl}_4 \cdot 3\text{H}_2\text{O}$ , reddish-brown, needle-shaped, hygroscopic crystals, which dissolves in water to give an acid solution. When these crystals are treated with concentrated aqueous hydrochloric acid, chlorine is given off, and a reddish-brown solution obtained which contains both hexachlororuthenic acid,  $\text{H}_2\text{RuCl}_6$ , and pentachlororuthenious acid,  $\text{H}_2\text{RuCl}_5$ , whilst the ammonium salts of these two acids are formed if the tetrachloro-oxyruthenic acid is treated with ammonium chloride solution. A series of colour changes occurs when ammonia is added to a solution of tetrachloro-oxyruthenic acid, with the ultimate formation of a violet solution containing the compound



which has been isolated as a violet powder.

Ammonium chlororuthenate,  $(\text{NH}_4)_2\text{RuCl}_6 \cdot 0.5\text{H}_2\text{O}$ , may be prepared by the interaction of concentrated aqueous hydrochloric acid with ruthenium tetroxide, the solution being heated, saturated with a mixture of chlorine and hydrogen chloride, kept for some hours, and then again saturated with chlorine and hydrogen chloride. The mixture is then cooled in ice and treated with concentrated ammonium chloride solution, when the ammonium chlororuthenate separates in pale brown, star-shaped crystals belonging to the cubic system. These crystals dissolve in water to form a brown solution, which on dilution first turns yellow and then deposits a black precipitate owing to hydrolysis. The salt is slowly but completely decomposed by hydrogen sulphide, the whole of the ruthenium being precipitated. The blue colour test for ruthenium is not sensitive in this case. Potassium chlororuthenate,  $\text{K}_2\text{RuCl}_6$ , may be prepared similarly, and is anhydrous, but otherwise generally resembles the ammonium salt.

Potassium chlororuthenite,  $\text{K}_2\text{RuCl}_5$ , may be prepared by heating the chlororuthenate in dry hydrogen chloride at  $540^{\circ}$ . It is quite stable in solution, and exists in three modifications of which the present or  $\gamma$  form is different from both the ordinary  $\alpha$  form, and from the  $\beta$  form prepared by Howe (*A.*, 1902, ii, 86).

Ruthenium dioxide,  $\text{RuO}_2$ , may be prepared in the form of bluish-

black, lustrous crystals, by heating tetrachloro-oxyruthenic acid or ammonium chlororuthenate in a current of oxygen at a temperature not above 540°.

The reaction between hydrochloric acid and ruthenium tetroxide is best represented by the equations (i)  $\text{RuO}_4 + 6\text{HCl}(\text{gas}) = \text{H}_2\text{RuO}_5\text{Cl}_4 + \text{Cl}_2 + 2\text{H}_2\text{O}$ ; (ii)  $\text{H}_2\text{RuO}_5\text{Cl}_4 + 4\text{HCl} = \text{H}_2\text{RuCl}_6 + \text{Cl}_2 + 2\text{H}_2\text{O}$ ; (iii)  $2\text{H}_2\text{RuCl}_6 \rightleftharpoons 2\text{H}_2\text{RuCl}_5 + \text{Cl}_2$ . W. H.-R.

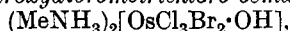
**Osmiridium and the Separation therefrom of Metals of the Platinum Group.** V. REKSCHINSKI (*Trans. Inst. Chem. Reagents, Moscow*, 1923, No. 2, 28—41).—Descriptive.

G. A. R. K.

**Osmium Tetroxide. I. Valency of Osmium in its Tetroxide.** F. KRAUSS and D. WILKEN (*Z. anorg. Chem.*, 1924, **137**, 349—364).—Digestion of osmium tetroxide with concentrated hydrochloric acid and potassium iodide results in the liberation of exactly 4 atoms of iodine per mol. of tetroxide. The solution contains a compound,  $\text{Os}(\text{OH})\text{Cl}_3$ , from which compounds may be prepared in which the osmium is combined with 4 atoms of chlorine. Hydrolysis of solutions of  $\text{Os}(\text{OH})\text{Cl}_3$  yields a black precipitate of  $\text{OsO}_2 \cdot 2\text{H}_2\text{O}$  identical with that obtained by Ruff by neutralising solutions of alkali osmates with sulphuric acid. This black compound absorbs 4 atoms of oxygen per mol. from potassium permanganate and is reconverted thereby into osmium tetroxide. These facts confirm the octovalency of osmium in its tetroxide.

The compound *osmium hydroxytrichloride*,  $\text{Os}(\text{OH})\text{Cl}_3$ , crystallises from the brown solution obtained by the action of hydrochloric acid on osmium tetroxide in the form of long, brown, hygroscopic needles containing water which is lost at 150°, leaving a black, sintered mass of the anhydrous compound. With alkali chlorides, a feebly acid solution of this compound yields *alkali hydroxypentachloro-osmates*  $\text{M}_2[\text{OsCl}_5 \cdot \text{OH}]$ , of which the potassium, rubidium, and caesium salts are only slightly soluble, thus resembling the corresponding hexachloroplatinates. The sodium salt crystallises in large, red octahedra, and the other salts in small, red to yellow, stellate aggregates of octahedra. *Ammonium hydroxypentachloro-osmate*,  $(\text{NH}_4)_2[\text{OsCl}_5 \cdot \text{OH}]$ , forms sparingly soluble, reddish-brown needles and the *methylammonium* salt,  $(\text{MeNH}_3)_2[\text{OsCl}_5 \cdot \text{OH}]$ , soluble, yellowish-red leaflets.

Recrystallisation of hydroxypentachloro-osmates from concentrated hydrochloric acid results in the formation of the darker coloured, more soluble hexachloro-osmates described by Gutbier (A., 1910, ii, 45). With concentrated hydrobromic acid, the methylammonium salt described above yields the corresponding *bromopentachloro-osmate*,  $(\text{MeNH}_3)_2[\text{OsCl}_5\text{Br}]$ , in glistening, deep red, six-sided leaflets. With methylammonium bromide, a feebly hydrobromic acid solution of osmium hydroxytrichloride gives light red leaflets of *methylammonium hydroxydibromotrichloro-osmate*,



which with concentrated hydrobromic acid gives *methylammonium trichlorotribromo-osmate*,  $(\text{MeNH}_3)_2[\text{OsCl}_3\text{Br}_3]$ , dark red leaflets.



Attempts to prepare hydroxypentabromo-osmates proved unsuccessful except in the case of the methylammonium salt, which is formed on adding methylammonium bromide to a solution of hydrated osmium dioxide in dilute hydrobromic acid. It crystallises in light brown needles.

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A. R. P.

## Mineralogical Chemistry.

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**Evolution of Iron Oxides.** A. BRUN (*Arch. Sci. phys. nat.*, 1924, [v], 6, 244—263; cf. A., 1917, ii, 497).—Lava passing from the vitreous to the crystalline stage traverses a period in which ferrous oxide is deposited as a new mineral, "iozite," the presence of which indicates the absence of water at the time of its formation. The ferrous oxide content of a lava is reduced by the oxidising action of air or steam; hence the magma in the crater is probably less highly oxidised than the lava outside. Metallic iron in a lava is considered to be primitive, and not reduced from an oxide.

S. K. T.

**Ferronickel and Troilite in Meteorites.** P. N. TSCHIRVINSKI (*Bull. Inst. Sci. Petrograd*, 1922, 5, 111—115; from *Chem. Zentr.*, 1924, i, 2507).—The ratio of ferronickel to troilite in 81 meteorites was found to approximate to 67.62 : 22.38.

G. W. R.

**Chemical Composition of Pallasite.** P. N. TSCHIRVINSKI (*Bull. Acad. Sci. Petrograd*, 1917, 387—398; from *Chem. Zentr.*, 1924, i, 2507).—The mean chemical composition of pallasite approximates to the formula  $R_2SiO_4 + 3(Fe, Ni)$ , where R = nickel or iron. The volume ratio of olivine to ferronickel is 7 : 3, which is equal to the ratio of the respective numbers of atoms in the two minerals.

G. W. R.

**Chlorophoenicite, a New Mineral from Franklin Furnace, New Jersey.** W. F. FOSHAG and R. B. GAGE (*J. Wash. Acad. Sci.*, 1924, 14, 362—363).—This is found as pale-green (by daylight; but purplish-red by artificial light), prismatic crystals in the franklinite-zincite ore. It resembles the pale-green willemite in appearance, but is readily distinguished from this by the fact that in the bulb-tube or before the blowpipe it blackens and fuses with difficulty only on the edges. The crystals are monoclinic and elongated in the direction of the axis of symmetry;  $n(\alpha)$  1.682,  $n(\beta)$  1.690,  $n(\gamma)$  1.697. Analysis :

As <sub>2</sub> O <sub>5</sub> .	MnO.	ZnO.	CaO.	MgO.	FeO.	H <sub>2</sub> O.	Total.
19.24	34.46	29.72	3.36	1.34	0.48	11.60	100.24

gives the highly basic formula,  $R_3As_2O_8 \cdot 7R(OH)_2$ . L. J. S.

**"Hydrozincite."** C. PERRIER (*Atti Soc. ital. Sci. nat. Milano*, 1915, 54, 188—222; from *Chem. Zentr.*, 1924, i, 2505).—The excess

of water in the compound, to which the formula  $2\text{ZnCO}_3, 3\text{Zn}(\text{OH})_2$  is given, is held by adsorption, since the water of constitution is not lost below  $165^\circ$ . Hydrazincites occur having colloid phases and excess of zinc hydroxide formed from the hydrolysis of zinc carbonate.

G. W. R.

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## Analytical Chemistry.

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**Micro-muffle.** F. PREGL (*Mikrochemie*, 1924, 2, 75—76).—A micro-muffle for heating organic compounds of metals with strong sulphuric acid consists of a horizontal tube 10 mm. in diameter having a piece of wire gauze wrapped round it at the point at which the burner is placed and a second tube, 15 mm. in diameter and bent at right angles, attached loosely at one end. The second tube has a piece of wire gauze round part of the vertical section, so that, by applying heat at this spot, a current of warm air is caused to pass over the substance which is heated in the boat in the horizontal tube.

A. R. P.

**Pipette for Microchemical Analysis.** A. NAGY (*Mikrochemie*, 1924, 2, 19—20).—The pipette consists of a narrow graduated glass tube to the upper end of which is attached a surgical glass syringe of about 1 c.c. capacity.

W. P. S.

**Centrifugal Filter.** F. PREGL (*Mikrochemie*, 1924, 2, 76—78).—The filter consists of a tube about 7 cm. long and 6 mm. in diameter having, about 2 cm. from one end, a conical constriction which reduces the bore at that point to 0.2—0.5 mm. The end nearest the constriction is opened out to make a flange and the other end is closed with a cork. A small piece of cotton wool is placed in the constriction at the shorter end of the tube, and on this are placed the liquid and precipitate. The whole is placed in a hand-operated centrifugal machine and, after centrifuging, the mother-liquor is removed by taking out the cork and the precipitate by withdrawing the filter plug.

A. R. P.

**Gravimetric Determinations with Filter-tubes.** H. HÄUSLER (*Z. anal. Chem.*, 1924, 64, 361—379; cf. Gartner, A., 1921, ii, 123).—A method for the gravimetric determination of precipitates involving the use of asbestos or spongy platinum in filter-tubes constructed of glass, porcelain, or platinum, by means of which filtration may be effected with the aid of suction, is described. The whole of the operations are carried out in a single vessel, which consists of the filter-tube and a precipitation vessel which are weighed together, the latter being a beaker or a crucible, according to the heat treatment required by the precipitate. The method is rapid, efficient, and accurate both for micro-analysis (2—10 mg.) and macro-analysis (0.1—0.2 g.). Details of the construction of the filter-tubes and the whole technique of the operation

are given, together with the results of both micro- and macro-determinations of most of the common ions, the results being in all cases satisfactory. J. W. B.

**Quantitative Microchemical Separations. I. Use of "Filter-tubes."** A. BENEDETTI-PICHLER (*Z. anal. Chem.*, 1924, **64**, 409—436; cf. preceding abstract).—"Filter-tubes" for microchemical filtrations consist of narrow capillary tubes having a bulb packed with fine, long asbestos threads sealed to the lower end. The upper end of the tube is attached by a rubber connexion to a glass tube, which passes into a pressure filtration flask and terminates just above a small test-tube in which the filtrate is collected. In filtering, the lower end of the tube is placed just below the surface of the liquid in the beaker and the whole contents are slowly sucked through the filter. The precipitate is washed by rinsing the walls of the beaker with the washing liquid and sucking this through the filter. The tube is eventually transferred to a drying oven at a suitable temperature and finally weighed with the precipitate. In case it is necessary to ignite the precipitate, a quartz filter-tube is used. For use in microchemical analysis, various types of beakers, crucibles, stirring rods, and washing apparatus are described and details are given of the procedure followed in the separation of silver from copper by precipitation as chloride, calcium from magnesium by the oxalate method, and potassium from sodium by the cobaltinitrite process. [Cf. *B.*, 1924, 892.] A. R. P.

**Use of Filter-paper Pulp in Analysis.** E. WILKE-DÖRFURT and E. LOCHER (*Z. anal. Chem.*, 1924, **64**, 436—441).—When using filter paper pulp to assist the filtration of iron or aluminium hydroxides or basic acetate the precipitate should not subsequently be digested with strong nitric or sulphuric acid, as organic complexes are thereby formed which hinder reprecipitation of the iron or aluminium by the usual hydrolysing agents and, in certain cases, may entirely prevent the formation of any precipitate. A. R. P.

**Micro Gas Analysis.** L. REEVE (*J. Chem. Soc.*, 1924, **125**, 1946—1954).—An accurate method of micro gas analysis is described in which the volumes (about 0.05 c.c.) are measured at atmospheric pressure in a calibrated capillary tube (cf. Timiriazeff, *Ann. Chim. Phys.*, 1877, [v], **12**, 355). Methods of analysing for carbon monoxide and dioxide, hydrogen, hydrocarbons, and formaldehyde are described; a method is also suggested for the direct micro-determination of oxygen. S. K. T.

**Correction Tube for Gas Burettes.** F. C. VILBRANDT (*Ind. Eng. Chem.*, 1924, **16**, 936—937).—The compensator (figured in the original) consists of two concentric tubes, the inner one being open at the bottom. The whole apparatus thus becomes compact enough to go inside the same water jacket as the gas burette.

W. A. S.

**Spiral Gas-washing Bottle.** L. H. MILLIGAN (*Ind. Eng. Chem.*, 1924, **16**, 889).—A gas-washing bottle designed particularly for the analysis of mixtures of the oxides of nitrogen consists of an outer cylindrical tube with ground glass stopper and gas outlet, and, sealed through this stopper and passing to the bottom of the cylinder, the gas inlet. Between the cylinder and the tube and concentric with them is an open-ended glass tube with spiral corrugations, held between the curved tip of the inlet tube and an expansion on its stem. The gas and liquid pass together up the outer space and the liquid returns down the inner space.

Absorption is efficient and the design is suited for quantitative work. C. I.

**Detection of Constant-boiling Mixtures.** T. R. BRIGGS (*J. Physical Chem.*, 1924, **28**, 644—650).—The method of detection consists in the fractional distillation of the azeotropic mixture at some other pressure, when partial separation of the constituents will take place until a constant-boiling mixture of different composition is obtained. The method has been satisfactorily tested by means of the azeotropic mixture of maximum b. p. obtained from hydrochloric acid and water, and that of minimum b. p. from methyl alcohol and benzene. It is suggested that the same effect might be obtained by evaporating in a current of air so as to reduce the partial pressure. M. S. B.

**Titration of Silver and Halogen Ions Using Dyes as Indicators.** K. FAJANS and H. WOLFF (*Z. anorg. Chem.*, 1924, **137**, 221—245).—An extension of earlier work (cf. Fajans and Hassel, this vol., ii, 61) in which the action of other dyes as indicators in the titration of silver with alkali halides has been examined. For the titration of chlorides, fluorescein gives the best results; for bromides eosin and for iodides di-iododimethylfluorescein. By the use of the latter indicator and a determination of the sum of the chlorine and iodine, using fluorescein as indicator, the iodide content of a solution containing chloride may be determined with an accuracy of 0.1%. Titration of silver in nitric acid solution with potassium bromide gives results accurate to 0.1—0.2%, using rhodamin-G as indicator, the end-point being marked by a change in the colour of the solution from violet to yellowish-red. [Cf. *B.*, 1924, 851.] A. R. P.

**Titration of Silver and Halogen Ions using Dyes as Indicators.** W. BÖTTGER and K. O. SCHMIDT (*Z. anorg. Chem.*, 1924, **137**, 246—248).—The method of Fajans and Wolff (cf. preceding abstract) has been examined in order to determine the magnitude of the indicator error. Titration of standard silver nitrate solution with standard sodium chloride, using 5 c.c. of 0.0125% fluorescein solution as indicator, gave almost exactly the same result as that obtained by the use of potassium chromate as indicator (after correction), but no exact figures could be obtained for the amount of silver required to give the colour change with fluorescein owing to the fact that the silver chloride used in the

blank titration was not so finely divided as that obtained in an analysis and did not, therefore, exert the same adsorptive action on the indicator. It is concluded, however, that the indicator error is not so serious as in the Mohr titration.

A. R. P.

**Electrometric Titration of Chlorides.** E. MÜLLER (*Z. Elektrochem.*, 1924, **30**, 420—423).—Chlorides may be titrated with a mercurous solution, the end-point being indicated by a sharp change in the potential of an amalgamated platinum electrode; 0.1*N*-mercurous perchlorate is recommended as standard. The titration vessel holding the electrode is connected by a siphon with a standard calomel electrode; a constant *E.M.F.* of 0.32 volt is applied, and the end-point is reached when a galvanometer in series shows no current.

W. A. C.

**Determination of Chloride Ions.** O. BARKUS (*Amer. J. Physiol.*, 1924, **68**, 349—353).—An apparatus is described whereby chloride-ion concentrations in body-fluids and living tissues can be observed and changes continuously (electrometrically) recorded. An appreciable amount of the chlorine present in gastric fluid is non-ionised.

A. A. E.

**Micro-determination of Sulphur.** O. WINTERSTEINER (*Mikrochemie*, 1924, **2**, 14—17).—A siphon arrangement is described for the collection of barium sulphate precipitates in a filter-crucible; the latter is supported in a tube entering the top of a filter flask and a second tube fitting over the first tube carries the short end of the siphon so that this reaches into the filter-crucible. A side tube on the second tube is connected by means of a length of rubber tubing and a T-piece with the side tube of the filter flask. By momentarily opening a spring clip on the rubber tubing, the liquid and the barium sulphate precipitate are drawn over into the crucible (suction being applied to the filter-flask) and, when the clip is closed, filtration proceeds.

W. P. S.

**Determination of Hydrogen Sulphide in Bacterial Cultures.** C. R. FELLERS, O. E. SHOSTROM, and E. D. CLARK (*J. Bact.*, 1924, **9**, 235—249).—The current of air, by which hydrogen sulphide is removed from acid solutions and passed into standard iodine solution, is passed through standard thiosulphate solution to recover volatilised iodine. Aëration for 15 minutes is sufficient to remove more than 99% of the hydrogen sulphide; ordinary bacterial volatile products do not interfere.

CHEMICAL ABSTRACTS.

**Analysis of Sodium Hyposulphite.** R. H. MCKEE and N. E. WOLDMAN (*Colour Trade J.*, 1924, **14**, 180—183).—A discussion of the methods available for the volumetric and gravimetric analysis of sodium hyposulphite. The most accurate method is that of Helwig (*Amer. Dyestuff Rep.*, 1920, **7**, ii, 12).

CHEMICAL ABSTRACTS.

**Detection and Differentiation of Thiosulphuric and Sulphurous Acids and Hydrogen Sulphide in Organic Liquids.** E. PITTARELLI (*Arch. Farm. speriment.*, 1924, **38**, 13—23).—If an

organic liquid evolves hydrogen sulphide within 5 or 6 hours after its treatment with powdered aluminium and sodium hydroxide, the presence of thiosulphuric acid is indicated; if the hydrogen sulphide is eliminated by addition of an alkaline lead solution and filtration, treatment of the filtrate with powdered zinc then results in further liberation of hydrogen sulphide if sulphurous acid is present. Thiosulphuric acid may be detected also by rendering the liquid acid to the extent of 1 c.c. of hydrochloric acid per 40—50 c.c. of the liquid, adding a few crystals of either *p*-aminophenol or *p*-methylaminophenol and, drop by drop, 10% ferric chloride solution; a deep orange-yellow coloration forms if thiosulphuric acid is present. This colouring matter may be extracted by amyl alcohol and unites with methylene-blue to form a green compound soluble in the alcohol or in chloroform. The reaction, the sensitiveness of which is 1:400,000, is not disturbed by sulphurous acid, but hydrogen sulphide yields a highly sensitive reaction with the same reagent and must be previously eliminated by means of a zinc salt. If to an acid thiosulphate solution *p*-phenylenediamine (or dimethyl- or diethyl-*p*-phenylenediamine) and naphthylamine are added and then, drop by drop, ferric chloride solution, a greenish-blue (or bluish-green or emerald-green) coloration is obtained; these colorations resist the action of such energetic reducing agents as hyposulphites.

Thiosulphuric and sulphurous acids in an organic liquid may be distinguished by addition of aurine, coralline, or rosolic acid strongly acidified with hydrochloric acid, the presence of sulphurous acid being indicated by instantaneous decolorisation; if this occurs, addition of aurine is continued until the liquid is saturated with it and becomes distinctly yellow. If this colour persists for 24 hours, only sulphite is present, but if the liquid undergoes decolorisation, it contains thiosulphate. The sensitiveness of this reaction, which is not shown in presence of hydrogen sulphide, is 1:500,000.

T. H. P.

**Bromometric Determination of Thiocyanate.** A. KURTENACKER and H. KUBINA (*Z. anal. Chem.*, 1924, **64**, 442—444).—Thiocyanate cannot be determined satisfactorily by titration with bromine, potassium bromide, or bromide-bromate mixtures owing to the extreme slowness with which hydrogen cyanide is converted into cyanogen bromide under the conditions of the experiment. [Cf. *B.*, 1924, 866.]

A. R. P.

**Determination of Hydrazine and its Derivatives.** A. KURTENACKER and H. KUBINA (*Z. anal. Chem.*, 1924, **64**, 388—392).—Satisfactory results are obtained when the methods in general use for the determination of hydrazine are applied to its derivatives, semicarbazide and phenylhydrazine. Most satisfactory are the methods involving the direct titration with 0.1*N*-bromate solution in the presence of potassium bromide and hydrochloric acid, using indigo as an indicator (cf. Kurtenacker and Wagner, *A.*, 1922, ii, 312), or with 0.1*N*-iodate solution in the presence of hydrochloric acid, using chloroform as an indicator (cf. Jamieson, *A.*, 1912, ii,



487). Good results may also be obtained by the addition of an excess of the bromate or iodate solution and titration of the excess by means of iodine and thiosulphate solution (cf. Treadwell and Mayr, A., 1916, ii, 264; Hale and Redfield, A., 1911, ii, 929). In the case of titrations with the bromate solution, the addition of potassium bromide is essential, otherwise the amino group is also attacked and high results are obtained. Determination by means of iodate in alkaline solution (cf. Rimini, A., 1906, ii, 897) yields low results unless the solution of the hydrazine derivative is first treated with the iodate, then made alkaline, followed by the addition of potassium iodide, acidification, and titration with thiosulphate. Unsatisfactory results are obtained for semicarbazide by this method. Details of procedure for each method are given. J. W. B.

**Standardisation of Nitrous Oxide.** I. W. D. HACKH (*J. Amer. Pharm. Assoc.*, 1924, **13**, 191—193).—A method is given for determining the air and other impurities not absorbed by water. The amount of "other oxides of nitrogen" should not exceed 10 parts per million. CHEMICAL ABSTRACTS.

**Hydrostrychnine Reagent for Nitrites and Nitrates.** I. M. KOLTHOFF (*Chem. Weekblad*, 1924, **21**, 423—424; cf. Denigès, A., 1911, ii, 655; Scales and Harrison, this vol., ii, 565).—The reagent gives positive results with various oxidising agents, but may be used both qualitatively and quantitatively for nitrates. Nitrites if present give a coloration before addition of sulphuric acid, and may be determined colorimetrically, an equal amount being then added to the control in the nitrate determination with addition of sulphuric acid. Ferric iron may be removed by means of sodium hydrogen carbonate. S. I. L.

**Determination of Reduction Products of Free Nitric Acid Solutions.** L. H. MILLIGAN (*J. Physical Chem.*, 1924, **28**, 544—578).—Methods have been devised for determining the following nitrogen compounds in the presence of one another: nitrogen peroxide, nitric oxide, nitrous oxide, nitrogen, nitrous acid, and salts of ammonia, hydroxylamine, and hydrazine. Methods of determining strongly reducing metallic salts, in the presence of some of these substances, are given. [Cf. B., 1924, 865.]

M. S. B.

**Bromometric Determination of Phosphorous and Hypophosphorous Acids.** W. MANCHOT and F. STEINHAUSER (*Z. anorg. Chem.*, 1924, **138**, 304—310).—The addition of sodium hydrogen carbonate or acetate greatly accelerates the oxidation of phosphites by bromine; both phosphites and phosphorous acid may be determined volumetrically by so treating their solution, and then titrating with excess of standard bromine solution. The free bromine is then determined by treatment with excess of a standard solution of arsenious oxide and subsequent titration with bromine, using indigo-carmin as indicator. Hypophosphites and hypophosphorous acid may be determined by treatment with excess of sodium acetate (but not with sodium hydrogen carbonate) and

then with excess of a standard solution of bromine. The mixture is heated at  $60^{\circ}$  for  $\frac{1}{2}$  hour in a stoppered flask, and the unchanged bromine determined by titration with arsenious acid. A mixture of phosphorous and hypophosphorous acids may be analysed by finding the total quantity of bromine necessary completely to oxidise the mixture, and then determining the total phosphate produced in the oxidation by precipitation as magnesium ammonium phosphate. In the determination of phosphorous acid by the mercuric chloride method (Treadwell, "Lehrbuch," 11th Ed., 1923), the oxidation is complete if the solution is treated with sodium acetate and acetic acid and heated for 1.5 hours at  $40-50^{\circ}$ . W. H.-R.

**Volumetric Determination of Phosphoric Acid. Application to the Study of Phosphatic Urinary Acidity.** L. LEMATTE and (MLLE.) A. DELACROIX (*Bull. Soc. Chim. biol.*, 1924, **6**, 521—533).—A technique is described by which the volumetric determination of phosphates by means of uranium nitrate solution, using potassium ferrocyanide as external indicator, gives results as accurate as those obtained by a gravimetric method. The reaction liquid is heated on the water-bath throughout, and in addition to sodium acetate a large excess of sodium chloride is added to promote precipitation of the uranium phosphate. Secondary phosphates present in urine are precipitated by addition of barium chloride: the primary phosphates, which remain in solution, are titrated, and the secondary phosphates thus found by difference. All normal specimens of urine and many pathological samples contain both primary and secondary phosphates. In the normal subject, 58% of the phosphoric acid is present as primary phosphate, and 42% as secondary phosphate. The primary phosphates contribute 40% of the total acidity in the urine as found by means of 0.1N-sodium hydroxide and phenolphthalein. G. M. B.

**Use of Amalgams in Volumetric Analyses. X. Determination of Phosphoric Acid with Uranyl Salts.** S. SAITO (*J. Chem. Soc. Japan*, 1924, **45**, 74—78).—In the determination of phosphoric acid by way of uranyl ammonium phosphate, filtration of the colloidal precipitate is difficult. The precipitate is obtained in the crystalline state by mixing a boiling solution of 2—10 c.c. of sodium phosphate, 15—30 c.c. of 30% acetic acid, and 30—70 c.c. of water with a boiling mixture of 10—40 c.c. of 0.1N-uranyl acetate (or sodium uranyl acetate), 5—25 c.c. of 30% acetic acid, 5—20 c.c. of ammonium acetate, and 5—50 c.c. of water. After 10 minutes, the mixture is diluted with the same volume of hot water and, after partial cooling, filtered by suction and washed. The concentration of acetic acid in the solution should be above 1.3N for formation of a crystalline precipitate, but since this solution slightly dissolves the precipitate, it is diluted with water until the concentration of the acid is below 0.7N. The solution should contain less than 0.1 g.  $P_2O_5$  per 200 c.c. For the determination of the acid, the precipitate is dissolved in warm 3N-sulphuric acid, reduced with liquid zinc amalgam in the presence of air, and titrated with 0.1N-potassium permanganate solution. K. K.

**Micro-analytical Determination of Phosphorus and Arsenic in Organic Substances.** H. LIEB and O. WINTERSTEINER (*Mikrochemie*, 1924, 2, 78—81).—The arsenic and phosphorus contained in organic compounds may be converted into arsenic and phosphoric acids, respectively, by heating the substance with strong hydrogen peroxide and sulphuric acid; the phosphoric acid is then determined microchemically as ammonium phosphomolybdate and the arsenic acid as magnesium ammonium arsenate. [Cf. *B.*, Nov. 28.] A. R. P.

**Determination of Arsenic in Pyrites, Sulphuric Acid, and Hydrochloric Acid.** C. MAYR (*Z. anorg. Chem.*, 1924, 137, 328—330).—Details are given for the separation of the arsenic as sulphide, which is collected and dissolved in ammonium carbonate and hydrogen peroxide, the solution evaporated to dryness, the residue dissolved in hydrochloric acid, and the solution distilled with potassium bromide and hydrazine sulphate. The distillate is diluted and titrated with potassium bromate. [Cf. *B.*, 1924, 865.] A. R. P.

**New Methods of Volumetric Analysis. V. Chlorometry as a Substitute for Iodometry and Other Analytical Methods.** K. JELLINEK and W. KRESTEV (*Z. anorg. Chem.*, 1924, 137, 333—348; cf. *A.*, 1923, ii, 871).—A solution of sodium hypochlorite retains its titre constant over long periods provided that a large excess of sodium hydroxide is present. Such a solution may be used in place of iodine solutions for the determination of tin, antimony, and arsenic, using 1 c.c. of a saturated solution of potassium bromide as indicator. In each case, the solution should be standardised against a known weight of pure metal or oxide. The presence of ferrous salts interferes with the titration in each case.

Aluminium and lead salts may be titrated with trisodium phosphate, using methyl-red as indicator, to an accuracy of 0.5%. Calcium and barium salts cannot be accurately titrated with sodium sulphite and methyl-red, and titration of ferric salts with trisodium phosphate and potassium thiocyanate also gives erratic results. Phosphoric acid, in the presence of iron, may be accurately determined by precipitation with magnesia mixture if the solution contains ammonium tartrate. [Cf. *B.*, 1924, 892.]

A. R. P.

**Critical Studies on Methods of Analysis. XII. Boron.** L. A. CONGDON and J. M. ROSSO (*Chem. News*, 1924, 129, 219—221).—In the determination of boron, trustworthy results are obtained only by Gooch's methyl borate method and by titration with alkali hydroxide in the presence of glycerol. A. R. P.

**Electrometric Titration of Boric Acid in presence of Polyphenols and Organic Acids.** M. G. MELLON and V. N. MORRIS (*Proc. Indiana Acad. Sci.*, 1924, 35, 85—91).—Electrometric titration of a mixture of boric acid with pyrocatechol or pyrogallol is not successful, since no sudden change occurs at the neutralisation

point, probably owing to the formation of oxidation products of complexes. Glycollic, gallic, and tannic acids probably form complexes with boric acid, but two distinct changes are observed in the neutralisation.

CHEMICAL ABSTRACTS.

**Hydrofluosilicic Acid. III. Method of Titrating and Properties.** C. A. JACOBSON (*J. Physical Chem.*, 1924, **28**, 506—509; cf. A., 1923, ii, 561; this vol., ii, 105).—The aqueous solution, containing not more than 0.1—0.2 g. of acid, cooled in ice, is titrated with *N*-alkali in presence of sodium or potassium chloride, using methyl-orange as indicator:  $\text{H}_2\text{SiF}_6 + 2\text{KCl} = \text{K}_2\text{SiF}_6 + 2\text{HCl}$ ;  $\text{HCl} + \text{KOH} = \text{KCl} + \text{H}_2\text{O}$ . The solution is diluted, heated until nearly boiling, and titrated with *N*-potassium hydroxide, using phenolphthalein as indicator:  $\text{K}_2\text{SiF}_6 + 4\text{KOH} = 6\text{KF} + \text{H}_4\text{SiO}_4$ . The second stage gives results slightly higher than the first.

Hydrofluosilicic acid is non-volatile and appears to exist only in aqueous solution. At the ordinary temperature it may be concentrated to approximately 61%;  $d^{25}_4$  1.4634,  $n$  1.3465. In dilute aqueous solution it is quite stable. M. S. B.

**Determination of, and Protection against, Carbon Monoxide in Air.** E. TASSILLY (*Bull. Sci. Pharmacol.*, 1923, **30**, 513—524; from *Chem. Zentr.*, 1924, i, 2455).—The most trustworthy method for the determination of carbon monoxide in air depends on the formation of carbon monoxide-hæmoglobin. The iodic anhydride method gives good results in the absence of methane. An apparatus for protection against carbon monoxide poisoning is described. G. W. R.

**Volumetric Determination of Total Carbonic Acid in Dilute Solutions of Calcium Hydrogen Carbonate or in Hard Tap-waters.** E. M. CROWTHER and W. S. MARTIN (*J. Chem. Soc.*, 1924, **125**, 1937—1939).—The determination of the total carbonic acid in dilute calcium hydrogen carbonate solutions by precipitation with calcium or barium hydroxide, the excess of the latter being determined volumetrically, gives low results. Accurate results are obtained when the precipitation is carried out with calcium hydroxide and chloride solution to which a small quantity of solid calcium carbonate has been added. S. K. T.

**Crystal Reactions of Potassium, Ammonium, and Magnesium.** L. ROSENTHALER (*Mikrochemie*, 1924, **2**, 29—32).—Potassium, ammonium, and magnesium chloride solutions yield characteristic crystals when treated with sodium benzenesulphonate solution, sodium nitrophenoxide solutions, or silicotungstic acid solution. Magnesium may be detected in the presence of potassium and ammonium salts by means of sodium benzenesulphonate, whilst silicotungstic acid is suitable for the detection of potassium chloride, and of ammonium chloride in the presence of sodium chloride and potassium chloride. W. P. S.

**Use of Cæsium Chloride in Microchemistry.** E. H. DUCLOUX (*Mikrochemie*, 1924, 2, 108—120).—The following double compounds of cæsium chloride with other metallic chlorides are useful for the microchemical detection of the metal concerned:  $\text{AgCl}_2 \cdot 2\text{CsCl}$ , small cubes from ammoniacal solution, rapidly darkening on exposure to light;  $\text{HgCl}_2 \cdot \text{CsCl}$ , cubic or rhombic crystals;  $\text{AuCl}_3 \cdot \text{CsCl} \cdot 0.5\text{H}_2\text{O}$ , monoclinic, light yellow, feebly dichroic prisms exhibiting positive double refraction;  $\text{PtCl}_2 \cdot \text{CsCl}$  and  $\text{PtCl}_2 \cdot 2\text{CsCl}$ , needles and tetragonal prisms respectively;  $\text{PdCl}_2 \cdot 2\text{CsCl}$ , short, orange-yellow, right-angled prisms with regular cleavage;  $2\text{AsCl}_3 \cdot 3\text{CsCl}$ , greyish-yellow prisms and hexagonal tablets; bismuth chloride yields dirty white double salts of high refractive index which crystallise as hexagonal or rhombic tablets or prisms similar to the antimony compound,  $2\text{SbCl}_3 \cdot 3\text{CsCl}$ ;  $\text{CdCl}_2 \cdot \text{CsCl}$ , small colourless double pyramids;  $\text{CuCl}_2 \cdot 2\text{CsCl}$ , thin, yellow to yellowish-red prisms or tablets belonging to the rhombic system;  $\text{AlCl}_3 \cdot \text{CsCl}$ , tetragonal crystals; ferric chloride gives a double salt which crystallises in deep yellow dichroic tablets;  $\text{ZnCl}_2 \cdot 2\text{CsCl}$ , long, thin, deliquescent needles;  $\text{NiCl}_2 \cdot 2\text{CsCl}$ , bright yellowish-green, lenticular crystals;  $\text{MnCl}_2 \cdot \text{CsCl} \cdot 2\text{H}_2\text{O}$ , colourless prisms, hexagonal prisms, or radiating clusters;  $\text{CoCl}_2 \cdot \text{CsCl}$  and  $\text{CoCl}_2 \cdot 2\text{CsCl}$ , light blue rhombic and hexagonal tablets, respectively;  $\text{CaCl}_2 \cdot \text{CsCl}$ , colourless triclinic dendrites;  $2\text{TlCl}_3 \cdot 3\text{CsCl}$ , colourless, hexagonal crystals;  $\text{CeCl}_3 \cdot \text{CsCl}$ , colourless crystals with a high refractive index;  $\text{InCl}_3 \cdot 3\text{CsCl}$ , colourless, crystalline granules. A. R. P.

**Solubility of Silver Chloride and Gay-Lussac's Silver Titration.** R. LORENZ and E. BERGHEIMER.—(See ii, 757.)

**Micro-electrolytic Determination of Silver and Zinc.** K. NEUMANN-SPALLART (*Mikrochemie*, 1924, 2, 157—158).—By the use of Pregl's micro-electrolytic apparatus, silver may be deposited quantitatively from alkaline cyanide solutions and zinc from solutions of zinc hydroxide in alkali hydroxide. A current density of 4—5 amp. per 20 sq. cm. of cathode area at 4 volts is used and, in the case of zinc, the cathode should be silvered. [Cf. B., Nov. 28.] A. R. P.

**Use of Ammoniacal Silver Solutions in Qualitative Micro-analysis.** G. DENIGÈS (*Mikrochemie*, 1924, 2, 82—84).—When a drop of an ammoniacal solution of silver nitrate is added to a drop of a solution containing an anion which yields an insoluble salt with silver, the mixture begins to deposit the silver salt in a crystalline form around the edges of the liquid provided that enough ammonia is present to dissolve the precipitate on mixing the liquids. [Cf. B., Nov. 28.] A. R. P.

**Gravimetric Determination of Calcium as Anhydrous Calcium Oxalate.** C. DÍAZ VILLAMIL (*Anal. Fis. Quím.*, 1924, 22, 264—274).—A study of the principal methods used for the determination of calcium by way of the oxalate. Whilst the volumetric method with permanganate tends to give low results, the gravimetric method, depending on ignition of calcium oxalate

to calcium oxide, may give high results owing to absorption of carbon dioxide. The most trustworthy results are given by weighing the calcium as sulphate, but the method is inconvenient. A convenient method, which gives trustworthy results, consists in drying the calcium oxalate precipitate without removal of ammonium salts, igniting in a current of dry air at  $300^{\circ}$  for 1 hour, and weighing as anhydrous calcium oxalate, which is shown to be perfectly stable under the above conditions of ignition. G. W. R.

**Detection and Determination of Small Quantities of Calcium and Magnesium by Means of Ammonium Ferrocyanide, and a New Nephelometric Method for the Determination of the Hardness of Water.** F. FEIGL and F. PAVELKA (*Mikrochemie*, 1924, 2, 85—91).—Calcium and magnesium salts yield a micro-crystalline precipitate with ammonium ferrocyanide in neutral solutions containing 50% of alcohol; the reaction serves to detect 1 part of either metal in 1,000,000 parts of solution. In extreme dilutions, the precipitate appears as a white turbidity and the process may then be used for the nephelometric determination of either or both metals in water, *i.e.*, for the determination of the hardness of the water. [Cf. *B.*, Nov. 28.] A. R. P.

**Determination of Calcium Carbide.** J. Y. YEE and H. J. KRASE (*J. Amer. Chem. Soc.*, 1924, 46, 1389—1393).—Calcium carbide is treated either with sodium chloride solution or, if sulphides are present, with lead nitrate solution, and the evolved acetylene passed into neutral or ammoniacal silver nitrate solution. In the former case, the acid liberated ( $C_2H_2 + 3AgNO_3 \rightarrow C_2Ag_2, AgNO_3 + 2HNO_3$ ) is titrated with alkali; in the latter, the excess of silver is determined with thiocyanate solution after filtering off the silver carbide. Phosphides must, however, be absent. H. T.

**Action of Hydrogen Chloride on Calcium Cyanamide. Determination of Nitrogen in Calcium Cyanamide.** C. MONTEMARTINI and L. LOSANA (*Giorn. Chim. Ind. Appl.*, 1924, 6, 325—326).—The reaction,  $CaCN_2 + 6HCl = CaCl_2 + CCl_4 + 2NH_3$ , which proceeds quantitatively at a red heat, forms the basis of a rapid and accurate method for the determination of nitrogen in calcium cyanamide. [Cf. *B.*, 1924, 866.] T. H. P.

**Sensitive Colour Reaction for Magnesium.** F. L. HAHN, H. WOLF, and G. JÄGER (*Ber.*, 1924, 57, [B], 1394—1396).—An alcoholic solution of 1 : 2 : 5 : 8-tetrahydroxyanthraquinone acquires a cornflower-blue colour in the presence of magnesium which permits the ready detection of  $1 \mu g.$  of the metal in 1 c.c. of solution. With somewhat greater content of magnesium a pure blue precipitate separates. The reaction is less sensitive in the presence of ammonium salts or of phosphates. It is adapted to the detection of traces of magnesium in aluminium, since the latter metal can be retained in solution by the presence of an excess of sodium hydroxide or of tartrate and sodium hydroxide. H. W.

**Use of Molybdenum as Indicator in the Volumetric Determination of Zinc.** L. FERNANDES (*Giorn. Chim. Ind. Appl.*, 1924, 6, 334—335).—Alkali molybdates are not precipitated by, but give an intense red coloration with, potassium ferrocyanide in acetic acid solution. They may therefore be used as indicators in the titration of zinc with ferrocyanide, the accuracy of the results obtained being thus enhanced. The application of this method to zinc ores is described. [Cf. *B.*, 1924, 893.] T. H. P.

**Microchemical Detection of Cadmium and Zinc as Double Pyridine Compounds.** I. M. KOLTHOFF and H. HAMER (*Mikrochemie*, 1924, 2, 92—93).—Zinc and cadmium give with pyridine and ammonium thiocyanate characteristic crystalline precipitates which may be used for the microchemical detection of the elements (cf. Spacu, A., 1923, ii, 879). Similar precipitates are obtained if bromide is substituted for thiocyanate, and in this case copper does not interfere. The cadmium compounds consist of short, thick needles which often cross one another at an acute angle, whereas the zinc compounds are long, thin needles. A. R. P.

**[Ferrocyanide Test for Copper.]** E. D. CRITTENDEN.—(See i, 1175.)

**Gravimetric Determination of Copper.** E. WILKE-DÖRFURT and U. RHEIN (*Z. anal. Chem.*, 1924, 64, 380—388).—The large positive error occurring in the determination of copper by precipitating with hydrogen sulphide and igniting the sulphide to oxide is shown to be due not, as previously supposed, to the presence of sulphate (which is only present when washing of the precipitate is incomplete), but to carbon produced by the incineration of the filter-paper and occluded by the precipitate in such a manner as to prevent its oxidation. Accurate results are therefore obtained by this method if the use of filter-paper be avoided by employing either Zsigmondy membrane filters (cf. Zsigmondy, A., 1919, ii, 520; Jander and Jander, this vol., ii, 269) fitted into a weighed porcelain crucible, or the new porcelain filter crucibles (cf. Hüttig, this vol., ii, 247). J. W. B.

**Determination of Copper with Permanganate.** L. CUNY (*J. Pharm. Chim.*, 1924, [vii], 30, 240—242).—Copper in aqueous solution may be rapidly determined by the addition of an excess of ammonium thiocyanate solution and a small quantity of pyridine. A very sparingly soluble green compound,  $\text{Cu}(\text{CNS})_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ , is formed, and the excess of thiocyanate in the filtrate is determined by titration with permanganate in acid solution. The process is not accurate unless the concentration of the copper lies within narrow limits (0.2—0.5 g. per litre). P. M.

**Microchemical Detection. III. Copper, Alkaloids, and the "Psicain" Base.** L. ROSENTHALER (*Mikrochemie*, 1924, 2, 121—124).—An alkaline solution of copper in potassium cyanide turns a 1% alcoholic solution of guaiacum resin blue, a similar aloin solution red, and a benzidine solution green. The tests will detect

0.6  $\mu$  of copper in 0.1 c.c. of solution. Potassium bismuthithiocyanate solution, stabilised with mannitol, and potassium mercurithiocyanate solution give visible white precipitates with 0.01% solutions of quinine or strychnine hydrochloride. The "psicain" base (*d*- $\psi$ -cocaine) may be distinguished from cocaine by the following reactions: the formation of crystalline clusters of needles with sodium nitrate, an immediate crystalline precipitate with potassium iodide, and the slow formation of crystalline rods and prisms with the copper-lead nitrite reagent. With the same reagents, cocaine yields, respectively, no precipitate, oily drops which crystallise on rubbing, and an immediate precipitate of short but broad, green prisms. [Cf. *B.*, Nov. 28.] A. R. P.

**Micro-analytical Determination of Copper and Nickel.** R. STREBINGER and I. POLLAK (*Mikrochemie*, 1924, 2, 125—130).—For the micro-analysis of solutions containing both copper and nickel, the solution is rendered ammoniacal and the nickel precipitated at 70—80° with dimethylglyoxime. The filtrate is treated with a few drops of a 1% alcoholic solution of benzoinoxime to precipitate the copper. Both precipitates are dried at 100° and weighed. [Cf. *B.*, Nov. 28.] A. R. P.

**Iodometric Determination of Cuprous Oxide in Presence of the Cupric Ion. Application to the Determination of Reducing Sugars.** A. BLANCHETIÈRE (*Bull. Soc. Chim. biol.*, 1924, 6, 509—514).—The conversion of cuprous oxide into cupric iodide on which the iodometric method of Shaffer and Hartmann (*A.*, 1921, ii, 417) depends is not complete, but by using oxalic in place of sulphuric acid for acidifying the iodide-iodate mixture the reaction is made quantitative even with concentrations of the cupric ion up to 0.5*M*. The application of this method to the determination of reducing sugars is described. G. M. B.

**Titration of Manganous Salts with Permanganate.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1924, 61, 1141—1149).—The reaction  $3\text{Mn}^{++} + 2\text{MnO}_4' + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$  is quantitative in neutral or faintly acid solution in presence of a small quantity of zinc oxide or a zinc salt. Ferric salts must be precipitated, zinc oxide being most suitable for this purpose; excess of zinc oxide must be avoided, since the precipitate formed does not settle readily, the solution being then acidified with acetic acid. S. I. L.

**Application of Ferric Oxalate to the Separation of Iron and Calcium.** J. BARLOT.—(See i, 1162.)

**Titration of Ferrous Iron with Permanganate.** I. M. KOLTHOFF and N. SMIT (*Pharm. Weekblad*, 1924, 61, 1082—1095).—In presence of sulphuric acid the titration gives accurate results at all concentrations of iron or acid, and is not affected by temperature. In presence of hydrochloric acid, the results are always inaccurate. The error is lower the longer the time taken for titration, but increases inversely with the concentration of the iron, and directly with the concentration of hydrochloric acid to a maxi-



num. Addition of neutral chlorides including barium and magnesium chlorides, or of phosphates, has little effect. At higher temperatures, the error is greater if the concentration of hydrochloric acid be high. Addition of manganous salts reduces the error, but under the most favourable conditions the error in titrating a 0.01N-solution may be more than 1%. S. I. L.

**Diphenylamine Indicator in the Volumetric Determination of Iron.** W. W. SCOTT (*J. Amer. Chem. Soc.*, 1924, **46**, 1396—1398).—Ferrous iron solutions containing hydrochloric acid, stannous chloride, mercurous chloride, etc., can be satisfactorily titrated with potassium permanganate solutions, using diphenylamine solution as an internal indicator. The best results are given by using not more than 0.2 c.c. of Knop's preparation (this vol., ii, 351), and 0.1N-permanganate, the volume not exceeding 300 c.c.

H. T.

**Use of Liquid Amalgams in Volumetric Analysis. I. Use of Zinc and Bismuth Amalgams.** K. SOMEYA (*Z. anorg. Chem.*, 1924, **138**, 291—303).—Bismuth amalgam reduces ferric salts to the ferrous state in an atmosphere of carbon dioxide, whilst quinquivalent vanadium in solution is reduced to the quadrivalent state both in carbon dioxide and in air. A differential titration of a mixture of iron and vanadium may be carried out by reducing one portion of the solution with bismuth amalgam and then titrating with permanganate by the method of Zimmermann and Reinhardt; a second portion of the solution is treated similarly after reduction with zinc amalgam, which reduces the vanadium to the bivalent state (cf. Nakazono, A., 1921, ii, 596). In air, the reduction of ferric salts by bismuth amalgam is incomplete, but, in the presence of molybdate, the reduction of the ferric salt is complete, the molybdate being reduced to quinquivalent molybdenum. This reaction must not be carried out in an atmosphere of carbon dioxide or the molybdate is reduced too far. A differential titration of molybdenum and iron is again possible by reducing two portions of the solution with zinc and bismuth amalgam, respectively. Titanium sulphate in solution is reduced by bismuth amalgam at 60° if hydrochloric acid is present, and the reduced solution may be titrated with permanganate. The amalgams used contained about 3% of bismuth or zinc respectively. W. H.-R.

**Copper as Reducing Agent in Iron Determinations.** J. M. HENDEL (*Ind. Eng. Chem.*, 1924, **16**, 951).—The reduction of ferric sulphate solution previous to titration with permanganate is conveniently effected by boiling with a piece of copper gauze (99.8% purity). It is necessary, after cooling, to draw a current of air through the solution for 3—10 minutes, otherwise results up to 0.4% too high are obtained owing to the presence of cuprous ion. The acidity during reduction should not exceed 0.25N. No error is introduced by the presence of titanium. C. I.

**Micro-determination of Nickel.** I. POLLAK (*Mikrochemie*, 1924, **2**, 17—19).—Five c.c. of the nickel solution, containing from

0.5 to 3 mg. of the metal, are treated with a few drops of very dilute ammonia and a slight excess of 1% alcoholic dimethylglyoxime solution; a further few drops of dilute ammonia are then added, the mixture is heated at 100° for 30 minutes, and the precipitate is collected on a micro-filter.

W. P. S.

**Titanous Salts as Reducing Agents.** E. KNECHT.—(See i, 1183.)

**Detection of Zirconium in the Presence of Titanium.** I. BELLUCCI and G. SAVOIA (*Atti. I. Congr. naz. Chim. pur. appl.*, 1923, 483—488; from *Chem. Zentr.*, 1924, i, 2531).— $\alpha$ -Nitroso- $\beta$ -naphthol and also  $\beta$ -nitroso- $\alpha$ -naphthol give with zirconium salts coloured complex salts of the composition  $[C_{10}H_6O_2N]_2ZrO$ . Titanium salts also give coloured complex salts in neutral solutions, but not in the presence of hydrochloric acid. The coloration with zirconium salts is not affected by the presence of hydrochloric acid or aluminium chloride.

G. W. R.

**Microchemical Reactions of Zirconium and Some Related Elements.** F. STEIDLER (*Mikrochemie*, 1924, 2, 131—156).—Zirconium oxychloride solutions yield a yellow precipitate of indefinite composition with picric acid. Prolonged washing of the precipitate with water either before or after drying results in complete removal of the picric acid, leaving a residue of zirconium hydroxide. Zirconium, titanium, molybdenum, niobium, and tantalum yield colours of various shades of brown on linen or artificial silk that has been dyed with turmeric, but the reaction is not very delicate with respect to tantalum and niobium; the fabric impregnated with zirconium or titanium is turned a yellowish-green colour when dipped into an alkaline solution of  $\alpha$ -nitroso- $\beta$ -naphthol, that impregnated with molybdenum a dark-brown to greenish-grey in hydrogen sulphide solutions, and that impregnated with titanium an intense orange colour with 1:8-dihydroxynaphthalene-3:6-disulphonic acid which becomes bright yellow with alkalis. The effect of various metallic compounds and of boric acid and alkalis on the pleochroism of natural and artificial fibres dyed with turmeric has been determined. The behaviour of zirconium salts in the above test is not affected by the presence or absence of hafnium compounds.

A. R. P.

**Micro-determination of the Oxide Content of Colloidal Gold.** P. A. THIESSEN.—(See ii, 768.)

**Colorimetric Determination of Platinum by Potassium Iodide.** E. G. R. ARDAGH, F. S. SEABORNE, and N. S. GRANT (*Can. Chem. Met.*, 1924, 8, 117—120; 140—142).—Directions are given applying the formation of red iodoplatinate ions (from chloroplatinate and potassium iodide) to the colorimetric determination of platinum in solutions containing about 0.2 mg. in 50 c.c. In 1 hour, 90% of the maximum colour intensity is reached; both assay and control solutions must therefore be kept for this

period at the ordinary temperature. The rate of development, but not the maximum intensity, of the colour varies with the age of the solution. Acids (except hydrochloric) and heavy metals interfere. The quantity of potassium iodide used, if greater than the minimal, has little effect.

CHEMICAL ABSTRACTS.

#### Determination of Glycerol and of Trimethylene Glycol.

S. FACHINI and S. SOMAZZI (*Chim. et Ind.*, May, 1924 [special number], 510—514).—The glycerol and trimethylene glycol in the crude products may be rapidly determined by oxidation with potassium dichromate and sulphuric acid, the carbon dioxide which is evolved being weighed in a suitable absorbent. With the additional knowledge of the amount of dichromate reduced, the relative proportions of the constituents in mixtures of these two alcohols may be calculated.

S. K. T.

#### Apparently Specific Test for Tannins. A. H. WARE

(*Analyst*, 1924, 49, 467—471).—Tannin alone is completely precipitated when equal volumes of neutral iron ammonium citrate solution (0.25% of the B.P. reagent in tap-water), and ammonium citrate (30%) are added to the same volume of the aqueous extract to be tested, after partial removal, if necessary, of resin, chlorophyll, etc. with 10% ammonium acetate solution. Combined with the modified method of Stiasny, the reaction may be used for the qualitative separation of phlobotannin, gallotannin, and gallic acid in solution. [Cf. *B.*, Nov. 28.]

D. G. H.

#### Modifications of the Picric Acid Method for Sugars.

J. J. WILLAMAN and F. R. DAVISON (*J. Agric. Res.*, 1924, 28, 479—488).—Rose's method (*A.*, 1921, ii, 465; 1918, ii, 24) is modified as follows. The standard sugar solution suggested is a 0.08% dextrose solution, or a 0.076% sucrose solution in saturated picric acid. This deteriorates after about a week. If dextrose-picric acid solution be heated previous to reduction in a sodium carbonate solution a greater colour value is obtained. A standard dilution of the test colour is necessary, since the intensity is not proportional to the dilution. The intensity of the colour produced is not proportional to the amount of sugar present and colour factors for 8 sugars are given. Previous clarification of the sugar solutions is often unnecessary.

A. G. P.

#### Determination of Dextrose in presence of Lactose by means of Copper Acetate.

P. FLEURY and P. TAVERNIER (*J. Pharm. Chim.*, 1924, [vii], 30, 225—231).—A solution of copper acetate in acetic acid containing sodium acetate is readily reduced by dextrose, but not at all by lactose, when heated for 10 minutes on a boiling water-bath. The method cannot, however, be applied to the determination of dextrose in the presence of lactose, as in that case the amount of copper reduced by the dextrose is considerably increased. Alkali and alkaline-earth chlorides greatly diminish the amount of copper acetate reduced by the dextrose, the addition of only 0.8% of sodium chloride diminishing the amount of copper reduced to

58% of its normal value. Chlorides should therefore be removed by treatment with silver acetate. This effect is not produced by sulphates or nitrates. P. M.

**Determination of Dextrose by a Modification of the Method of Fontès and Thivolle.** P. SPEHL (*Compt. rend. Soc. Biol.*, 1924, **90**, 638—640; from *Chem. Zentr.*, 1924, i, 2725; cf. A., 1921, ii, 563).—The method of Fontès and Thivolle is modified by using an excess of the copper tartrate reagent. A control tube without dextrose is used and each determination is checked by titration. The persistence of a pink coloration is taken as the end point. G. W. R.

**Determination of Maltose in the presence of other Reducing Sugars by means of Barfoed's Solution.** P. NOTTIN (*Compt. rend.*, 1924, **179**, 410—413).—Barfoed's solution of copper acetate and acetic acid is slowly reduced by maltose, and accordingly the values obtained by Le Grand (A., 1921, ii, 355) with this solution do not represent the true amounts of dextrose present. If  $G$  represents the amount of dextrose and  $M$  the amount of maltose present in a mixture, the reducing values for Barfoed's solution ( $A$ ) and Bertrand's solution ( $T$ ) can be expressed:  $A = G + aM$  and  $T = G + bM$ . The values of the coefficients  $a$  and  $b$  have been found by experiment to be 0.070 and 0.572, respectively. The value for  $a$  determined for maltose concentrations below 1% diminishes at higher concentrations (to 0.053 for 10% of maltose); the value of  $b$  also varies with the concentration of the maltose. Using these values, the amounts of maltose and dextrose present can be calculated from the equations:  $M = 1.995(T - A)$ ;  $G = A - 0.07M$ , and the values obtained are in close agreement with the results obtained with the polarimeter. R. B.

**[Determination of] Methylpentosans in Cereals.** G. TESTONI (*Staz. sperim. agrar. ital.*, 1923, **56**, 378—385; from *Chem. Zentr.*, 1924, i, 947).—The method of Tollens for the determination of methylpentosans in cereals is inexact, since starch and certain constituents of bran yield on distillation with hydrochloric acid, hydroxymethylfurfuraldehyde, which reacts with phloroglucinol and aniline acetate similarly to methylfurfuraldehyde. This error may be obviated by redistillation before precipitation with phloroglucinol. G. W. R.

**Cellulose Nitrate.** B. RASSOW and E. DÖRR (*J. pr. Chem.*, 1924, [ii], **108**, 113—186).—For the determination of pentosans in cellulose nitrate, it is necessary first to denitrate the latter, as furfuraldehyde is destroyed by nitric acid. For this purpose, alcoholic potassium and, particularly, ammonium hydrosulphide solutions give satisfactory results, the cellulose being recovered in practically theoretical amount, whilst the pentosans do not pass into solution. The furfuraldehydephloroglucide obtained in the determination of pentosans in denitrated cellulose nitrate contains methylfurfuraldehyde, derived from cellulose degradation products

formed during nitration. This can be extracted with alcohol, the insoluble portion giving the true pentosan content. The deviation of actual from theoretical yields of cellulose nitrate increases with increasing pentosan content of the latter. Celluloses poor in pentosan undergo little change with respect to this constituent through nitration and subsequent denitration, whilst those richer in pentosan lose a considerable proportion of this material. Pentosans are hydrolysed by the nitrating acids, the hydrolysis being greater the higher the temperature and weaker the acid, but up to 2% of pentosan always remains in the cellulose nitrate. Low yields of cellulose nitrate from wood and straw celluloses are also due in part to the presence of degraded cellulose formed during purification. Wood gum and pure xylan can be nitrated only with strong acids, weaker acids yielding soluble hydrolysis products. Nitropentosans are soluble in the usual solvents for cellulose nitrate, provided that the formation of hard, horny agglomerations is avoided during drying (cf. Will and Lenze, A., 1898, i, 227). [Cf. B., 1924, 863.]

F. G. W.

**Microchemical Detection of Acetaldehyde in Fruits.** C. GRIEBEL (*Z. Unters. Nahr. Genussm.*, 1924, 47, 438—441).—A few mg. of the fruit (e.g., pear) are placed in a shallow glass vessel, and this is covered with a microscope slide bearing on its under surface a drop of *p*-nitrophenylhydrazine hydrochloride solution (in 15% acetic acid); after about 30 seconds, particularly if the vessel is heated slightly, characteristic crystals of acetaldehyde-*p*-nitrophenylhydrazone are formed in the drop. The reaction may be obtained with 0.001 mg. of acetaldehyde. Other volatile aldehydes and ketones also yield crystals with the reagent.

W. P. S.

**Tests for Acetone and Aldehydes.** H. LEFFMANN (*Amer. J. Pharm.*, 1924, 96, 507—509).—In Frommer's test for acetone (*Berlin Klin. Woch.*, 1905, 42, 1008) vanillin can be substituted for salicylaldehyde. A few c.c. of a 10% alcoholic solution are added to 10 c.c. of acetone, together with a small piece of solid sodium hydroxide; a marked red ring forms above the alkaline solution. Gillet's test (A., 1923, ii, 442) is applicable only in fairly pure solutions. For accurate determinations the conditions under which aldehydes and acetone react with hydroxylamine and hydrazine require further investigation (cf. Pittarelli, A., 1920, ii, 639).

H. T.

**Detection of Ethyl Phthalate.** H. LEFFMANN (*Amer. J. Pharm.*, 1924, 96, 503—505).—A review of the existing methods of detecting ethyl phthalate. Utz's modification of Lyon's method (this vol., ii, 574) can give misleading results. Andrews' procedure (A., 1923, ii, 663) was found consistently satisfactory.

H. T.

**Rapid Determination of Cyanogen in Complex Iron Cyanides.** I. BELLUCCI and B. RICCA (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 476—482; from *Chem. Zentr.*, 1924, i, 2532).—In the determination of cyanogen in complex cyanogen compounds

of iron, the solution of the complex salt is boiled with a suspension of mercuric oxide. Sodium chloride is added to facilitate filtration, and by addition of potassium iodide to the filtrate the cyanogen is obtained in the form of cyanide. Sulphuric acid is added and the hydrogen cyanide is distilled into 1% sodium hydroxide and titrated with standard silver nitrate solution. G. W. R.

### **Iodometric Determination of Ferri- and Ferro-cyanides.**

R. LANG (*Z. anorg. Chem.*, 1924, **138**, 271—277).—In the determination of ferricyanides by treatment with zinc sulphate and potassium iodide, and titration of the liberated iodine with thiosulphate (cf. Mohr, *Annalen*, 1858, **105**, 60), the presence of excess of zinc sulphate causes too much iodine to be liberated owing to the surface effect of finely divided zinc ferricyanide causing auto-oxidation of the iodide. The error may be prevented by the addition of the zinc salt after the titration is practically completed. Ferrocyanides may be similarly determined if first oxidised to ferricyanide by the action of permanganate in acid solution, the excess of permanganate being destroyed by the action of hydrazine sulphate in the presence of potassium bromide, or by the action of nitrite and carbamide. An alternative method is to oxidise the ferrocyanide in acid solution by means of nitrite and to destroy the excess of the latter with carbamide. [Cf. *B.*, 1924, 940.] W. H.-R.

**Titration of Aniline and Homologues.** D. O. JONES and H. R. LEE (*Ind. Eng. Chem.*, 1924, **16**, 948—949).—The titration of, e.g., aniline with a standard nitrite solution takes a considerable time and nitrous acid is lost, even at 0°, because it decomposes (reversibly) into nitric acid and nitric oxide. By adding nitric acid, this decomposition is inhibited. The determination of aniline, toluidine, etc. is best carried out by adding to the cold (0°) acid solution of the compound (or a technical liquor) an excess of standard nitrite solution, nitric acid free from nitrous acid having previously been added, and after 30 minutes, titrating with a standard *p*-nitroaniline solution. W. A. S.

**Amino-acids containing Sulphur. I. Determination of Cystein.** Y. OKUDA (*J. Chem. Soc. Japan*, 1924, **45**, 1—18; cf. *J. Tokyo Chem. Soc.*, **37**).—The cystein solution containing hydrochloric or sulphuric acid and sodium bromide is titrated with 0.05*N*-potassium bromate solution until the light yellow colour developed does not disappear for 5 minutes. One c.c. of the bromate solution corresponds with 0.00606 g. of cystein. The concentrations of cystein and sodium bromide and the presence of sodium or zinc chloride have no influence on the result. In the absence of cystine, tyrosine, and tryptophan, this method is accurate. Of the amino-acids obtained by the hydrolysis of protein, only cystein reacts actively with iodine in acid solution. Cystein may therefore be titrated in acid solution with potassium iodate solution in the presence of iodide. In this case, the mol. proportion between cystein and iodine is not simple and is mainly governed by the concentration of the acid. K. K.

**Amino-acids containing Sulphur. II. Determination of Cystine.** Y. OKUDA (*J. Chem. Soc. Japan*, 1924, 45, 18—31).—When amino-acids are treated with nascent hydrogen, only cystine and cystein react with iodine. 1.01 G. of cystine is reduced to 1.0 g. of cystein by zinc dust and hydrochloric acid. The protein is hydrolysed by boiling with hydrochloric acid, treated with charcoal, filtered, and cooled. After keeping for thirty minutes in contact with zinc dust, it is filtered, diluted, and the acid content adjusted to 2%. The cystein is then determined volumetrically (cf. preceding abstract). When the sample contains cystein and cystine, the former is determined before reduction by the method previously described. If the amount of cystine is less than 1 mg. in 20 c.c. of 2% hydrochloric acid, the method gives a positive error. K. K.

**Determination of Allylthiocarbimide [in Mustard].** MORVILLEZ and MEESEMAECKER (*J. Pharm. Chim.*, 1924, [vii], 30, 236—240).—The powdered mustard is digested at 35° with aqueous alcohol and the product distilled into ammonia solution. After treatment with silver nitrate solution and heating at 85°, the silver sulphide may be collected on a tared filter, or the excess of silver nitrate may be determined volumetrically. An alternative process is to acidify the neutralised distillate with sulphuric acid, and then to add 0.1*N*-iodine solution and to set aside for 15 minutes in the dark. After the addition of chloroform, the excess of iodine is titrated with thiosulphate solution. This process is as trustworthy as the former, and more rapid. [Cf. *B.*, 1924, 922.] P. M.

**Microchemical Detection of Mustard Oils.** A. PIETSCHMANN (*Mikrochemie*, 1923, 2, 33—46).—The presence of mustard oils in a distillate may be detected by the allylthiocarbamide and phenylhydrazine reactions. The distillate is treated in a closed vessel with concentrated ammonia and, after 12 hours, the mixture evaporated to a small volume. A drop of this concentrated solution is then evaporated on a slide; crystals of allylthiocarbamide are obtained which may be identified by the usual reactions. If a drop of the distillate is mixed with a drop of 10% phenylhydrazine solution in glycerol and a drop of 10% sodium acetate solution in glycerol, yellow or brown crystals are obtained after some days. Determinations of mustard oil in *Alliaria officinalis* and *Armoracia lapathifolia*, by the ammoniacal silver nitrate method showed that the oil predominates in the outer portions of the tubers; in the case of *A. officinalis*, the distribution of the oil varies with the age of the plant and eventually the whole of the oil is found in the ripe seeds.

W. P. S.

**Analysis of Dehydrothio-*p*-toluidinesulphonic Acid.** H. R. LEE and D. O. JONES (*Ind. Eng. Chem.*, 1924, 16, 930—931).—The “nitrite-figure” for dehydrothio-*p*-toluidinesulphonic acid is best determined as follows. To an ice-cold solution of the acid (as technically isolated ammonium salt) an excess of a standard solution of sodium nitrite is added, followed by sufficient hydrochloric acid, then nitric acid (free from nitrous acid); the last addition is to prevent

loss of nitrous acid by decomposition. After 10 minutes, the solution is titrated with a standard *p*-nitroaniline solution.

W. A. S.

**Purification, and Identification by Micro-analysis, of Vegetable Poisons isolated from Bodies.** C. A. YLLNER (*Ark. Kemi, Min., Geol.*, 1924, **9**, No. 6, 1—11).—Alkaloids may be readily separated from animal organs which have become more or less putrid by treating the aqueous tartaric acid extract of the organs with a reagent prepared by dissolving 1.35 g. of mercuric chloride and 5 g. of potassium iodide in 100 g. of water. With most of the alkaloids, the precipitate obtained is soluble in dry acetone and is thus separable from the slimy material precipitated at the same time; morphine, however, requires special treatment. The details of the subsequent procedure for the identification of the alkaloids are described. [Cf. *B.*, Nov. 28.]

T. H. P.

**Dragendorff's Reagent [for Alkaloids].** G. CAPPELLI (*Annali Chim. Appl.*, 1924, **14**, 261—264).—Contrary to the statement of Ogier and Kohn-Abrest ("Traité de Chimie toxicologique," 1924, ii, 119), Dragendorff's reagent serves as an excellent reagent for the alkaloids in general and reacts well with narceine, theobromine, veratrine, and solanine. In preparing the reagent, it is necessary to use sublimed bismuth tri-iodide, which may be obtained by allowing iodine to fall, little by little, on to bismuth fused in a current of dry carbon dioxide and kept in continual agitation; the sublimed tri-iodide is collected in receivers, the carbon dioxide being freed from entangled fine crystals by passage through "vaseline" oil.

T. H. P.

**Determination of Morphine in Body Fluids and Organs.** T. TAKAYANAGI (*Arch. Exp. Path. Pharm.*, 1924, **102**, 167—175).—A method for the determination of morphine in urine, fæces, and organs involves a preliminary purification which varies with the organ, fluid, etc., concerned. The morphine is extracted with chloroform, transferred to water, precipitated by the addition of a solution containing potassium phosphate, ammonium molybdate, and oxalic and nitric acids, collected, and weighed in a Gooch crucible. The error is not greater than 5%. The method may be applied to the determination of other alkaloids by modifying the extractive solvents used.

J. P.

**Determination of Uric Acid in Poultry Excreta.** H. E. WOODMAN (*J. Agric. Sci.*, 1924, **14**, 413—427).—The fresh sample is extracted twice with cold alcohol and then with ether and the residue boiled with dilute hydrochloric acid. The liquor is evaporated and kept. The precipitated uric acid is collected, washed with cold water, and boiled with a dilute solution of lithium hydroxide, and the insoluble residue extracted with lithium hydroxide solution. The combined lithium hydroxide extract is evaporated, ammonium chloride is added, and the precipitated ammonium urate, washed with saturated ammonium chloride solution and dissolved in dilute



hydrochloric acid, is concentrated to 20 c.c., and kept. The uric acid is filtered off, washed, and either weighed or titrated with permanganate solution.

A. G. P.

**Determination of Bile Pigments in Urine.** G. SABATINI (*Klin. Woch.*, 1923, 2, 2031—2033; from *Chem. Zentr.*, 1924, i, 1425).—The pigments are determined colorimetrically, biliverdin being extracted by amyl alcohol in which it is soluble in acid solution, whilst bilirubin is insoluble.

G. W. R.

**Determination of Urobilin in Urine and Faecal Materials.** P. DESCOMPS, GOIFFON, and BROUSSE (*J. Pharm. Chim.*, 1924, [vii], 30, 97—113).—The urine, or an aqueous extract of the faeces, is oxidised with iodine, any excess of the latter being destroyed with thiosulphate after 30 seconds. An alcoholic solution of zinc acetate is added, and the mixture filtered. The concentration of urobilin is then determined by comparison, in a specially designed apparatus, of the intensity of the fluorescence of the solutions with that of a standard solution of pure urobilin in a solution of sodium acetate. The method is accurate to within 1.5%.

W. T. K. B.

**Test for Bile Pigments in Urine, Bile, and Blood-serum.** R. KAPSINOV (*J. Amer. Med. Assoc.*, 1924, 82, 687—688).—A solution of ferric chloride in concentrated hydrochloric acid gives a deep green colour, not extractable by chloroform, in presence of bile pigments.

CHEMICAL ABSTRACTS.

**The Guareschi Reaction with Proteins.** G. LO PRIORE (*Staz. sperim. agrar. ital.*, 1923, 56, 285—301; from *Chem. Zentr.*, 1924, i, 947).—The reaction with Hofmann-violet, decolorised by sulphuric acid, is not specific for proteins, but is given generally by nitrogen compounds of slight acidity or alkalinity.

G. W. R.

**New Possibilities of Acidimetry applied to Proteins and their Hydrolytic Products.** P. HIRSCH (*Biochem. Z.*, 1924, 147, 433—480).—An investigation of the possibility of applying acidimetric methods to the determination of proteins and derived products, based on a theoretical consideration of the titration curves of ampholytes in general, and an experimental investigation of the curves obtained for the acidic and basic groups of several amino-acids both singly and in mixtures, and for albumin, gliadin, and casein. From these latter curves, and from those obtained on titration of the total mixed hydrolysis products of the two first-mentioned proteins and of gelatin, it is considered that the original protein may be characterised.

J. P.

**Determination of Albumins and Globulins.** K. GUTZEIT (*Z. ges. exp. Med.*, 1924, 39, 397—406; from *Chem. Zentr.*, 1924, i, 2805).—From investigations with pure albumin and globulin solutions, using dialysis, it has been shown that albumins can change spontaneously into globulins within 2 to 4 days. The refractometric-viscosimetric method of Rohrer and the interferometric method of Hirsch are not applicable to the determination

of albumins and globulins. Directions are given for the separation of globulins from albumins by salting out with saturated sodium sulphate solution.

G. W. R.

**Microchemical Determination of Lipoids by Bang's Method.**

H. FORSTER (*Biochem. Z.*, 1924, **146**, 562—563).—Methods are described whereby certain of the difficulties in the determination of blood lipoids by Bang's method may be overcome (cf. this vol., ii, 359).

J. P.

**Determination of Lipoids.** E. HERZFELD (*Schweiz. med. Wochs.*, 1923, **53**, 797—798; from *Chem. Zentr.*, 1924, i, 2804).—The method is based on the turbidity produced on adding a mixture containing 90 c.c. of 10% phosphotungstic acid and 10 c.c. of concentrated hydrochloric acid to a diluted ethyl-alcoholic extract of the substance under examination. The turbidity is produced with as little as 0.008 mg. of lipid substances in 1 c.c. of extract.

G. W. R.

**Colorimetric Determination of Humic Matter in Mineral Soils.** T. EDEN (*J. Agric. Sci.*, 1924, **14**, 469—472).—The sample (5 g.) is treated with 50 c.c. of 10% hydrochloric acid, 20 c.c. of 50% sodium hydroxide solution are added, and the volume is adjusted to 100 c.c. plus the soil volume, and the mixture heated on a water-bath for 15 min. The extract is filtered and 20 c.c. are used to prepare a test solution which is compared colorimetrically with a standard made from Acidum Humicum (Merck).

A. G. P.

**Determination of Colloidal Material in Soils by Adsorption.**

P. L. GILE, H. E. MIDDLETON, W. O. ROBINSON, W. H. FRY, and M. S. ANDERSON (*U.S. Dept. Agric. Bull.*, 1924, **1193**, 41 pp.; cf. Moore, Fry, and Middleton, A., 1921, ii, 608).—The adsorptive capacities for water vapour, malachite green, and ammonia of a number of soils were determined and compared with those of the colloidal material extracted from the same soils by centrifuging after removal of the coarser particles by settling. The ratio of the adsorption per g. of soil to the adsorption per g. of colloid multiplied by 100 is taken as the percentage of colloidal material present. The chief errors are due to the difficulty of extracting a representative sample of the colloid and to a change taking place in the adsorptive capacity of the colloid after extraction. By applying a correction, good agreement was obtained with determinations made gravimetrically and microscopically.

C. T. G.

**Determination of "Bayer 205" in Serum, Urine, and Tissues.** O. STEPPUHN and X. UTKIN-LJUBOWZOW (*Klin. Wochs.*, 1923, **3**, 154—155; from *Chem. Zentr.*, 1924, i, 1246).—A method for the determination of "Bayer 205" is described in which the material containing this substance is boiled with an alkali. The components thus liberated are coupled with diazo compounds, and the resultant colouring matters determined colorimetrically.

G. W. R.

## General and Physical Chemistry.

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**Quantum Defect and Atomic Number.** L. A. TURNER (*Phil. Mag.*, 1924, [vi], 48, 384—394).—A modification of Bohr's assignments of quantum numbers to optical orbits is proposed, to apply at least to heavier elements of groups I and II of the periodic table. The quantum defect for orbits of the second kind (*i.e.*, penetrating orbits) does not vary smoothly with atomic numbers if the Bohr assignment is followed, but the relation becomes linear for the alkali metals if the quantum numbers of the *s* and *p* orbits of rubidium and caesium are increased by one and two, respectively. Similar changes are suggested for group II.

Quantum defects for the terms of ionised atoms are less than those of the corresponding neutral atoms. S. B.

**Quantum Defect and Atomic Number.** L. A. TURNER (*Phil. Mag.*, 1924, [vi], 48, 1010—1014; cf. preceding abstract).—A linear relation exists between the atomic number and the quantum defects computed from the ionising potentials of the rare gases, from the second ionising potentials of the rare gases, and from the ionising potentials of the hydrogen halide molecules. On the basis of these relations the following critical potentials are predicted: ionising potential neon,  $27.5 \pm 1.5$  volts; ionising potential hydrogen fluoride,  $17.9 \pm 0.5$  volts; appearance of a blue spectrum of neon,  $45.2 \pm 1.2$  volts. C. W. B.

**Stability of the Atom.** D. N. MALLIK (*Phil. Mag.*, 1924, [vi], 48, 884—895).—A mathematical paper showing that Larmor's condition for the permanent stability of a system of electrons, *i.e.*, that the vector sum  $|\dot{e}v|$  shall be constantly zero, is a necessary consequence of the quantum conditions postulated by Sommerfeld in the case of a Bohr atom of hydrogen. C. W. B.

**Absorption of Radiation by Multiply Periodic Orbits, and its Relation to the Correspondence Principle and the Rayleigh-Jeans Law.** I. Extensions of the Correspondence Principle. II. Calculation of Absorption by Multiply Periodic Orbits. J. H. VAN VLECK (*Physical Rev.*, 1924, 24, 330—346, 347—365).—I. Theoretical. The quantum theory aspects of the problem are considered, and the correspondence principle is extended to include absorption as well as spontaneous emission. The general correspondence principle basis for Kramers' dispersion formula is also discussed.

II. A presentation of the mathematical analysis on which the foregoing is largely based. A. A. E.

**Fine Structures in Non-hydrogenic Atoms.** A. E. RUARK, F. L. MOHLER, and R. L. CHENAULT (*Nature*, 1924, 114, 575).—The fine structures of non-hydrogenic lines arise from transitions between  
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the components of complex spectral levels. Save for a few isolated examples, fine structures are not due to isotopy. In some cases it is necessary to introduce a fine quantum number,  $f$ , the values of which characterise the different components of a complex level. Fine structures may be due to relativity, magnetism, or unknown dynamical peculiarities of the element. A. A. E.

**Fine Structure of Mercury Lines and the Isotopes.** H. NAGAOKA, Y. SUGIURA, and T. MISHIMA (*Jap. J. Phys.*, 1923, 2, 121—162).—The distribution of intensity of light in interference points produced by crossed spectra of interferometers is discussed and the method of reduction for determining  $\delta\lambda$  given. Reasons are given for the hypothesis that the mercury atom consists of a central mass with a proton quasi-elastically connected with it. The appearance of satellites is traced to the existence of isotopes. The fine structure of the line  $\lambda = 2537$  is discussed in detail in relation to alteration of strength of exciting current, position in the arc, and the influence of a magnetic field and a third electrode. The line  $\lambda = 3131.84$ , which does not obey the formula for isotopes, is found to be due to the packing of nuclear electrons. The deviation from Coulomb's law of electric action at very small distances is discussed, together with the probable variation of the formula for electric mass in such a field of force. L. J. H.

**Spectroscopic Evidence of Isotopy.** H. NAGAOKA and Y. SUGIURA (*Jap. J. Phys.*, 1923, 2, 167—278).—It is suggested that the non-series lines of spectra may have their source in nuclear vibrations which set the whole group of electrons in vibration. On this view, when atomic encounters occur, coupled vibrations are set up and the frequency of any resulting light emission will be affected by the masses of the nuclei. Different varieties of such atomic encounters can be easily conceived in ionised gases even for monatomic elements, and must be frequent in diatomic elements during the formation of molecules. When isotopes are present symmetric and asymmetric encounters are possible; thus for chlorine two symmetric pairs (35, 35) and (37, 37) and one asymmetric pair (35, 37) are possible, giving rise to triplets. Formulæ are developed for the difference in wave-length for the different cases which generally amount to many Ångström. The spectra of lithium, neon, silicon, chlorine, argon, zinc, copper, bromine, and rubidium were examined for such differences, and strong support for the hypothesis is submitted in more than 90 pages of tables. By reversing the calculation, it is possible to test for unknown isotopes from spectroscopic data. Probably isotopes of sodium (21) and calcium (44) exist. The presence of an isotope of barium is doubtful. L. J. H.

**Fine Analysis of the Stark Effect in Balmer's Series by Lo Surdo's Method.** J. S. FOSTER (*Physical Rev.*, 1923, 21, 710).—The use of a new form of Lo Surdo discharge tube enabled observations to be extended to  $H\epsilon$ . Among the  $p$ -components for  $H\gamma$ , the undisplaced line grows weaker with increasing field and

finally disappears. The outside  $s$ -components for  $H\gamma$  are very weak in all fields up to the maximum value of 60 kv./cm. and are about equal in intensity.

A. A. E.

**Broadening of Spectral Lines Caused by Increased Current Density and their Stark Effects.** M. KIMURA and G. NAKAMURA (*Jap. J. Phys.*, 1923, 2, 61—75).—A qualitative comparison is made of the broadening of some lines of various elements produced by using a high current density with the Stark effect recorded by others.

L. J. H.

**Regularity in the Distribution of the Spectral Lines of Iron and Intra-atomic Magnetic Field.** H. NAGAOKA and Y. SUGIURA (*Jap. J. Phys.*, 1923, 2, 1—52).—In a vertical arc, with sufficiently high potential, a steep potential gradient is found near the lower electrode, whether anode or cathode. By comparing spectral photograms of this region with different metals certain characteristics of electrical separation were noted, which made it possible to observe to which group the lines belonged, and many regularities were observed. The different types of regularities are summarised in tables. Regular separation (of quadruplets) suggests an intra-atomic magnetic field which was tentatively calculated at  $7 \times 10^6$  gauss. This agrees with the value deduced by Weiss from experiments on the magnetic quality of iron at high temperatures.

L. J. H.

**Pole-effects and Pressure-shifts in the Lines of the Spectra of Zinc and Calcium.** R. E. HARRIS (*Astrophys. J.*, 1924, 59, 261—273).—For zinc, electrodes of zinc, brass, and carbon filled with zinc chloride were used; for calcium, electrodes of metallic calcium, and carbon filled with calcium chloride. With calcium, the pole-effect differed for the two sources, being greater at the positive pole with calcium, and greater at the negative with calcium chloride. Similar effects were observed in the case of zinc and zinc chloride.

A. A. E.

**Self-reversal of the Lines  $H_\alpha$  and  $H_\beta$  of Hydrogen.** M. KIMURA and G. NAKAMURA (*Jap. J. Phys.*, 1923, 2, 53—59).—The influence of the introduction of foreign vapours (water, oxygen, chlorine, iodine, and mercury) on the self-reversal of the lines  $H_\alpha$  and  $H_\beta$  was studied. These substances, at a pressure of a few millimetres, broaden out the lines considerably, and in some cases a faint reversal of the line  $H_\beta$  is observed. Further addition of hydrogen reverses the line  $H_\alpha$  easily. The broadening of the lines which is observed if the side, instead of the centre, of the capillary image is focussed on the slit is considered in relation to the Stark effect. It is supposed that the atoms near to the wall of the capillary tube are exposed to a greater inter-molecular field.

L. J. H.

**Intensity Relations in the Hydrogen Spectrum produced by Electron Impacts.** A. L. HUGHES and P. LOWE (*Physical Rev.*, 1923, 21, 202).—The distribution of intensity in the hydrogen spectrum produced by the impact of electrons of energy between

29 and 110 volts was measured. The density of  $H_\alpha$  remained constant, whilst that of  $H_\beta$ ,  $H_\gamma$ , and  $H_\delta$  increased rapidly at first, and then tended to a constant value. The densities of the band lines 6327, 6225, 6135, 6122, 6030, and 6018 Å. decreased very rapidly as the energy of the electron was increased, whilst those of 5013, 4934, 4929, 4632, 4743, and 4205 exhibited a maximum between 30 and 40 volts. It is inferred that the proportion of dissociating collisions to non-dissociating collisions increases rapidly with the energy of the impacting electrons between 29 and 110 volts, and that the higher the energy of impact the more likely is the electron within the atom to be displaced to the remoter Bohr orbits as the molecule is being dissociated by electron impacts.

A. A. E.

**Spectrum of Helium at Very Low Pressures.** R. T. DUFFORD and L. THOMPSON (*Physical Rev.*, 1923, 21, 212—213).—At pressures corresponding with a parallel spark gap of 1—4 cm., the brightest helium lines belong to the helium and parhelium principal series, and the next to the first subordinate series, with the helium lines brighter than the parhelium lines. Only one faint line (4713 Å.) of the helium second subordinate series is observed, and one (5048 Å.) of parhelium. None of the enhanced lines of helium appear. An essential difference between the spectra and those obtained at higher pressures is the marked shift of energy towards the violet among the lines of any one series.

A. A. E.

**Relative Intensities of Helium Lines as a Function of Current.** B. CURRY (*Physical Rev.*, 1923, 21, 203).—The current-intensity curves are of the form  $y = ax^n$ , where  $a$  and  $n$  are constant for a given line between definite limits of the current. The results confirm Kayser's observation of a shift of energy towards the violet, but do not show even qualitative relations to the Wien displacement law of black-body radiation.

A. A. E.

**Regularities in the Spectra of the Alkaline Earths.** F. A. SAUNDERS and H. N. RUSSELL (*Physical Rev.*, 1923, 22, 201).—Many lines of calcium, strontium, and barium are combinations between terms of the known series and other triple or single terms. Combination series of type  $2\pi - m\sigma$ ,  $2\pi - m\delta$  have been found in the spark spectra of calcium and barium. A new  $pp'$  group in calcium, near 2560 Å., indicates that the neutral atom can contain more than enough energy to ionise it; probably both valency electrons are shifted to outer orbits and when both fall back a single quantum is radiated. Each element has three  $d'$  triplets with inner quantum numbers 2, 1.0; 3, 2.1; 4, 3.2. The separation of corresponding triplets increases with atomic weight; those between the triplets are nearly constant.

A. A. E.

**Spectra of Constricted Arc of Metals.** T. TAKAMINE and M. FUKUDA (*Jap. J. Phys.*, 1923, 2, 111—119).—Spectra of arcs in vacuum between metal electrodes were examined in which the arc was mechanically constricted by passage through a narrow hole near the anode. At the constricted portion, many series of lines appeared which are usually forbidden by the principle of selection. It is

concluded that this, as well as the broadening of the diffuse series of lines also observed, is due to the powerful intermolecular field produced by the high concentration of the ions and electrons caused by the constriction. In the case of mercury, a certain group of arc lines, of which the series relations are unknown, appeared with marked intensity. With thallium many new combination lines were found, and with cadmium and zinc the diffuse series lines are observed up to higher term numbers than have previously been given.  
L. J. H.

**Standard Wave-lengths and Regularities in the Spectrum of the Iron Arc.** W. F. MEGGERS (*Astrophys. J.*, 1924, 60, 60—75).—The relative values of 27 sets of spectral terms have been calculated to 8 significant figures; about 800 lines from 2276 Å. to 9768 Å., and including most of the internationally adopted standards, are represented with precision. Critical tests of the accuracy in relative values of such standards show that most of the lines in any one multiplet are relatively correct to 1 in  $2 \times 10^6$  or  $3 \times 10^6$ , except in the ultra-violet, where the error is 1 in  $4 \times 10^5$ . Pressure shifts and pole effects can be eliminated and the accuracy of standard wave-lengths increased by the adoption of the iron arc in a vacuum as the source of secondary and tertiary standards.  
A. A. E.

**Regularities in the Spectrum of Ionised Titanium.** N. K. SUR (*Nature*, 1924, 114, 611).—The chief lines in the spectrum of ionised titanium can be arranged as quartet groups, and the lowest levels are given by three  $p$ -terms with the frequency differences 861 and 509 (*i.e.*, 5:2.96, whilst Landé's ratio would be 5:3). The separations of the  $d$  terms, which should be 7:5:3 are 98.40:69.46:45.86 = 7:5:3.1. The ionisation potential of ionised titanium appears to be about 13 volts.  
A. A. E.

**Vacuum Spark Spectrum of Silicon, 2100—6700 Å.** R. A. SAWYER and R. F. PATON (*Physical Rev.*, 1923, 21, 203).—Previous results (A., 1923, ii, 804) have been verified and extended by the use of an improved apparatus. About 300 lines attributed to silicon have been carefully measured; of these, 200 are new, 100 being faint and therefore doubtful.  
A. A. E.

**Electrodeless Discharge.** P. D. FOOTE and A. E. RUARK (*Nature*, 1924, 114, 750).—The spark spectrum of potassium was excited, in the electrodeless ring discharge, by reduction of the pressure, *e.g.*, to 0.002 mm. mercury. The fact that only five or six members of the Balmer series were observed in the case of hydrogen is probably due to the fact that collisions of electrons, of velocity comparable with the ionisation potential, with hydrogen molecules usually result in excitation or ionisation without dissociation. Among the experimental details recorded is a suggestion for the possible separation of the isotopes of mercury by a deposition method. The ring discharge is an effective means of producing active nitrogen; evidence is quoted in support of the view that this consists of nitrogen molecules in a metastable condition.  
A. A. E.

**Spectrum Observations on the Copper Arc.** F. SIMEON and E. S. DREBLOW (*Nature*, 1924, **114**, 751).—With the copper arc, practically no pole effects were observed above 2800 Å.; changes in intensity, below this wave-length, between the centre of the arc and the poles are tabulated. Minimal or zero intensity was observed at the negative pole. By means of Hartmann's formula the following wave-lengths were interpolated: 2138.49, 2105.03, 2104.70, 2079.53. The line given by Hasbach at 2085.22 Å. was not observed.  
A. A. E.

**Series in the Spectra of Aluminium and Magnesium in the Extreme Ultra-violet.** T. LYMAN (*Nature*, 1924, **114**, 641—642).—Certain lines in the spectra of aluminium and magnesium in the extreme ultra-violet appear to be higher members of series discovered by Paschen (this vol., ii, 672) and Fowler ("Series in Line Spectra," p. 120), and the identifications are tabulated.  
A. A. E.

**Colloidal Supports for [Solutions when] Obtaining Emission Spectra.** J. ERRERA (*Bull. Soc. chim. Belg.*, 1924, **33**, 449—451).—A modification of Gramont's method for detecting small quantities of a metal by the most persistent lines of the emission spectrum, the latter being obtained by striking an arc between two drops of a very dilute solution of a salt of the metal placed at the ends of two silica capillary tubes (Gramont, A., 1908, ii, 3). A gelatinised solution of the salt is used in the form of two electrodes fixed into brass carriers. The ultimate rays are still visible at high dilutions and, in the case of silver, may be obtained for dilutions of the order of one part in a million.  
M. S. B.

**Band Lines in the Secondary Spectrum of Hydrogen.** G. S. FULCHER (*Physical Rev.*, 1923, **21**, 375—376).—Additional band lines have been discovered; each group consists of five regularly spaced lines. The wave-length differences are more constant than the frequency differences; all are low-voltage lines, and no Zeeman effect has been observed.  
A. A. E.

**Band Spectra and Molecular Structure.** Y. TAKAHASHI (*Jap. J. Phys.*, 1923, **2**, 95—110).—Theoretical, with special application to iodine, the alkaline-earth fluorides, helium, and the Fulcher band of hydrogen. The moments of inertia for these molecules are calculated.  
L. J. H.

**Infra-red Band Spectrum of Methane.** J. P. COOLEY (*Physical Rev.*, 1923, **21**, 376—377).—All three absorption regions of methane ( $7.7\ \mu$ ,  $3.31\ \mu$ , and  $2.35\ \mu$ ) have been partly resolved into lines; about fifty lines in the second region fit into two parabolic series, one on each side of the centre of the band. Between these and masking the first line of the positive or longer wave-length series lies a narrow region of intense absorption corresponding with the "zero branch"; the lines are too closely packed to admit of resolution. The band at  $7.7\ \mu$  is similar in structure. The moment of inertia of the molecule in the first rotational state represented in the region at  $3.31\ \mu$  is computed to be  $5.6 \times 10^{-40}\ \text{g.cm.}^2$  and in the region at  $7.7\ \mu$ ,  $9.0 \times 10^{-40}\ \text{g.cm.}^2$   
A. A. E.



**Rotational Specific Heat of Hydrogen.** R. C. TOLMAN (*Physical Rev.*, 1923, **22**, 202—203).—Consideration of infra-red rotation-oscillation spectra indicates that the lowest possible azimuthal quantum number for the non-oscillating rotating molecule of the "dumb-bell" model can have only the values 0, 1, or  $\frac{1}{2}$ . The rotational specific heat is calculated for the third possibility. It is considered that the simple dumb-bell model cannot be more than a first approximation and that the results do not yet warrant the conclusion that half-quantum numbers are to be preferred.

A. A. E.

**Line and Band Spectra of Fluorine.** H. G. GALE (*Physical Rev.*, 1923, **21**, 711—712).—The stronger lines previously observed (A., 1923, ii, 803) have been re-measured, together with a number of fainter lines also ascribed to fluorine. Five strong bands have heads at approximately 5100, 5390, 5730, 6100, and 6520 Å., and six fainter bands at 5580, 5720, 5850, 6480, 6930, and 6980, respectively. The bands are all degraded towards the red. Silicon tetrafluoride gives a band spectrum of eleven bands between 4240 and 4600 Å., the bands being degraded towards the red and falling into three groups.

A. A. E.

**Active Modification of Nitrogen.** M. N. SAHA and N. K. SUR (*Phil. Mag.*, 1924, [vi], **48**, 421—428).—It is suggested that nitrogen in the active form discovered by Strutt consists of  $N_2$  molecules in a metastable condition, loaded with an energy corresponding to 8.5 volts. This view is based on the fact that the spectrum of active nitrogen shows only those positive nitrogen bands attributed by Wien to the un-ionised  $N_2$  molecule, and none of the line spectrum of nitrogen, or even the negative bands supposedly due to  $N_2^+$ .

The excitation of the spectra of other materials by active nitrogen is due to the transference of the energy of the metastable state to the atoms of the other substances. It appears that, in accordance with this view, no lines requiring more than 8.5 volts for their excitation are developed.

S. B.

**Active Nitrogen.** R. T. BIRGE (*Nature*, 1924, **114**, 642—643).—An investigation of the band spectrum of nitrogen has given a partial indication of the form of the molecule responsible for the emission of  $\alpha$ -group bands. The results suggest that the particular state of electronic excitation corresponding with the initial state of the molecule when emitting the first positive group bands is metastable for ten, eleven (particularly), and twelve units of vibrational energy. The assumption of the metastable state is essential. Saha and Sur's assumption (cf. preceding abstract) that active nitrogen is merely a nitrogen molecule excited with 8.5 volts energy is untenable, since it precludes the possibility of emission of the  $\alpha$ -group bands, and offers no explanation of the distinction between the  $\alpha$ -group of the afterglow and the ordinary first positive group. The effect of the presence of an electro-negative element in removing electrons and thus prolonging the life of active nitrogen is considered. Oxygen may to some extent produce an excited form of nitric oxide which

reverts to the stable form with the emission of  $\beta$ -bands; these excited molecules may be metastable, and may be accompanied by different excited nitric oxide molecules which revert to the stable form with the emission of the  $\gamma$ -bands. It is not possible, however, to arrive at definite conclusions regarding the mode of excitation of the  $\beta$ - and  $\gamma$ -groups.

A. A. E.

**Fluorescence and Channelled Absorption Spectra of Bismuth Vapour at High Temperatures.** A. L. NARAYAN and K. R. ROW (*Nature*, 1924, **114**, 645).—Bismuth vapour at  $1300^{\circ}$  yields an absorption spectrum composed of a very great number of bands shading off towards the red, and presenting a fine structure; they extend from 6500 to 4500 Å. The vapour emits an orange-yellow fluorescence, the spectrum of which contains 24 bands from 6600 to 5050 Å.

A. A. E.

**Structure of the Absorption Bands of certain Organic Gases and Vapours in the near Infra-red.** C. F. MEYER and D. W. BRONK (*Physical Rev.*, 1923, **21**, 712—713).—The region of  $3.3\ \mu$  has been investigated for ethylene, benzene, ethyl alcohol, and ethyl ether. The bands exhibit decided structure; ethylene shows maxima at  $3.1970$ ,  $3.2412$ ,  $3.3169$ , and  $3.3722\ \mu$ , of approximately the same intensity, the group somewhat suggesting a double doublet. Benzene shows maxima at  $3.2331$ ,  $3.2784$ , and  $3.3722\ \mu$ , the central one being the most pronounced. Ethyl ether has maxima at  $3.3513$  and  $3.4802\ \mu$ , of equal intensity, and a smaller maximum at  $3.3973\ \mu$ . Ethyl alcohol has one decided maximum at  $3.3571\ \mu$ , and several less intense. Relationships in wave-length differences are indicated between the maxima for the compounds.

A. A. E.

**Absorption Spectra and Co-ordination of some Cupric Compounds.** I. (MISS) H. S. FRENCH and T. M. LOWRY (*Proc. Roy. Soc.*, 1924, **A**, **106**, 489—512).—An attempt to decide the presence or absence of co-ordination in doubtful cases. Quantitative measurements of the absorption spectra of a number of organic copper compounds were made. Data are given for (i) solutions in alcohol and in chloroform of copper derivatives of diketones, viz., acetylacetone, ethyl acetoacetate, and benzoylcamphor, (ii) for solutions of copper salts of monobasic fatty acids, viz., solutions in water of the formate, acetate, and propionate, in alcohol of the series acetate to caproate, and in chloroform of the series propionate to caproate. For the purpose of comparison, measurements were also made of the extinction-coefficients of certain solutions of inorganic copper salts. The absorption spectra are all dominated by two main factors, as follows: (i) a "copper" band in the red or infra-red, the position and intensity of which vary with the radicals associated with the metal, but without destroying the general character of the band, (ii) a band or general absorption in the ultra-violet which is determined almost entirely by the organic radicals, although the metal with which they are associated influences in a secondary way the position of the band or the intensity of the general absorption. The behaviour of these factors and their influence on the colours of

the solutions are discussed. The evidence obtained supports the view that the copper salts of the fatty acids in the undissociated state are just as much co-ordinated as the more stable organic copper derivatives, *i.e.*, of the type copper acetylacetone, generally admitted to be co-ordinated. Some of the compounds are decomposed by water, yielding hydrated copper ions, which, however, are also co-ordinated.

L. F. G.

### **Influence of Constitutional Variation in Dyes on their Relative Absorption in Aqueous and Alcoholic Solutions.**

W. C. HOLMES (*J. Amer. Chem. Soc.*, 1924, **46**, 2118—2124).—The relative absorption of dyes in dilute aqueous and alcoholic solutions does not conform to Kundt's rule, but is primarily dependent upon constitutional factors. The term *alcopositive* is applied to dyes of which the absorption band is displaced toward the red in passing from aqueous to alcoholic solution, dyes exhibiting the opposite behaviour being termed *alconegative*. Most azo dyes appear to be alcopositive, the proportion of alconegative dyes increasing with the complexity of the dye molecule, and in the trisazo class alconegative dyes appear to predominate. In the triphenylmethane dyes, alkyl substitution in the amino group exerts an alconegative influence and most of the acid dyes of the diamino type, including all hydroxyamino derivatives, are alconegative. Sulphonation in the non-aminated nucleus has an alconegative effect but its influence is less with the triamino derivatives. Substitution of phenyl groups in the amino group exerts an alcopositive influence, and the behaviour of the acid triamino dyes of this group depends chiefly on the nature of the substituted amino group. Similar influences are observed with the rhodamines, rhodamine chloride itself being moderately alcopositive. Esterification exerts an alcopositive influence, and a similar effect is observed in the phthaleins. Halogenated phthaleins substituted in the resorcinol nucleus are less alcopositive than those substituted in the phthalic anhydride residue. Most thiazine and oxazine dyes are alconegative, the proportion of alcopositive dyes being greater in the azine class. The influence of alkyl substitution in the amino groups in dyes of this class is very pronounced, and the influence of ethyl groups appears to be rather more alconegative than that of methyl groups. In the indigo group, sulphonation exerts an opposite effect to that observed with diaminotriphenylmethane derivatives. It is suggested that the absorption of dyes is dependent on the distribution of residual affinity in the molecule, which is affected by interplay of the residual affinities of the solvent and solute (cf. Baly, *J. Amer. Chem. Soc.*, 1915, **37**, 979). R. B.

### **Luminescence of Solid Nitrogen and the Auroral Spectrum.**

L. VEGARD (*Nature*, 1924, **114**, 715; cf. this vol., ii, 713).—The luminescence of solid nitrogen shows two bands in the green,  $N_1$  and  $N_2$ . McLennan and Shrum (this vol., ii, 642) consider that the auroral line has no connexion with this band, since it does not coincide with any of the three maxima. The maxima cannot, however, be treated in this way as ordinary spectral lines, since they have no definite positions. The band  $N_1$  is regarded as a manifestation of

the same effect as that which, in the limiting case of molecular magnitude, is responsible for the auroral line; it is necessary to consider the spectrum as a whole. The green afterglow obtained, according to McLennan and Shrum, with pure argon is actually due to traces of nitrogen. A. A. E.

**Rotatory Dispersion of Derivatives of Tartaric Acid. I. Methylene Derivatives.** P. C. AUSTIN and V. A. CARPENTER.—(See i, 1164.)

**Rotatory Dispersions of *d*-Camphorimide, *d*-Camphorbenzylimide, Benzyl-*d*-camphoramic Acid, and their Derivatives.** B. K. SINGH and A. C. BISWAS.—(See i, 1211.)

**Absorption Spectra of Camphor, Benzylidenecamphor, and Camphorquinone. Optical Evidence of Two Types of Conjugation.** T. M. LOWRY and H. S. FRENCH.—(See i, 1212.)

**Abnormal Rotatory Dispersion of Acid Solutions of Nicotine in Relation to Hydrogen-ion Concentration.** (MLLE.) J. LIQUIER (*Compt. rend.*, 1924, 179, 269—271).—Similar results to those obtained by Gennari (A., 1896, ii, 286) in the case of mixtures of nicotine and acetic acid are given in dilute solution on addition of varying quantities of different acids to an aqueous solution of nicotine. As the ratio of molecular concentration of acid to that of nicotine increases, the laevorotation becomes smaller, disappears when the ratio is between 0.7 and 0.8 (corresponding with  $p_H$  values of 7.79 and 7.54), and subsequently becomes of opposite sign. The hypothesis is put forward that although undissociated nicotine is laevorotatory, the cations of its salts are of the opposite sign. H. J. E.

**Mutarotation. III. Solution Volume and Refraction Constants of  $\alpha$ - and  $\beta$ -Glucose.** C. N. RIIBER (*Ber.*, 1924, 57, [B], 1599—1604; cf. A., 1922, ii, 807; 1923, ii, 811).—From the data recorded previously, the molecular solution volume of  $\alpha$ - and  $\beta$ -glucose in aqueous solution (10%) is calculated to be 111.230 and 111.648 ml. respectively; since the values vary somewhat with the dilutions, they are calculated for infinite dilution to be 111.795 and 111.218 ml. The molecular refraction, calculated by the Gladstone-Dale formula, is 62.676 and 63.066 for  $\alpha$ - and  $\beta$ -glucose, respectively, in 10% solution and 62.532 and 62.923 for infinitely dilute solution; these values are for the sodium *D* line. H. W.

**Theory of Constitutive Colour.** E. ZINTL and A. RAACH (*Ber.*, 1924, 57, [B], 1739—1744).—The colour of compounds has been attributed to the vibration of atoms or the oscillatory change in valency within the molecule of constitutively coloured substances. Attempts are described to examine this theory experimentally in the cases of the higher oxides of lead with the aid of radioactive indicators. If such oscillations occur in a compound containing inactive quadrivalent lead and induced active bivalent lead a regular distribution of the radioactive isotopes over all the lead atoms is to be expected. A preparation of lead sesquioxide with incited bivalent lead yields, after treatment with nitric acid, bi- and quadri-valent

lead of equal activity, but the experiment is regarded as inconclusive since atomic exchange during the production or decomposition of the sesquioxide is not improbable. If, however, lead sesquioxide is obtained by the precipitation of a 3*N*-alkaline solution of inactive plumbate with a 3*N*-alkaline solution of radioactively incited plumbite and the precipitate, after being illuminated during 3 hours, is dissolved in 12*N*-alkali hydroxide a solution is obtained from which barium hydroxide precipitates barium plumbate of such small activity that it can be attributed only to co-precipitated barium plumbite. An oscillatory exchange in the molecule,  $\text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , is therefore considered not to occur under the influence of light.

H. W.

**Sensitising Action of Heat on Photographic Plates for the Infra-red.** O. MASAKI (*Jap. J. Phys.*, 1923, 2, 163—165).—The sensibility of the photographic plate increases with rise of temperature and reaches a maximum at 105°.

W. E. G.

**Spectral Characteristics of Test Solutions used in Heterochromatic Photometry.** K. S. GIBSON (*J. Opt. Soc. Amer.*, 1924, 9, 113—121).—The integrated light transmissions of solutions of potassium dichromate (72 g. per litre) and of copper sulphate (57 g. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  per litre) have been found to be equal within 1%. These solutions may be used in work involving visual photometry of sources emitting different wave-lengths, to eliminate personal errors of observation.

S. B.

**Ionisation Potentials of Hydrogen as Interpreted by Positive-ray Analysis.** T. R. HOGNESS and E. G. LUNN (*Proc. Nat. Acad. Sci.*, 1924, 10, 398—405).—The minimum potential necessary for the ionisation of hydrogen by the impact of electrons emitted by a hot tungsten filament has been determined. By observing the combined effect of an electric and magnetic field, the ratio of the charge to the mass for each type of ion has been measured by a method similar to Dempster's (*Physical Rev.*, 1918, 11, 316). Three different types have been obtained,  $\text{H}^+$ ,  $\text{H}_2^+$ , and  $\text{H}_3^+$ ; but since the ionisation potentials for  $\text{H}^+$  and  $\text{H}_3^+$  are practically identical, namely 16.6 volts, it seems probable that  $\text{H}_3^+$  is formed by the combination of  $\text{H}^+$  and  $\text{H}_2$ . The ionisation potential for the formation of  $\text{H}_2^+$  is 15.7 volts. The results obtained are in agreement with those of Olsen and Glockler (*A.*, 1923, ii, 455).

M. S. B.

**Ionising Potentials of Multiatomic Gases.** C. A. MACKAY (*Physical Rev.*, 1924, 24, 319—329).—Ionising potentials were measured by accelerating photo-electrons from a nickel target through a gauze and collecting positive ions from the ionisation chamber on a fine platinum wire electrode. The following results, in volts, were obtained: helium, 24.5; hydrogen, 15.8; nitrogen, 16.3; oxygen, 12.5, 16.1; hydrogen chloride, 13.8; hydrogen bromide, 13.2; hydrogen iodide, 12.8; water, 13.2; ammonia, 11.1; chlorine, 13.2; bromine, 12.8; iodine, 10.0; nitric oxide, 9.4; carbon dioxide, 14.3; carbon monoxide, 14.1, 15.6; hydrogen

sulphide, 10.4. The results of thermochemical considerations are inconsistent with the view that the first ionisation involves molecular dissociation, certain consistencies being regarded as fortuitous.

A. A. E.

**Stages in the Development of the Iodine Spectrum and Related Critical Potentials.** F. L. MOHLER and P. D. FOOTE (*Physical Rev.*, 1923, 21, 382).—In undissociated vapour below 10 volts there are apparently two stages in the excitation of the band spectrum, whilst above 10 volts both line and band spectra are obtained. Above 21 volts a second line spectrum appears. Dissociated vapour emits only pure line spectra. Critical radiation potentials are 10.5, 21, and 52 volts; ionisation was observed at 10.5 volts, but no increase at 21 volts.

A. A. E.

**The Striated Discharge in Mercury Vapour.** W. H. MCCURDY (*Phil. Mag.*, 1924, [vi], 48, 898—917).—The striations which occur in the positive column of the discharge in a monatomic gas under low pressure are due to the presence of impurities; also the current in the positive column of the discharge is due to the motion of electrons under the influence of the electric field, whilst that in the Faraday dark space and the negative glow is due to the diffusion of the electrons and positive ions produced in the negative glow by fast electrons from the Crookes dark space.

C. W. B.

**Disappearance of Gas in the Electric Discharge.** RESEARCH STAFF OF THE GENERAL ELECTRIC COMPANY, LONDON (N. R. CAMPBELL and E. G. NEW) (*Phil. Mag.*, 1924, [vi], 48, 553—580).—An attempt has been made to find a relation between the rate of absorption of gas in a discharge tube and the rate of ionisation of its molecules. The results are complicated by the existence of other modes of absorption and evolution of gas, which are independent of ionisation. In nitrogen, and in carbon monoxide, the rate of absorption is proportional to the rate of ionisation, and nearly independent of the gas pressure, and of the voltage applied, shape of electrodes, etc. It depends greatly on the condition, but not on the material, of the walls of the tube. In argon and in hydrogen, the relation between absorption and ionisation, if existent, is obscured by other effects. All existing theories of the mechanism of the absorption are open to grave objections. The experiments were carried out in triode tubes of about 150 c.c. capacity, the potential drop being 50—350 volts, and the initial gas pressure 0.001 mm.

S. B.

**Absorption of Hydrogen in Potassium Vapour Arcs.** R. D. RUSK (*Physical Rev.*, 1923, 21, 720).—Potassium was made the anode of a two-electrode tube, and ionisation currents were obtained between a coated filament and the anode, through potassium vapour and hydrogen, absorption being obtained with currents of a few milliamperes. Absorption appears to set in at a potential corresponding with a particular type of ionisation of the hydrogen.

A. A. E.

**Electron Emission from Tungsten, Thorium, Molybdenum, and Tantalum.** S. DUSHMAN, H. N. ROWE, and C. A. KIDNER (*Physical Rev.*, 1923, **21**, 207—208).—Suitably corrected emission data gave results in satisfactory agreement with the equation:  $I = 60 \cdot 2 T^2 \epsilon^{-b_0/T}$  amps./cm.<sup>2</sup> (cf. *ibid.*, 1922, **20**, 109). The emission at 2000° Abs. was: tungsten,  $9 \cdot 12 \times 10^{-4}$ ; thoriated tungsten, 9.55; molybdenum,  $3 \cdot 31 \times 10^{-3}$ ; tantalum,  $1 \cdot 95 \times 10^{-2}$ . The values are in agreement with those of Davisson and Germer (*ibid.*, 1922, **20**, 300). A. A. E.

**Variation of the Thermionic Emission with Temperature and the Concentration of Free Electrons within Conductors.** A. T. WATERMAN (*Physical Rev.*, 1924, **24**, 366—376).—The following free electron concentrations ( $\times 10^{17}$  per c.c. at 0°) are incidentally obtained: sodium, 1.0; copper, 1.7; platinum, 1.5; silver, 1.4; lead, 1.1; bismuth, 1.0. Molybdenum disulphide,  $1 \cdot 3 \times 10^{12}$ ; calcium oxide,  $2 \cdot 3 \times 10^9$ . The values decrease with increase of temperature. A. A. E.

**Scattering of Electrons by Platinum and by Magnesium.** C. DAVISSON and C. H. KUNZMAN (*Physical Rev.*, 1923, **21**, 385).—Up to 350 volts the electron scattering patterns for platinum are simple and similar in form to those required by the assumption of a nucleus surrounded by a single shell of electrons, but above 350 volts the distribution breaks up into a series of lobes. Patterns were also obtained with magnesium deposited by vaporisation on the platinum target. The results indicate a concentration of 7 or 8 electrons in the magnesium atom at a distance of about  $1 \cdot 5 \times 10^{-9}$  cm. from its centre. A. A. E.

**Electrometer Method for Measuring Dielectric Constants of Liquids.** A. P. CARMAN (*Physical Rev.*, 1924, **24**, 396—399).—A differential idiostatic electrometer is described for the measurement of dielectric constants of liquids. The dielectric constant of water at 25° for an alternating *E.M.F.* of 60 cycles is 78.07, a result which is in agreement with accepted values. A. A. E.

**Electric Moment of Gaseous Molecules of Hydrogen Halides.** C. T. ZAHN (*Physical Rev.*, 1924, **24**, 400—417).—Measurements by an improved heterodyne null method from the liquefaction point to 300° give results well represented by Debye's equation,  $(\epsilon - 1)vT = AT + B$ , where  $v$  is the specific volume,  $T$  the absolute temperature,  $A$  is for hydrogen chloride, 0.001040; hydrogen bromide, 0.001212; hydrogen iodide, 0.001856; and  $B$  is 0.895, 0.52, and 0.12 respectively. The electric moments of the molecules, in  $10^{-18}$  c.g.s.u., are, respectively, 1.034, 0.788, and 0.382. Incidentally, the following dielectric constants,  $(\epsilon - 1) \times 10^6$ , were measured: air, 572; nitrogen, 581; hydrogen, 265; oxygen, 518 ( $\pm 0.5\%$ ) at 0° and 760 mm. Since the limit for the infra-red absorption data for hydrochloric acid is 6 times the value from the Debye classical theory and 13 times that from the Pauli quantum theory, it is not possible to decide between the two theories.

A. A. E.

**Electric Moments of Organic Molecules.** C. P. SMYTH (*J. Amer. Chem. Soc.*, 1924, **46**, 2151—2166).—The electric moments of the molecule of a substance calculated from the author's formula (*Phil. Mag.*, 1923, [vi], **45**, 849; 1924, [vi], **47**, 530) are always smaller than those deduced from a consideration of the hypothetical molecular structure. This is due to a shifting of charges caused by the attractive and repulsive forces within the molecule. The moments of the alcohols, ethers, aldehydes, and ketones are comparable with the moment of the water molecule, but ammonia and the amines have smaller moments than water because the electrons around the nitrogen nucleus are more easily displaced than those around the oxygen nucleus. The moments of analogous hydrogen and organic halides decrease in the order: chloride, bromide, iodide. Saturated hydrocarbons and hydrocarbons with double bonds have very small moments; the influence of the introduction of successive methyl groups is irregular. The effect on the moment of two groups in the same molecule is discussed in detail. S. K. T.

**Specific Inductive Capacity of Colloidal Solutions.** J. ERRERA (*Bull. Soc. chim. Belg.*, 1924, **33**, 422—431, 432—449).—The specific inductive capacity of vanadium pentoxide sols has been determined by a bridge method (cf. Joachim, A., 1920, ii, 465; King and Patrick, A., 1922, ii, 109). A freshly made solution, containing 31 parts of oxide per 1000, had a specific inductive capacity of 74.7, and this increased with age. A solution 5 years old, containing 14 parts per 1000, had a specific inductive capacity of 400. The liquid remaining after ultrafiltration gave a value of 82.9. After dilution the sol does not reach immediately a state of equilibrium, but a portion gradually passes into the molecular disperse state and, at the same time, diminution of the specific inductive capacity takes place. By increasing the intensity of the oscillating circuit used as a source of alternating current, and therefore the strength of the electric field, the specific inductive capacity increases, whereas for water under the same conditions it remains constant. With rise of temperature the specific inductive capacity diminishes.

The phenomena observed have the same origin as the optical anisotropy of vanadium pentoxide sols. The particles of the latter assume the form of small rods the longitudinal axis of which is coincident with the optical axis. Under the influence of an electric field the particles are orientated so that the axis is parallel to the lines of force, and this effect opposes the Brownian movement, which, however, is again increased by rise of temperature. The appearance of optical anisotropy, and the accompanying increase in the specific inductive capacity indicate the first stage in the process of coagulation. The use of a metallic container appears to accelerate coagulation, possibly on account of contact potentials. Passage of an electric current ages the sol artificially.

Vanadium pentoxide behaves exceptionally compared with other non-solvated sols, since the latter have, in general, a specific inductive capacity very little different from that of water. The explan-



ation given for the behaviour of vanadium pentoxide is supported by measurements made with varying frequencies of the alternating current. These show that, at high frequencies, the specific inductive capacity decreases to a little less than that of water. It increases, however, as the frequency diminishes, to a maximum value, and then decreases again because of the absorption of energy by the particles which begin to migrate under the action of the current. This behaviour may be attributed to the fact that, at high frequencies, there is no time for the field to exert its directive action on the colloidal particles before inversion takes place, and so Brownian movement has full play. The time required for the particles to respond to the field is approximately  $10^{-7}$  sec. By comparison with the dielectric constants of electrolytic solutions of similar conductivity, it is shown that the conductance has no influence on the result. No interference is produced by placing the sol in an external field acting at right angles to the internal field. M. S. B.

**Change of Conductance of Selenium due to Electronic Bombardment.** R. DE L. KRONIG.—(See ii, 849.)

**Hall Effect in Silicon-Iron Alloys.** T. C. MACKAY (*Physical Rev.*, 1923, **21**, 720).—The increment in the Hall effect is approximately proportional to the percentage of silicon up to about 5%.  
A. A. F.

**Hall Effect and Specific Resistance of Evaporated Films of Silver, Copper, and Iron.** J. C. STEINBERG.—(See ii, 857.)

**Magnetism of Oxygen and the Molecule  $O_4$ .** G. N. LEWIS (*J. Amer. Chem. Soc.*, 1924, **46**, 2027—2032).—The magnetic susceptibility of oxygen does not obey Curie's law, but a quantitative explanation of the effect of temperature on its magnetic properties is possible if it is assumed that both  $O_2$  and  $O_4$  molecules exist. The molecule of  $O_2$  is paramagnetic and obeys Curie's law, whilst that of  $O_4$  is not paramagnetic. The heat of dissociation is approximately 128 calories per mol. of  $O_4$ . At the temperature of liquid air, about one-half by weight is in the associated form, whilst at room temperature the associated fraction is only a few hundredths of 1%. The heat of dissociation is responsible for the diminution in the specific heat of liquid oxygen with rise of temperature.

W. H.-R.

**Barkhausen Effect [in Steel].** E. P. T. TYNDALL (*Physical Rev.*, 1924, **24**, 439—451).—Experiments with steel containing 4.2% Si support Barkhausen's theory that magnetic materials magnetise discontinuously, but do not support the suggestion that each discontinuity is due to a single crystal.  
A. A. E.

**Magnetic Susceptibility of Helium, Neon, Argon, and Nitrogen.** L. G. HECTOR.—(See ii, 854.)

**Magnet Steel with Especial Reference to the Relation between the Carbon Content and Magnetic Properties.** G. HANNACK (*Stahl u. Eisen.*, 1924, **44**, 1237—1243).—The maximum

induction of tungsten steel falls linearly with increasing carbon content whilst the coercivity increases; these effects are much more marked in the case of chromium steel, but the curves showing the relations between carbon content and magnetic properties are not straight lines. [Cf. *B.*, 1924, 946.] A. R. P.

**Thermal Conductivity of Bismuth in a Transverse Magnetic Field.** F. A. WARD (*Phil. Mag.*, 1924, [vi], 48, 971—977).—The average diminution of the thermal conductivity of bismuth is 3.22% in a transverse magnetic field of 5370 c.g.s. units, and of the order 5% in a field of 6260 c.g.s. units. C. W. B.

**Separation of Isotopes.** J. KENDALL (*Physical Rev.*, 1923, 21, 389—390; cf. *A.*, 1923, ii, 282).—The ionic migration and discharge potential methods are referred to; it is believed that the freezing-point method would be successful in an extreme case such as that of lithium. A. A. E.

**Possible Isotopes of the Elements.** S. R. COOK (*Physical Rev.*, 1923, 22, 203).—An application of general equations to elements based on helium, the hydrogen molecule, and the hydrogen atom. A. A. E.

**Mass-spectra of Cadmium, Tellurium, and Bismuth.** F. W. ASTON (*Nature*, 1924, 114, 717).—Cadmium, examined by the use of an anode containing cadmium fluoride, has the isotopes 114, 112, 110, 113, 111, 116, in reasonably good agreement with the chemical atomic weight, 112.41. The group is remarkably similar to that of tin, a fact which may be significant in connexion with the relative stability of the nuclei of isotopes. The masses appear integral with that of iodine. Tellurium gives lines at 126, 128, and 130, the intensities of the latter two being equal and double that of the first. It is probable that the mean atomic weight is greater than 128; the element is unique in that all its mass numbers probably form members of isobaric pairs. Bismuth is a simple element of mass number 209. A. A. E.

**Structure of Silver.** H. COLLINS (*Chem. News*, 1924, 129, 222—223).—Speculative. A. R. P.

**Structure of Antimony.** H. COLLINS (*Chem. News*, 1924, 129, 267—269).—Speculative. A. A. E.

**Radioactivity of Basalts and other Rocks.** J. H. J. POOLE and J. JOLY (*Phil. Mag.*, 1924, [vi], 48, 819—832).—Values are given for the radium and thorium contents of more than one hundred basic, ultra-basic, intermediate, and acid rocks from widely different localities. C. W. B.

**Complexity of the Elements. II.** A. S. RUSSELL (*Phil. Mag.*, 1924, [vi], 48, 365—378).—The complexity of the elements of even atomic number between selenium and lead has been investigated with the help of the postulates developed in a previous paper (this vol., ii, 445). It is suggested that relations, of the same type

as Fajans'  $\alpha$ - and  $\beta$ -ray rules, exist between the mass number and life period of isotopes, both for radioactive and ordinary elements. For elements of odd atomic number the isotope of lowest mass number has the longest period. The relations suggested for elements of even atomic number are more complex, and less definite. Predictions are attempted of the isotopes of elements not yet examined in the mass spectrograph. S. B.

**Need for Redetermination of the Atomic Weights of Uranium, Thorium, and Radium.** A. S. RUSSELL (*Nature*, 1924, **114**, 717—718).—The assumption of the existence of an isotope of uranium of mass greater than that of uranium does not account for the discrepancy between the calculated and experimental values of the atomic weight of uranium. It seems likely that in the transformations between uranium-*I* and radium- $\Omega'$  a mass of 0.11 is gradually lost in addition to the mass of the 8  $\alpha$ -particles expelled, giving a mass for radium of 0.14 greater than the experimental value. There is a *prima facie* case for the redetermination of the atomic weights of uranium, thorium, and radium.

A. A. E.

**Distribution of the Active Deposit of Radium in Helium and Argon in an Electric Field.** G. H. BRIGGS (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 249—255).—A continuation of previous work (cf. *Phil. Mag.*, 1921, **41**, 367) on the distribution of the active deposit of radium and thorium in electric fields in various gases (e. g., air, carbon dioxide, nitrous oxide, methane, acetylene, ammonia, ethylene, hydrogen sulphide). In helium and argon, as in all other gases investigated, negative particles are not present in sufficient numbers to be detected. The value of  $(c-d)/(c+d)$ , where *c* and *d* are the cathode and anode deposits after a long exposure to the gas mixed with radium emanation in a parallel plate vessel, is 0.964 for helium and 0.755 for argon, and is independent of the voltage from 400 to 5000 volts and 400 to 8000 volts respectively. The fractions of radium-*A* and radium-*B* initially positively charged are 0.936—0.939 and 0.964—1.0 respectively in helium and 0.618 and 0.818 respectively in argon.

W. T. K. B.

**Range of  $\alpha$ -Particles in Rare Gases.** L. F. BATES (*Proc. Roy. Soc.*, 1924, **A**, **106**, 622—632).—The ranges of  $\alpha$ -rays, from sources of thorium-*B* and -*C*, in helium, neon, argon, krypton, and xenon were determined by a scintillation method. The stopping power of helium, compared with that of air as unity, is 0.1757 for  $\alpha$ -rays having a range of 4.29 cm. in air. The stopping powers of neon, argon, krypton, and xenon are 0.586, 0.930, 1.330, and 1.804, respectively, for  $\alpha$ -rays having a range of 4.15 cm. in air. From a comparison of the observed stopping powers and those calculated by Fowler's method (*Proc. Camb. Phil. Soc.*, 1923, **21**, 521) the deduction is made that Henderson's theory (*Phil. Mag.*, 1922, **44**, 680), on which Fowler's method is based, accounts for only about 75% of the energy loss suffered by  $\alpha$ -rays on passing through the several gases.

L. F. G.

**Collision of  $\alpha$ -Particles with Light Atoms.** M. AKIYAMA (*Jap. J. Phys.*, 1923, 2, 279—286).—If the conservation of momentum holds good the track of the  $\alpha$ -particle before and after impact and that of the recoil atom will lie in one plane, but anomalous cases are observed in which this apparently is not the case. Other anomalies are considered and the possibility that very hard  $\gamma$ -rays are produced at collision is tentatively discussed. L. J. H.

**Recoil of Radioactive Atoms.** M. AKIYAMA (*Jap. J. Phys.*, 1923, 2, 287—289; cf. preceding abstract).—On disintegration of actinium-*A* and -*B* the tracks of the recoil atom and expelled  $\alpha$ -particle are not always exactly opposite on the same straight line. The maximum deviation recorded is  $15^\circ$ , and 22 out of 82 observations show deviations of more than  $8^\circ$ . L. J. H.

**Origin and Nature of Long-range Particles from Radium-*C*.** E. RUTHERFORD and J. CHADWICK (*Phil. Mag.*, 1924, [vi], 48, 509—526).—In previous experiments (A., 1919, ii, 260) on the passage of  $\alpha$ -particles from radium-*C* (range 7 cm.) through nitrogen and oxygen, particles of range 9 cm. were observed, which produced scintillations brighter than those due to hydrogen nuclei.

It is now shown that the appearance of these particles is independent of the nature of the gas in their path, and that they originate in the radium-*C*. Magnetic deflection methods prove that they are  $\alpha$ -particles. They are ascribed to a previously unknown mode of disintegration of radium-*C*. Similar conclusions are reached regarding a small number of particles which have been detected, of range 11.2 cm. The observation of Bates and Rogers (this vol., ii, 84) of particles of range 13.3 cm. is not supported.

S. B.

**The Double Bond.** W. H. CAROTHERS (*J. Amer. Chem. Soc.*, 1924, 46, 2226—2236).—The suggestion of Lewis (A., 1916, ii, 310) that dissociation may occur at non-polar linkings, producing parts more or less polar and reactive, is developed in conjunction with the octet theory to account for the reactions of the double bond. In compounds containing a double bond, dynamic equilibrium is assumed to exist between an inactive form and an active form. In the former the double bond is represented by two typical non-polar unions, whilst in the latter, dissociation of one of the bonds has occurred, leaving one atom with only six electrons. The amount of the active form present is always small and is determined by the nature of the compound (that is, by the effective nuclear charges of the two atoms) and varies with the temperature, concentration, etc. On dissociation, the atom having the higher effective nuclear charge retains the extra electron; the result is the same when the doubly linked atoms are attached to other atoms or groups, the additional electron being retained by the atom carrying the groups with the higher nuclear charge. These assumptions, in combination with the octet theory, are used to interpret addition, selective addition, conjugation and 1:4-addition, Markovnikov's rule,

reduction, catalytic hydrogenation, promotor action, and other reactions of the double bond. Esterification is discussed on the same theory. The double bond, although usually polar, is not necessarily so, and its reactivity is not chiefly due to polarity (cf. Lowry, T., 1923, 123, 822; Noyes, this vol., ii, 102). R. B.

**X-Ray Absorption Coefficients of Cobalt and Nickel.** F. K. RICHTMYER and F. W. WARBURTON (*Physical Rev.*, 1923, 21, 721).—The X-ray mass absorption coefficients ( $\mu/\rho$ ) for cobalt and nickel, respectively, are  $124\lambda^3 + 0.17$  and  $144\lambda^3 + 0.20$ . The constant  $K$  in the equation  $\mu/\rho = K\lambda^3 + \sigma/\rho$  is therefore a function, not of the atomic weight, but of the atomic number. A. A. E.

**Effect of Canal-rays on Crystals.** W. FEITKNECHT (*Helv. Chim. Acta*, 1924, 7, 825—842; cf. A., 1908, ii, 1007; 1909, ii, 718).—Microscopical observations were made of the surface changes of cathodes under the influence of impinging positive rays. The gas used in the bulb was generally argon at 0.05—0.15 mm. pressure; when hydrogen is substituted, the effects are the same, although not so marked. The *P.D.* across the discharge bulb varied between 1000 and 2500 volts, giving a current of about 0.35 ma. The metals and alloys were all polished before examination. The rate of removal of atom-layers by positive rays depends on the crystallographic situation of the face attacked and on the density of packing of the atoms. The rate of ejection of atoms will be greater as the thickness of the "inner transitional layer" (cf. A., 1920, ii, 295) increases. For silver and copper, the action of the rays varies according as the metal is recrystallised before exposure or the solidified regulus used directly. In the latter case, a short exposure reveals the crystalline structure. Projections are formed on the surface which consist of pulverised metal thrown back on the cathode. When the recrystallised metal is given a long exposure, cavities are produced, which resemble the "etching figures" produced by the attack of liquid solvents. The more complete the recrystallisation, the more easily are the cavities developed. The action on silver-copper alloys depends on the composition. When silver is in excess, the eutectic comes into prominence, for copper is less easily pulverised than silver, of which, in this case, the primary crystals consist. When copper is in excess, the arborescent primary crystals of copper become prominent. W. E. E.

**Crystal Structure of Benzene.** J. K. MORSE (*Physical Rev.*, 1923, 22, 525; cf. A., 1923, i, 1189).—Plane spacings calculated by Hull's method for the centred orthorhombic lattice of benzene agree with Broomé's results for the lattice constants  $a_1 : b_1 : c_1 = 5.809 : 6.884 : 6.186$  in Å. The means of the adjacent angles for two pairs of lines are  $21^\circ 21.5'$  and  $23^\circ 39.5'$ , respectively. The scattering angles for liquid benzene for the  $K_\beta$  and  $K_\alpha$  radiation of iron are  $21^\circ 21'$  and  $23^\circ 39'$ ; hence these regions are identified with the liquid. A. A. E.

**Diffraction of X-Rays in Liquids, Fluid Crystals, and Amorphous Solids.** C. V. RAMAN and K. R. RAMANATHAN (*Proc. Indian Assoc. Cultiv. Sci.*, 1923, 8, 127—162).—The diffraction haloes photographically observed when monochromatic X-radiation passes through a film of liquid are explained by considering the positions of the molecules to possess a certain degree of regularity. X-Ray diffraction haloes for liquid mixtures, anisotropic liquids, and amorphous solids are also dealt with.

CHEMICAL ABSTRACTS.

**Scattering of X-Rays by Liquid Benzene, Mesitylene, and Octane, and by Diamond Splints.** C. W. HEWLETT (*Physical Rev.*, 1923, 21, 477).—The scattering curve for octane shows three maxima due respectively to general radiation, and the first and second order reflection for the *K*-radiation of molybdenum. Benzene and mesitylene curves show the general radiation, but it is not resolved from the *K*-radiation. Mesitylene shows two maxima for the *K*-radiation, giving spacings for the atomic planes of 6.2 Å. and 4.1 Å. Small differences were observed in the curves for diamond splints at ordinary temperatures and at 300°. A. A. E.

**Atomic Structure according to Bohr and Isomorphogenism of Metals of the Rare Earths with those of the Calcium Group.** F. ZAMBONINI (*Atti R. Accad. Lincei*, 1924, [v], 33, ii, 16—20).—Bohr's conception of the structure of the atoms of different elements serves to explain the peculiar chemical behaviour of the rare-earth metals. As with the alkaline-earth metals, the external envelope of a rare-earth metal contains only two electrons. The tervalent character of yttrium and of the elements from lanthanum to lutecium is determined by the fact that the adjacent internal orbit comprises, in addition to the two groups, each of four electrons, found with calcium and its analogues, also an isolated electron, which is able to act as a valency electron. The tervalency of these metals cannot, however, be as pronounced as that of aluminium, gallium, indium, thallium, etc., which have three valency electrons in the outermost sphere. Thus, alums are formed by aluminium and the other typically tervalent elements but not by the rare-earth metals. That thallium is able to replace part of the aluminium of alums is due to the presence of three valency electrons in the outermost envelope. The limited character of the isomorphogenism between the rare-earth metals and those of the aluminium group is indicated also by the compositions of various minerals. The structure given by Bohr furnishes likewise a satisfactory interpretation of the behaviour of thorium.

The above considerations are in complete accord with the compositions of the gases resulting from the action of water on the carbides of the different metals. Thus, the carbides of cerium, lanthanum, praseodymium, and samarium yield gases containing from 67.19 to 72.16% of acetylenic hydrocarbons, and hence resemble calcium carbide, whereas of the gas obtained from thorium carbide only 15.16 to 15.22% consists of acetylenes. T. H. P.

**Carbon Atom in Crystalline Structure.** (SIR) W. H. BRAGG (*J. Franklin Inst.*, 1924, 198, 615—625).—An address delivered at the University of Pennsylvania reviewing the present position.

W. E. G.

**Crystal Structure of Aluminium Carbide, determined without the use of X-Rays.** M. L. HUGGINS (*Physical Rev.*, 1923, 21, 716).—A knowledge of the general tendencies operative in crystal formation, determined from a study of the positions of valency electrons in crystals of known atomic arrangement, of the empirical formulæ, number of valency electrons, the crystal symmetry, and sometimes other crystallographic data, is sufficient to determine the most probable structure of many crystals. From the fact that it forms yellow, rhombohedral crystals,  $d$  2.36, and is stable in a vacuum up to  $1400^\circ$ , aluminium carbide,  $\text{Al}_4\text{C}_3$ , is considered to have each aluminium atom surrounded by 3 carbon atoms and each carbon by 4 aluminium atoms, all at tetrahedron corners. The average aluminium-carbon distance is 2.02 Å. It is predicted that  $c/a$  will be about 1.225, and that the (0001) faces will be found to be polar.

A. A. E.

**Crystal Structure of the Rhombohedral Forms of Selenium and Tellurium.** A. J. BRADLEY (*Phil. Mag.*, 1924, [vi], 48, 477—496).—The structures of selenium and tellurium crystals have been determined by the X-ray "powder" method. They may be regarded as simple rhombohedral structures with interaxial angles of almost  $90^\circ$ , in which each atom is slightly displaced towards two of the six adjacent atoms. The resulting structure is a threefold spiral, composed of three interpenetrating simple triangular lattices.

The crystal structures of elements of groups IV, V, and VI differ from group to group in virtue of the difference in negative valency, which regulates the direction of displacement from the simple cubic structure.

S. B.

**Structure of the Isomorphous Ammonium Zirconium and Ammonium Hafnium Fluorides.** O. HASSEL and H. MARK (*Z. Physik*, 1924, 27, 89—101).—The isomorphous ammonium zirconium and ammonium hafnium fluorides,  $(\text{NH}_4)_3\text{MF}_7$ , crystallise in the cubic system; four molecules are contained in the crystal unit, the side of which is 9.35 Å. for the former and 9.40 Å. for the latter. The spacing is of the  $O_h^4$  type with three parameters, the four metal atoms and four of the fluorine atoms showing a  $D_{3d}$  symmetry, the twelve nitrogen atoms a  $C_{2v}$  symmetry, and the remaining twenty-four fluorine atoms a  $C_s$  symmetry. From the density of the impure hafnium salt (containing 15% of the zirconium salt) the atomic weight of this metal is found to be  $179 \pm 5.4$ .

S. K. T.

**Crystal Structure and Absorption Spectra. The Cobaltous Compounds.** R. HILL and O. R. HOWELL (*Phil. Mag.*, 1924, [vi], 48, 833—847).—By examining and comparing the absorption spectra of solutions with those of solid compounds of known crystalline structure, the nature of the association of the atoms in

solution can be elucidated. Examination of the structure of magnesium oxide shows that the magnesium is surrounded by six oxygen atoms. Cobalt pink, in which cobalt replaces magnesium, has an absorption spectrum comparable with the absorption spectra of the solutions of cobalt chloride, sulphate, or nitrate, the latter being among themselves almost identical. It is concluded that the cobalt ion in these solutions is surrounded by six water molecules. Similarly, spinel is shown to contain the magnesium atom surrounded by four oxygen atoms; cobalt spinel is blue and has an absorption spectrum to which those of the many cobalt pigments examined closely approximate. Moreover, solutions of cobalt thiocyanate in ether, and cobalt oxide in potassium hydroxide, are blue, and their absorption spectra are similar. It is concluded that the cobalt atom in the solid blue compounds is associated with four other atoms or groups. The same arrangement accounts for the colour of the blue solutions. Constitutions are given to the well-known cobaltous pigments. C. W. B.

**Deformation of Tungsten Single Crystals under Tensile Stress.** RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD. (F. S. GOUCHER) (*Phil. Mag.*, 1924, [vi], 48, 800—819).—A combined X-ray and microscopical study is made of the deformed crystals—in particular the fractured crystals—which are produced by the extension and fracture of fine tungsten wires composed of crystals, many of which occupy locally the complete volume of the wire. The deformation may be accounted for in all cases by slip on the (112) planes and in the [111] direction, with the single exception of a crystal subject to special constraints which slipped as well on the (100) planes and in the [100] direction. The results are in accord with the direction of easiest slip in the case of single crystals of metals involving other types of lattice. C. W. B.

**Some Properties of Single Metal Crystals.** P. W. BRIDGMAN (*Proc. Nat. Acad. Sci.*, 1924, 10, 411—415).—A preliminary note. The elasticities, linear compressibilities, thermal expansions, and electrical resistances, in various directions, of single crystals of antimony, bismuth, cadmium, tellurium, tin, zinc, and (in part) tungsten, are recorded and discussed. Two new polymorphic forms of cadmium, produced by pressure, are noted. W. A. S.

**Crystalline Structure of Calcium Oxide, Sulphide, and Selenide.** W. P. DAVEY.—(See ii, 858.)

**Crystalline Structure of Barium and Strontium Selenides.** M. K. SLATTERY.—(See ii, 859.)

**Crystal Structures of some Sulphides, Selenides, and Tellurides.** M. L. HUGGINS.—(See ii, 849.)

**Crystal Structure of "Metallic" Selenium and Tellurium.** M. K. SLATTERY.—(See ii, 849.)

**Crystal Structure of Hard Steel.** K. HEINDLHOFFER.—(See ii, 863.)



**Course of Recrystallisation of Silver.** G. GLOCKER and E. KAUPP.—(See ii, 857.)

**Crystallographic Identity of the Two Forms of Mercuric Oxide.** G. R. LEVI.—(See ii, 860.)

**Crystal Lattice of Manganous Oxide.** G. R. LEVI.—(See ii, 862.)

**Crystal Structure of Manganese Dioxide.** A. ST. JOHN.—(See ii, 862.)

**Crystal Structures of some Tetragonal Crystals.** M. L. HUGGINS.—(See ii, 866.)

**Crystal Structures of Alumina, Ferric Oxide, and Chromic Oxide.** W. P. DAVEY.—(See ii, 861.)

**Crystal Structure of Iron-Nickel Alloys.** L. W. MCKEEHAN.—(See ii, 863.)

**Crystal Structure and Density of Cuprous Selenide and Zinc Selenide.** W. P. DAVEY.—(See ii, 860.)

**Internal Structure of Crystallised Carbon and of Benzene.** J. BECKENKAMP.—(See ii, 754.)

**Structure of "Black Diamonds" [Carbonado].** W. GERLACH.—(See ii, 753.)

**Crystal Structure of Calcium Hydroxide.** G. R. LEVI.—(See ii, 757.)

**Crystalline Lattices of the Rhombohedral Carbonates of Bivalent Metals.** G. R. LEVI and A. FERRARI.—(See ii, 760.)

**Critical Densities of Salts.** R. LORENZ and W. HERZ.—(See ii, 755.)

**Study of Secondary Valency [Tri-iodides] by X-Rays.** G. L. CLARK and W. DUANE.—(See ii, 855.)

**Atomic Radii.** M. L. HUGGINS (*Physical Rev.*, 1923, 21, 205—206).—The following atomic radii (distance from nucleus to valency electron-pair) have been computed (in Å.): beryllium, 1.00; carbon, 0.77; oxygen, 0.65; magnesium, 1.29; silicon, 1.17; sulphur, 1.04; chlorine, 0.96; manganese (bivalent), 1.39; iron (bivalent), 1.23; copper (univalent), 1.42; zinc, 1.31; germanium, 1.22; selenium, 1.12; bromine, 1.10; silver, 1.60; cadmium, 1.49; tin, 1.40; tellurium, 1.23; iodine, 1.22; and the conditions under which they are strictly comparable are specified. The correctness of the above values is dependent on the value assumed for sulphur surrounded by four positive bivalent elements. The radius of the hydrogen atom in ice is 0.73 Å.; in the centred cubic forms of ammonium chloride and bromide, the hydrogen diameter is 1.67 Å. and 1.64 Å., respectively. A. A. E.

**Determination of Molecular Diameters from Surface Tension Measurements.** S. MOKROUSHIN (*Phil. Mag.*, 1924, [vi], 48, 765—768).—The molecular diameter is expressed as a function of the surface energy:  $d = \sqrt{J(L - RT)/(\pi N \sigma)}$ , where  $L$  = latent heat of vaporisation per mole. Values of  $d \times 10^8$  quoted in the paper, viz., nitrogen, 4.94, hydrogen, 4.48, oxygen, 4.6, water, 5.12, chlorine, 5.24, bromine, 5.82, are hence independent of any determination of the mean free path. C. W. B.

**Polymorphic Transformation Energies.** A. HARE (*Phil. Mag.*, 1924, [vi], 48, 412—421).—The heats of the polymorphic transformations of several salts have been determined by a cooling curve method. The values obtained are, in kg.-cals. per g.-mol.: potassium sulphate (569°), 2.57; potassium chromate (664°), 2.45; lead sulphate (866°), 4.06; lithium sulphate (566° and 569°), 6.77 and 6.96; sodium molybdate (440°), 14.60; sodium tungstate (579°), 9.51. It was found that, except with sodium molybdate, the heat of transformation could be obtained equally well either from a cooling or a heating curve. Sodium molybdate, however, required 24 hours to recover its normal state after heating. S. B.

**Dependence on Pressure of the Adiabatic Cooling of some Organic Substances.** N. A. PUSHIN and E. V. GREBENSHCHIKOV (*J. Chem. Soc.*, 1924, 125, 2043—2048).—The changes of temperature produced by the adiabatic expansion or compression of phenol, *p*-toluidine, benzene, urethane, ethyl alcohol, glycerol, and castor oil in the liquid state have been determined by the method described previously (T., 1923, 123, 2717). The coefficient  $dt/dp$  decreases with increasing pressure. At 64.4° and under a pressure of 2250 kg./cm.<sup>2</sup>, phenol passes into a denser modification,  $dt/dp$  becoming almost zero at this pressure. Mixtures of benzene with urethane and of phenol with *p*-toluidine have also been examined; with the latter mixtures the formation of a phenoxide of *p*-toluidine is indicated. S. K. T.

**Determination of Heat Content of Some Condensed Gases.** A. EUCKEN and E. KARWAT (*Z. physikal. Chem.*, 1924, 112, 467—485).—The molecular heats of a number of gases, in the solid and liquid states, have been determined, by means of the vacuum calorimeter, between 25° Abs. and a temperature approaching the boiling point. Transition temperatures (tr.) and melting points are indicated by sudden changes in the variation of molecular heat with temperature, and are as follows in absolute temperatures: hydrogen chloride, tr. 98.75°, m. p. 159°; hydrogen bromide, tr. 90° and 118°, m. p. 187.0°; hydrogen iodide, tr. 72° and 124°, m. p. 220°; nitric oxide, m. p. 110°; chlorine, m. p. 170.8°; ammonia, m. p. 195.5°; methane, m. p. 90.5°. The heats of transition and fusion at these temperatures have also been measured. The values of  $C_p$  at low temperatures have been employed to calculate, from Debye's equation, the characteristic temperature  $\theta_m$  for hydrogen chloride and bromide, nitric oxide, and ammonia. Values have also been given for  $K$  calculated from Lindemann's melting-

point formula  $\theta_m = K\sqrt{T_s/MV_m^{\frac{2}{3}}}$ , where  $T_s$  is the melting point. For gases, the constant  $K$  is about 180.  $K$  may therefore be used to determine  $\theta_m$  when  $C_p$  is not known at a low enough temperature to admit of the application of Debye's formula. With the help of the latter, extrapolation values of  $C_p$  at temperatures down to  $10^\circ$  Abs., have been calculated for the gases under consideration. Values of the total heat content  $J = \int_0^T C_p dT$  at  $10^\circ$  intervals, and of the double integral  $\int_0^T \int_0^T C_p dT/T^2 \cdot \int_0^T C_p dT = \phi$  are also tabulated.

M. S. B.

**Method of Measuring Specific Heats of Metals at High Temperatures.** K. K. SMITH and L. I. BOCKSTAHLER (*Proc. Nat. Acad. Sci.*, 1924, **10**, 386—388).—Improvements have been made in the method previously devised (Smith and Bigler, *Physical Rev.*, 1922, **19**, 268) of determining specific heat by measurements of the thermionic emission from an incandescent filament. The mean of a number of determinations of the specific heat of tungsten, at temperatures between  $2375^\circ$  and  $2475^\circ$  Abs., is  $0.045$  (atomic heat =  $8.3$ ), which is in agreement with the results obtained by Worthing (*ibid.*, 1918, **12**, 199) and Gaehr (*ibid.*, 1936) by different methods.

M. S. B.

**Heat of Combustion of Natural and "Sulphuric Acid"** Caoutchouc. F. KIRCHHOF and O. MATULKE.—(See i, 1213.)

**Heat of Combustion of Glycogen.** W. K. SLATER.—(See i, 1047.)

**Specific and Latent Heats of Iron and Steel.** A. MALLOCK.—(See ii, 764.)

**Joule-Thomson Effect for Helium.** J. H. PERRY (*J. Physical Chem.*, 1924, **28**, 1108—1112).—A mathematical paper, in which the equation of state derived by Keyes,  $P = RT/(V + \delta) - A/(V + 1)^2$ , is applied to helium for  $T = 50^\circ$  to  $375^\circ$  and for pressures up to 105 atm. Good agreement is obtained between observed and calculated values. The Joule-Kelvin coefficient is calculated for pressures of 1, 5, 25, 50, and 100 atmospheres. The inversion temperature at atmospheric pressure is slightly below  $100^\circ$  Abs., and decreases with increase of pressure.

L. L. B.

**Joule-Thomson Effect in Carbon Dioxide.** E. S. BURNETT (*Physical Rev.*, 1923, **21**, 372).—Curves have been obtained from which the Joule-Thomson effect and other thermal quantities can be derived for carbon dioxide for pressures from 0 to 100 atm., and for temperatures between  $-54^\circ$  and  $120^\circ$ .

A. A. E.

**Vapour Pressure of Solid Carbon.** J. J. VAN LAAR (*Rec. trav. chim.*, 1924, **43**, 598—599; cf. A., 1921, ii, 17).—By experiment Wertenstein and Jedrzejewski (A., 1923, ii, 632) have found the equation of the sublimation curve of carbon to be:  $\log_{10} p_{\text{atm.}} = -47000/T + 9.3$ . This is almost identical with the theoretical equation of Van Laar:  $\log_{10} p_{\text{atm.}} = -47120/T + 9.4$ . W. E. E.

**Vapour Pressure of Solid Hydrogen Chloride, Methane, and Ammonia.** E. KARWAT (*Z. physikal. Chem.*, 1924, **112**, 486—490).—Determinations of the vapour pressures at different temperatures of solid hydrogen chloride, methane, and ammonia have been made, and equations given which represent very accurately the experimental results. The melting points calculated from the vapour-pressure equations are in good agreement with the experimental values, as also are the heats of fusion (cf. ii, 820). M. S. B.

**Vapour-pressure Curves for Systems containing Alcohol, Ether, and Water.** E. A. LOUDER, T. R. BRIGGS, and A. W. BROWNE.—(See i, 1157.)

**Liquefaction of Gaseous Binary Systems: Sulphur Dioxide and Ethane.** W. MUND and P. HERRENT (*Bull. Soc. chim. Belg.*, 1924, **33**, 401—420).—Measurements were made of the variation in volume with pressure of three mixtures of sulphur dioxide and ethane;  $dv/dp$  is smaller in value for two-phase systems than for the homogeneous liquids at temperatures above  $87^\circ$ , in agreement with the conclusions of Kuenen (*Z. physikal. Chem.*, 1902, **41**, 43). W. E. G.

**Saturation Relations in Mixtures of Sucrose, Dextrose, and Lævulose.** R. F. JACKSON and C. G. SILSBEE.—(See i, 1168.)

**Solubility of Iodine in Chlorinated Hydrocarbons of the Aliphatic Group.** B. M. MARGOSCHES, W. HINNER, and L. FRIEDMANN.—(See ii, 749.)

**Influence of Nitric Acid on the Solubility of Nitrates in Water.** A. A. KASANCEV.—(See ii, 755.)

**Solubility of Magnesium Carbonate in Water containing Carbon Dioxide under High Pressure.** O. HAЕHNEL.—(See ii, 759.)

**Solubility of Strontium, Barium, and Heavy-metal Carbonates in Water under High Pressure of Carbon Dioxide.** O. HAЕHNEL.—(See ii, 758.)

**Solubility of Silver Chloride.** R. LORENZ and E. BERGHEIMER.—(See ii, 757.)

**Coefficients of Diffusion of certain Alkali Salt Vapours in the Bunsen Flame.** G. E. DAVIS (*Physical Rev.*, 1924, **24**, 383—395).—When a bead of salt is held in the non-luminous flame, a luminous streak, having a fairly well-defined boundary, is observed. The coefficient of diffusion,  $K$ , is given by  $K = \frac{1}{2}rv(dx/dr - 1)$ , where  $r$  is the radial distance from the bead to a point on the boundary,  $x$  is the vertical distance, and  $v$  the velocity of the flame gases, the last-named being determined by means of intermittent puffs of salt spray. Values of  $K$  ( $\pm 10\%$ ) for lithium chloride, 12.4;

lithium sulphate, 9.7; sodium chloride, 19.0; sodium sulphate, 16.4; potassium sulphate, 11.1; rubidium sulphate, 11.7; caesium sulphate, 8.4, are not in good agreement with those obtained by Wilson (A., 1912, ii, 744). Except for lithium salts, the value increases approximately in the inverse ratio of the square root of the atomic weight of the metal, and varies in a corresponding manner with the molecular weight. If the metallic atoms of the vapour are the source of luminosity, the results suggest that these are free during part of the time only.

A. A. E.

### Kinetic Theory of Viscosity, Conduction, and Diffusion.

S. CHAPMAN and W. HAINSWORTH (*Phil. Mag.*, 1924, [vi], 48, 593—607).—Pidduck (*Proc. Roy. Soc.*, 1922, A, 101, 101) has based a kinetic treatment of the viscosity etc. of gases composed of molecules with rotational as well as translatory energy on the assumption that the molecules are rigid elastic spheres, with perfectly rough surfaces. In the present paper the same properties are treated, allowing also for the varying closeness of approach of the molecules, according to the velocity of collision. Formulæ and tables are given for various quantities connected with thermal diffusion in a monatomic gas.

S. B.

**Density of Carbon.** H. C. HOWARD and G. A. HULETT (*J. Physical Chem.*, 1924, 28, 1082—1095).—The density of a porous body, determined by immersion in a liquid, varies with the liquid employed. Harkins and Ewing (A., 1922, ii, 123, 197) explain this by the assumption that the liquid at the surface of the charcoal is compressed, and that the magnitude of the compression is greatest in the most compressible liquid, whilst Cude and Hulett (A., 1920, ii, 309) assume that the liquid penetrates the capillaries to varying degrees. The experimental method used is a modification of the volumeometer method, using helium, which has been shown to be only very slightly adsorbed, as a filling fluid. The density of active coconut charcoal is found to be of the order of 2.1, and an accuracy of 1 in 200 is claimed. The densities of charcoals from various sources show a wide variation, depending on the purity, low densities being attributed to the presence of hydrocarbons. Samples heated at 1400° are found to show abnormally low densities. The values for the density of charcoal found by this method confirm the conclusions of Debye and Scherrer and of Asahara, that all carbons consist of graphite contaminated with hydrocarbons, and the hypothesis of Harkins and Ewing is not confirmed.

L. L. B.

**Comparison of Molecular Volume Numbers.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, 138, 281—284).—The equations previously deduced by the authors (this vol., ii, 520) have been used to calculate the molecular volumes of oxygen, nitrous oxide, carbon disulphide, chloroform, ethyl ether, ethyl bromide, ethyl alcohol, and benzene in the liquid and gaseous states at the b. p. The molecular volumes calculated from the indices of refraction agree fairly well with those calculated from the dielectric

constants, except in the case of substances of which the molecules have a dipolar character; large differences then occur owing to the fact that such substances show anomalous dispersion.

W. H.-R.

**Molecular Lowering of the Freezing Point of Liquid Ammonia.** L. D. ELLIOTT.—(See ii, 750.)

**Optical Absorption of Dissolved Salts.** H. VON HALBAN and L. EBERT (*Z. physikal. Chem.*, 1924, **112**, 321—358).—Measurements of the molecular extinction coefficient,  $\epsilon$ , for light of definite wave-length, have been made for a number of salts by means of the photoelectric cell (cf. von Halban and Siedentopf, A., 1922, ii, 332; von Halban and Geigel, A., 1921, ii, 145). This method is capable of a very high degree of accuracy, even for very small values of  $\epsilon$ . At low concentrations, the limits of which vary for different salts, Beer's law is obeyed. The effect on  $\epsilon$  of the addition of non-absorbing salts varies both in magnitude and in sign for different wave-lengths, so that deformation of the absorption curve takes place, and the position of the maximum may be altered. Similar deviations may be produced by increase in the concentration of the pure salt alone. Measurements made on sodium picrate dissolved in water and in methyl alcohol, by use of the König-Martens spectrophotometer, show that the addition of another salt produces a much greater effect in alcohol than in water. Addition of dimethyl oxalate produces a definite change, but not that of hexane and glycerol. Water causes a deviation which increases with concentration, but not according to any simple rule, and the absorption eventually reaches a value greater than for pure water. The results have an important bearing on the "salt error" of indicators.

The results obtained support the view that the ionic properties of solutions of strong electrolytes are to be explained in terms of the electrostatic forces between the ions. These forces influence the properties of the ions to different degrees, so that there is not necessarily a parallelism between electrical conductivity, light absorption, ionic activity, etc.

M. S. B.

**Dielectric Constants of Solutions of Electrolytes.** O. BLÜH (*Z. Physik*, 1924, **25**, 220—229; cf. A., 1923, ii, 823).—The lowering of the dielectric constant of water, produced by dissolving in it potassium, sodium, or lithium chloride, has been calculated on the assumption that each ion is hydrated, or surrounded by a definite layer of water molecules, which, owing to their dipolar character, are oriented under the influence of the charged ion. They are thus rigidly fixed and unaffected by an outside field. The dielectric constant of this water is regarded as 1. The volume of attached water is deduced from Born's values (A., 1920, ii, 527) for the real and apparent radii of the ions, and the dielectric constant for the total water in solutions of different conductivity is then calculated by the mixture rule. The results show the same

relative variations as those obtained experimentally by other investigators, but the actual values are not the same.

It is suggested that, with more accurate determinations of the dielectric constants of solutions of electrolytes (cf. Fürth, *Z. Physik*, 1924, 22, 98), it should be possible to obtain trustworthy data on hydration, ionic radii, the adsorption layer on the surface of colloids, and so on.

M. S. B.

**Conductivity Measurements with the Aid of a Galvanometer.** P. A. THIESSEN (*Z. Elektrochem.*, 1924, 30, 473—474).—In place of a telephone, a rectifying valve is used and the anodic (direct) current passed through a delicate suspended-coil galvanometer. Zero current is thus indicated visually instead of by ear.

W. A. C.

**Ionisation of Strong Electrolytes.** W. H. RODEBUSH (*J. Physical Chem.*, 1924, 28, 1113—1117).—From the equation obtained by Debye (A., 1923, ii, 459, 724) for the partial molal free energy of a completely polar electrolyte in dilute solution, the author obtains the empirical expression given by Lewis and Linhart,  $\theta/1.86\Sigma_1 m = 1 - \beta n^\alpha$ , and gives values for the constants  $\alpha$  and  $\beta$ . In the case of uni-univalent salts, there is satisfactory agreement between calculated and experimental values. Another empirical rule, given by Lewis and Randall (A., 1921, ii, 427), that in dilute solutions the activity coefficient of a given electrolyte is the same in all solutions of the same ionic strength, is also derived. Debye's equation is applied to the activity of a slightly soluble salt in the presence of other electrolytes, and it is shown that it can be written  $\log_e \alpha/m = \beta_1 \Sigma (v_1 z_1^2)^{1/2} m^{1/2} + C_1$ . This linear relationship between the logarithm of the activity coefficient and the square root of the ionic strength in dilute solutions was shown by Lewis to hold for available data.

L. L. B.

**Conductivity of Weak Acids in Methyl Alcohol and Alcoholysis of Their Aniline Salts.** H. GOLDSCHMIDT and F. AAS (*Z. physikal. Chem.*, 1924, 112, 423—447).—The electrical conductivities of sodium salts of salicylic acid, 3 : 5- and 2 : 4-dinitrobenzoic acid, and dichloroacetic acid, as well as of the acids themselves, have been measured in pure methyl alcohol, and also in methyl alcohol containing added water, up to a concentration of 3N.  $\lambda_\infty$  has thus been calculated for the acids, and thence the affinity constants of the latter in solutions containing different proportions of water. The effect of the addition of water on the affinity constant in methyl alcohol is the same for all the acids (cf. A., 1916, ii, 210) and may be represented by

$$K_n = (K_0 n + 0.235)(1 + 0.9n + 0.15n^2)/0.235$$

where  $K_n$  is the affinity constant when the concentration of the water is  $n$ -normal and  $K_0$  its value in pure alcohol (cf. this vol., ii, 235). This formula is valid up to  $n=3$ , and for very small concentrations of water the last factor may be neglected.

The alcoholysis of aniline salts of the four acids in methyl alcohol

has been determined, by comparing the conductivity curves for the sodium and aniline salts (cf. A., 1922, ii, 135), on the assumption that  $\lambda_{\infty}$  is the same for both, or by multiplying the conductivity of the corresponding sodium salt by the experimentally determined ratio (conductivity of aniline picrate)/(conductivity of sodium picrate). If  $a$  be the total concentration of acid and base,  $x$  that of the undecomposed salt, and  $x_{\gamma}$  the concentration of ionised salt, then  $(a-x)/x_{\gamma}=K=\sqrt{K_B/K_s}$ , where  $K_s$  is the affinity constant of the weak acid and  $K_B=[\text{aniline}]\cdot[\text{H}^+]/[\text{aniline ion}]$ . The value of  $K$  diminishes with the addition of water, and the ratio  $K_0/K_n$ , where  $K_0$  and  $K_n$  are the values of  $K$  when the concentrations of water are 0 and  $n$ , respectively, is practically identical for all except 2:4-dinitrobenzoic acid.  $K_B$  for aniline in methyl alcohol is approximately  $10^{-6}$ , and the affinity constant of aniline in methyl alcohol is hence calculated to be  $2.27 \times 10^{-11}$ . The alcoholysis of salts of bases of the ammonia type with weak acids, in alcohols, is greater than the hydrolysis in water. This is due to the fact that the ionisation of the acid is less in alcohol than in water, although the base, on the other hand, is stronger, that is  $K_B$  is smaller, in alcohol.

M. S. B.

### Electrolytic Dissociation of Picric Acid in Aqueous Solution.

H. VON HALBAN and L. EBERT (*Z. physikal. Chem.*, 1924, **112**, 359—422; cf. ii, 824).—Optical measurements with the photo-electric cell have shown that, at very low concentrations,  $4-6 \times 10^{-4}N$ , the absorption of light by sodium picrate and picric acid is practically identical. Undissociated picric acid consists of two isomeric forms, a pseudo-acid, which does not absorb light in solution, and the normal acid. Assuming that the absorption of the normal form of the acid is the same as that of the picrate ion, it can be shown that the concentration of the pseudo-form is 2500 times greater than that of the non-ionised normal acid. Thus the degree of light absorption in the solution may be taken as a measure of the concentration of picrate ion. The degree of ionisation of picric acid, at concentrations  $10^{-2}$  to  $10^{-3}N$ , has been determined on the assumption that the absorption by hydrogen or sodium ions is negligible. The value thus found is considerably higher than the values given by other methods. When the optically determined values of the ionisation are used,  $K_c=\alpha^2c/(1-\alpha)$  increases with the concentration.

The thermodynamic mass action constant has been calculated in accordance with Bjerrum's theory of ionic activity. By determining the hydrogen-ion activity electrometrically, the activity of the picrate ion is found to be approximately 0.84. This large value is due to a lack of symmetry in the picrate ion and a consequent distribution of the charge near the surface (cf. Bjerrum, this vol., ii, 24). The resulting large electrostatic action is seen in the abnormally large precipitating power of the picrate ion, which is comparable with that of a multivalent ion. Data relating to the freezing-point lowering of water by picric acid, the equilibrium between picric acid and  $\beta$ -naphthol in solution, the partition



coefficient of the acid between water and various organic solvents, the solubility in salt solutions, and the electrical conductivity of picric acid solutions have been considered. Incidentally, it has been found that picric acid forms simple molecules in bromoform and chloroform. Measurements of the absorption of light by the acid in solutions of sodium chloride show that picric acid is more highly ionised in the salt solutions than in pure water.

The behaviour of picric acid in concentrated solutions of electrolytes is in agreement with Bjerrum's views on the hydration of ions (*Z. anorg. Chem.*, 1920, **109**, 275). The calculated solubility of picric acid in *N*-hydrochloric acid solution agrees with Stepanow's value (*A.*, 1910, i, 471). M. S. B.

**Ionisation of some Organic Acids Dissolved in Mixtures of Water and Ethyl Alcohol.** M. DUBOUX and D. TSAMADOS (*Helv. Chim. Acta*, 1924, **7**, 855—875).—The rate of inversion of sucrose catalysed by acetic, lactic, benzoic, salicylic, succinic, malic, and tartaric acids has been examined in aqueous-alcoholic solutions of varying composition. The reaction velocity in accordance with the dual theory is assumed to be expressed by the equation:

$$k = k_H[H'] + k_M(C - [H']).$$

For each alcoholic solution,  $k_M$  and  $k_H$  are obtained as previously described. The polarimetric readings give  $k$ , and hence  $[H']$  is determined. Substitution in Ostwald's dilution equation gives the dissociation constant  $K$ .

From similar measurements of the rate of decomposition of ethyl diazoacetate, it is found that  $k = k_H[H']$  holds good approximately (*Z. physikal. Chem.*, 1907, **60**, 202). From this, values of  $[H']$  and  $K$  are derived. The conclusion to which the present investigation leads agrees with that of Wakeman (*Z. physikal. Chem.*, 1893, **11**, 49) and Godlewski (*J. Chim. physique*, 1905, **3**, 393), viz. that the ionisation of an organic acid diminishes as the proportion of alcohol increases. The results of the two methods are in satisfactory quantitative agreement. W. E. E.

**Constitution of Solid Electrolytes.** J. N. FRERS (*Ber.*, 1924, **57**, [B], 1693—1697; cf. Tubandt, *A.*, 1920, ii, 279; 1921, ii, 480).—Examination of the system lead anode—lead chloride—silver chloride—lead chloride—platinum cathode at 210° shows that only the silver ion of silver chloride wanders. Similarly, in the system lead anode—lead chloride—platinum cathode, migration is confined to the chlorine ion of the lead chloride. These experiments show that certain ions are retained with extraordinary firmness in the lattice, whereas others are much more readily removed from the positions which they occupy in the lattice system. H. W.

**Mobility of Ions in Solid Cuprous Sulphide.** H. BRANNER and O. KAHN (*Z. physikal. Chem.*, 1924, **112**, 270—276).—The coefficient of diffusion of silver ions in solid cuprous sulphide containing a little silver sulphide has been measured at temperatures ranging from 223° to 919°; within these limits, the values found

are expressed by the equation  $D=113e^{-2285/T}$ . At  $223^\circ$ , cuprous sulphide containing a little cuprous selenide showed no detectable diffusion of selenium ions. S. S.

**Mixed Crystals.** H. G. GRIMM (*Z. Elektrochem.*, 1924, **30**, 467—473).—The conditions for isomorphous intermixture are (1) similarity in atomic configuration, (2) similarity in space-lattice, and (3) approximate equality of ionic distances in the crystals (difference less than 5%). Chemical analogy is not essential. Sodium bromide and chloride (but not rubidium bromide) are shown to be isomorphous with lead sulphide, in that solutions evaporated on fresh cleavage-surfaces of the latter deposit congruently oriented crystals. Mixed crystals of sodium chloride or bromide containing 10—12% of potassium hydroxide may be obtained. Precipitation of barium sulphate in concentrated solutions of potassium permanganate at  $50\text{--}100^\circ$  leads to crystallographically well-defined mixed crystals; the permanganate in these is remarkable for its almost complete chemical inertness. Other isomorphous combinations of permanganates with sulphates, selenates, chromates, and fluoborates are mentioned.

W. A. C.

[**Properties of Alums.**] F. MÜLLER (*Z. physikal. Chem.*, 1924, **112**, 161—166).—The refractive index of mixed crystals of ammonium alum and ammonium-iron alum follows approximately the mixture law. At the temperature of liquid air, chrome alums become paler, and iron alums coloured by a trace of manganese become colourless. The tension of water vapour over a number of alums has been determined by means of a modified Bremer-Frowein tensimeter. Potash alum under pressure loses water and at  $62\text{ t./cm.}^2$  gives a residue of the composition  $\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 18\text{H}_2\text{O}$ . The stability and constitution of alums are discussed. S. S.

**Potential of the Fluorine Electrode.** J. SIMONS and J. H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1924, **46**, 2223—2225).—Attempts to measure the *E.M.F.* of a cell consisting of hydrogen and fluorine electrodes in fused potassium hydrogen fluoride, and in a solution of potassium fluoride in liquid hydrogen fluoride, were unsuccessful. S. K. T.

**Drop Electrode in Molten Salt Electrolyte.** P. B. TAYLOR (*Physical Rev.*, 1923, **21**, 705).—Paschen's drop electrode has been studied in molten salt electrolyte. The cell

$\text{Hg}(\text{still})|\text{NaNO}_3, \text{KNO}_3, \text{LiNO}_3, \text{ternary eutectic}|\text{Hg}(\text{fine stream})$   
has an *E.M.F.* of  $0.66 \pm 0.02$  volt, still electrode positive. The cell  
 $\text{Hg}(\text{still})|\text{NaNO}_3, \text{KNO}_3, \text{LiNO}_3, \text{ternary eutectic}|$

amalgam  $\text{Hg } 0.85, \text{Bi } 0.15$  (fine stream)  
has an *E.M.F.* of  $0.735 \pm 0.002$  volt, still electrode positive. These values are independent of the temperature between  $138^\circ$  and  $220^\circ$  and  $158^\circ$  and  $172^\circ$ , respectively. The second cell, with mercury electrode positive and amalgam still, has an *E.M.F.*  $= 0.001110T \pm$

0.004 volt, between  $162^{\circ}$  and  $238^{\circ}$ , where  $T$  is the absolute temperature. The potential of the dropping electrode is independent of the metal of the electrode.

A. A. E.

**The Radical Theory.** C. A. KRAUS (*J. Amer. Chem. Soc.*, 1924, **46**, 2196—2204).—When the typical radicals are arranged in the order of their electro-affinities, it is seen that their properties correspond with those of the elements which have the same electro-affinity. Amphoteric properties are shown by those radicals which fall between the strongly positive ( $\text{NH}_4^+$ ,  $\text{NMe}_4^+$ ) and the strongly negative ( $\text{CN}^-$ ,  $\text{NO}_3^-$ ,  $\text{SCN}^-$ ) radicals; these intermediate radicals, if univalent, have a close resemblance to hydrogen. These conclusions are supported by a detailed consideration of the properties of the trimethylstannyl group, which forms compounds with both positive and negative elements. Whilst the former compounds are true salts of the weak acid  $\text{SnMe}_3\text{H}$  (cf. Kraus and Greer, A., 1923, i, 26), the latter cannot be regarded as true salts of the base  $\text{SnMe}_3\text{OH}$  (cf. Kraus and Callis, this vol., i, 25). The electrolytic properties of aqueous and alcoholic solutions of trimethylstannyl halides are readily accounted for by assuming the formation of an oxonium salt.

S. K. T.

**Dependence of Surface Tension on Density and Temperature.** W. L. LEVSHIN (*Z. physikal. Chem.*, 1924, **112**, 167—174).—Surface tension is expressed as a function of temperature and density by the relation  $\gamma = K(T_K - T)^{1/2}(D - d)^{2.36}$ , where  $\gamma$  is the surface tension,  $K$  a specific constant,  $T_K$  the critical temperature,  $T$  the temperature of observation,  $D$  the density of the liquid, and  $d$  that of the vapour. This equation reproduces with considerable accuracy the data of Ramsay and Shields for non-associated liquids. From the principle of corresponding states, it follows that

$$T_K^{1/2}/KM^{2/3}D_K^{1.693}$$

should have the same value for different liquids; the values of this quantity for a number of associated liquids agree within about 5% (cf. Macleod, *Trans. Faraday Soc.*, 1923, **19**, 38; Ferguson, *ibid.*, 407; Sugden, T., 1924, **125**, 32).

S. S.

**Connexion between Surface Tension and Density.** G. N. ANTONOFF (*Z. physikal. Chem.*, 1924, **112**, 461—466).—According to recent work (cf. MacLeod, *Trans. Faraday Soc.*, 1923, **19**, 38; Ferguson, *ibid.*, 1923, **19**, 407), the relation between surface tension and density can be expressed by the formula  $\alpha = k\delta^4$ , where  $\alpha$  is the surface tension and  $\delta$  the difference in density between liquid and saturated vapour. If  $\alpha$  be plotted against  $\delta$  for benzene, a curve is obtained showing discontinuities. In each section of the curve, the relation between  $\delta$  and the reduced temperature,  $T$ , may be represented by an exponential expression of the form  $Ae^{\lambda\delta} = T + B$ , where  $A$ ,  $\lambda$ , and  $B$  are constants for the section under consideration. Similar behaviour has been found over a large range of temperature for all the other liquids examined, for example, carbon tetrachloride, acetic acid, methyl alcohol, methyl acetate, ether, etc. This behaviour is explained by regarding the mole-

cules as electrical doublets and by supposing that a gradual combination of these takes place on cooling; for example,  $A + A + A + \dots \rightleftharpoons A_n$ ;  $A_n + A_n + A_n + \dots \rightleftharpoons A_{mn}$ , and so on, a break in the curve occurring when all the molecules have taken up a new arrangement. On this assumption, all liquids are associated, but whether the liquid is "abnormal" or "normal" depends on whether a new distribution of the electric charges, and a consequent large energy change, has taken place on combination or not.

M. S. B.

**Viscosity and Surface Tension of Solutions of Iodine and Potassium Iodide.** E. A. DANCASTER.—(See ii, 847.)

**Determination of Distribution of Particle Size.** W. J. KELLY (*Ind. Eng. Chem.*, 1924, **16**, 928—930).—A sedimentation tube, like that of von Hahn (*Kolloid-Z.*, 1923, **32**, 60), is used; the side tube is bent over so that the upper portion is at a small angle with the horizontal. Readings of the rate at which the level of the liquid in this arm falls can thus be easily made and dilute suspensions can be employed.

W. A. S.

**Stability of Colloidal Solutions. I. Aluminium Hydroxide Suspension.** K. C. SEN (*J. Physical Chem.*, 1924, **28**, 1029—1035).—An undialysed ferric hydroxide sol requires more electrolyte for coagulation than a corresponding dialysed sol. This has been attributed to the peptising action of the hydrochloric acid present. The stability of aluminium hydroxide sols peptised with benzoic, acetic, and propionic acids has been studied. Benzoic acid, which is found to be more readily adsorbed than acetic or propionic acid, is the most effective in its peptising action. The stability of the sol depends on the concentration of the hydroxide, as well as on the amount of acid present. With increase in acid concentration, the stability rises to a maximum, and for suspension of the same degree of purity, the stability decreases with the dilution. With hydrochloric acid, equilibrium is reached only after a long time.

The constitution of hydroxide colloids is briefly discussed.

L. L. B.

**Formation of Colloid Solutions by Electrical Pulverisation in the High-frequency Alternating Current Arc.** E. O. KRAEMER and T. SEDBERG (*J. Amer. Chem. Soc.*, 1924, **46**, 1980—1991).—The formation of colloidal sols of cadmium by electrical pulverisation in alcohol and ether has been studied, using a Tesla coil, a modified Poulsen circuit, and a transformer circuit; the results are compared with those obtained by Börjeson (*Dissertation*, Upsala, 1921, p. 117), using an induction coil. Under comparable conditions, pulverisation is more rapid with the Poulsen and transformer circuits than with the Tesla or induction coils; this is due to the shorter period occupied by the interruptions in the case of the Poulsen and transformer circuits. In the transformer and induction coil circuits, there is, superimposed on the oscillatory condenser discharge across the spark gap, a direct

low-frequency current which charges the condenser, and consequently the rate of pulverisation depends on the quenching of the discharge by the liquid and is less in ether than in alcohol. In the Tesla coil method, in which the two processes are separated, the rate of pulverisation is independent of the liquid. In this method, moreover, there is less decomposition of the liquid medium, and sols of greater purity are obtained.

W. H.-R.

**Physical Chemistry of the Globulins. V. Compounds of Globulin with Salts of Tervalent Ions.** M. ADOLF (*Koll.-Chem. Beihefte*, 1924, 20, 138—156; cf. A., 1923, i, 396; this vol., i, 101).—The solvent action on globulin of salts with a tervalent ion exceeds that of the alkali chlorides or hydrochloric acid and resembles that of the alkalis. With aluminium chloride or sodium citrate, globulin-salt compounds are probably formed, since other methods of combination are excluded by the changes in the conductivity and in the concentration of the hydrogen and chlorine ions. The aluminium chloride-globulin salt moves towards the cathode, whilst the sodium citrate compound moves in the opposite direction. Solutions of both compounds may be diluted or boiled without change. Hydrochloric acid precipitates the sodium citrate- but not the aluminium chloride-globulin. Partial mutual precipitation occurs when solutions of the two compounds are mixed. Aluminium citrate behaves differently and resembles an alkali chloride. Compounds of globulin with salts containing one tervalent ion behave differently from those formed with salts containing ions of the same valency.

E. M. C.

**Influence of Electrolytes on the Stability of Red Blood-corpuscle Suspensions.** J. OLIVER and L. BARNARD (*J. Gen. Physiol.*, 1924, 7, 99—122).—The charge on red blood-cells in isotonic sucrose solutions with and without the addition of metallic salts has been determined by cataphoresis. The cells are much less susceptible to electrolytes than is collodion, a difference attributed to their chemical constitution. The valency of the cations of the electrolytes is not sufficient to account completely for the changes in charge observed. With certain electrolytes, notably those yielding tervalent ions, not only may the charge be reduced until the isoelectric region is reached, but a reversal of charge may also occur. Curves showing the variation in charge with concentration of various electrolytes are given and discussed. In weak solutions of electrolytes, the stability of suspensions of the cells depends on the electric charge of the cells and the suspensions become unstable when the potential difference falls below 32 millivolts. In concentrated solutions of electrolytes, the stability bears no relation to the charge. The view that agglutination by disodium arspenamine may be due to changes in the electrical properties of the cells is confirmed.

O. O.

**Combination of Salts and Proteins. I.** J. H. NORTHROP and M. KUNITZ (*J. Gen. Physiol.*, 1924, 7, 25—38).—Ion activity ratios for the inside and outside of gelatin particles calculated on

Donnan's theory agree with *E.M.F.* measurements. The ratios of the total concentrations of calcium, magnesium, potassium, and zinc, however, do not agree with the calculated ratios, and this discrepancy is attributed to the formation of complex ions with the protein. In the case of zinc, combination is rapidly and completely reversible, and hence is not considered to be a surface effect. Protein combines more readily with zinc than with chlorine, so that addition of zinc chloride to isoelectric gelatin should give rise to an unequal distribution. This is shown to be the case by an increase in swelling, osmotic pressure, and viscosity. O. O.

**Physical Chemistry of the Proteins. III. Relation between the Amino-acid Composition of Casein and its Capacity to Combine with Base.** E. J. COHN and R. E. L. BERGGREN (*J. Gen. Physiol.*, 1924, 7, 45—79).—From a study of ten casein preparations it appears that the base-combining capacity is influenced by the method of preparation. When the casein has not been exposed to an alkalinity greater than that in which it exists naturally, it is calculated that 1 g.-mol. of sodium hydroxide combines with 735 g. of casein. When the method of preparation entails exposure to high concentrations of base, the weight of combined casein is only 535 g. On the basis of these figures, native casein with a minimal molecular weight of 12,800 must contain eighteen acid groups; and six additional groups are liberated in alkaline solution. Of these twenty-four, nineteen groups can be accounted for by the known amino-acid constituents of the protein, and if the phosphorus be assumed to exist as phosphoric acid, nine further acid groups are possible. The methods proposed for the determination of base-combining capacity are discussed in some detail. O. O.

**Physical Chemistry of the Proteins. IV. Relation between the Composition of Zein and its Acid and Basic Properties.** E. J. COHN, R. E. L. BERGGREN, and J. L. HENDRY (*J. Gen. Physiol.*, 1924, 7, 81—98).—The methods used for casein (cf. preceding abstract) have been applied to the measurements of the base-combining and acid-combining capacities of zein. From these it appears that the protein has no basic groups, the low solubility in water and dilute acids and alkalis indicating that zein is a remarkably inert protein. O. O.

**Foam Systems.** O. BARTSCH (*Koll. Chem. Beihefte*, 1924, 20, 1—49).—The foaming power of two-phase systems increases with the surface-activity of the dissolved substance and generally increases with dilution. Solutions of maximum foaming power have approximately equal surface tensions. These foams behave as negatively charged lyophobic sols towards electrolytes and protective colloids. The foaming of three-phase systems is to be ascribed to the formation of aggregates of gas bubbles and solid particles and is primarily determined by the concentration of the foam stabiliser. It is suggested that the maximum stability of a foam containing a solid phase and oleic acid is associated with the

formation of a unimolecular layer of oleic acid on the surface of the solid. [Cf. *B.*, 1924, 971.] E. M. C.

**Chemical Adsorption.** G. STADNIKOV (*Kolloid-Z.*, 1924, 35, 228—233; cf. *A.*, 1922, ii, 619).—Further experiments on the adsorption of mixtures of hydrochloric and nitric acids by aniline-black have given values smaller than those previously found. After regeneration by treatment with excess of ammonia, the adsorptive power of aniline-black is reduced. Oxalic acid shows a maximum adsorption of 3 mols. per mol. of aniline-black. Acetic acid is only slightly absorbed, but monochloroacetic acid is absorbed to a considerable extent and affords evidence of adsorption in accordance with Henry's law, in addition to the formation of a chemical compound. E. M. C.

**Negative Adsorption. VII. Action of Saturated Solutions of Salts on Dried Gelatin.** M. A. RAKUSIN and L. A. ITZKIN (*Biochem. Z.*, 1924, 149, 232—234).—Dry gelatin added to saturated solutions of various salts does not cause the salt to separate from solution; it dissolves slowly in calcium chloride solution, rapidly in strontium chloride solution (cf. Rakuzin and Gönke, *ibid.*, 1923, 137, 341). J. P.

**Adsorption. VI. Methods for Distinguishing the Different Types of Adsorption.** P. N. PAVLOV (*Kolloid-Z.*, 1924, 35, 221—225).—A recapitulation of methods based on the form of the distribution curve. E. M. C.

**Adsorption. VII. Nature of the Adsorption of Acetic Acid by Charcoal.** P. N. PAVLOV (*Kolloid-Z.*, 1924, 35, 225—228).—The isotherm obtained for the adsorption of acetic acid by charcoal is independent of the volume of solution and of the quantity of charcoal employed. The log-log curves for the original sample of charcoal and a finer material prepared by air separation are parallel. The author concludes that the acid is not adsorbed on the surface but is probably combined with active substances present in solid solution in the charcoal. E. M. C.

**Adsorption of the Complement by Dyes.** F. KLOPSTOCK (*Biochem. Z.*, 1924, 149, 331—338).—Various dyes—eosin, Congo-red, light-green, magenta-red, methylene-blue, night-blue, nigrosin, rivanol, trypanflavine, trypan-blue, water-blue—carrying both positive and negative charges, adsorb the complement. The proteins of inactive normal serum act as protective colloids in inhibiting the adsorption, whilst the presence of the lipoid of Wassermann antigen greatly increases the adsorption of the complement by the dyes, whether these carry a positive or a negative charge. J. P.

**Influence of Dissolved Substances on the Swelling of Gelatin.** F. V. VON HAHN (*Z. Elektrochem.*, 1924, 30, 453—457).—Capillary tubes of gelatin have been repeatedly used as viscosimeters for pure water, until constancy of the time of reflux was attained. It was found necessary to age each capillary for at

least 18 hours before bringing into use. Dilute solutions of various organic substances were then compared with respect to their swelling or shrinking effect on the gelatin. With most substances, swelling occurs, but the gelatin returns to its normal state when rinsed with water. Chloroform and ether solutions cause shrinkage. With atropine hydrochloride and paracetaldehyde, swelling occurs, followed, after rinsing, by shrinkage to below normal. There is no apparent connexion with the surface tension and consequently no evidence in support of the view (Brinkman, A., 1923, i, 974) that surface tension influences the permeability of membranes.

W. A. C.

**Sensitive Method for Measuring Swelling.** F. V. VON HAHN (*Kolloid-Z.*, 1924, **35**, 215—218).—Solutions of gelatin and similar materials are cooled in a glass tube, resembling a viscosimeter, and the resulting gels pierced by a needle. The rate of flow of a liquid through the capillary so formed gives a measure of its effect on the swelling of the gel. The apparatus described is sensitive to changes of 0.01% of the volume of the gel.

E. M. C.

**Theory of Liesegang Rings.** J. TRAUBE and K. TAKEHARA (*Kolloid-Z.*, 1924, **35**, 245—247; cf. following abstract).—The formation of Liesegang rings is to be ascribed solely to the changes of concentration in the salt solutions which occur as the result of the formation of a precipitate membrane and of the subsequent diffusion processes.

E. M. C.

**Electrolyte Reactions in the Presence of Gelatin, and Liesegang Rings.** K. TAKEHARA (*Kolloid-Z.*, 1924, **35**, 233—245).—A close resemblance is found between the formation of Liesegang rings in gelatin gels and the formation of precipitates in gelatin sols at a slightly higher temperature. In the latter case, precipitates are formed only when critical salt concentrations are exceeded. In some cases, change of the salt concentration leads to a sudden change of colour in the sol, and the colours then correspond with those of the Liesegang rings in the gel.

E. M. C.

**Rhythmic Bands.** S. ODÉN and G. KÖHLER (*Ark. Kemi, Min., Geol.*, 1924, **9**, No. 10, 1—4).—A simple experiment illustrating the formation of zones of precipitation in jellies is described. The formation of zones depends on the action of light, especially of the blue and violet regions, and is retarded by strong electrostatic fields.

T. H. P.

**Rhythmic Crystallisation.** E. SCHUBERT (*Kolloid-Z.*, 1924, **35**, 219—220).—Sulphanilic acid-sulphuric acid mixtures, *p*-tolunitrile, salol, and methylsalicylic acid exhibit rhythmic crystallisation on cooling.

E. M. C.

**Ultramicroscopical Investigation of Linear Elements. I. Azimuth Effect.** A. SZEGVARI (*Z. physikal. Chem.*, 1924, **112**, 277—294).—The cardioid condenser of an ultra-microscope was fitted



with a diaphragm which allowed light of a definite azimuth to illuminate the specimen. Rod-like particles which lie at right-angles to the direction of the incident light scatter more effectively and are more easily detected. The instrument is also of use in the examination of fibres, since the azimuth of the incident light can be adjusted to show the surface structure of a particular fibre. S. S.

**Ultramicroscopical Investigation of Linear Elements. II. Sols with Rod-shaped Particles.** A. SZEGVARI (*Z. physikal. Chem.*, 1924, **112**, 295—316).—Sols of vanadium pentoxide, benzo-purpurin, chrysophenin, cotton-yellow, and soap were investigated by means of the cardioid ultra-microscope with controlled azimuth illumination (preceding abstract). Vanadium pentoxide and benzo-purpurin contain particles arranged in swarms, in which all the rod-like particles are parallel. The particles are not fixed in the swarm, but each exhibits characteristic Brownian movement; the swarming is not due to incipient coagulation, since it is exhibited by stable concentrated benzopurpurin sols, freed as far as possible from electrolytes. Chrysophenin and cotton-yellow sols show rod-like particles irregularly distributed; soap shows a similar distribution, but in addition contains disc-shaped particles. Sols of silver, Berlin-blue, copper oxide, osmium dioxide, stannic acid, and a specially prepared aluminium hydroxide sol contain non-spherical particles of ultra-microscopic dimensions. S. S.

**Membrane Equilibria and the Electric Charge of Red Blood-cells.** C. B. COULTER (*J. Gen. Physiol.*, 1924, **7**, 1—18).—The Donnan equilibrium determines the distribution of  $H^+$  and  $Cl^-$  ions between the cell and the surrounding fluid. The distribution of  $HPO_4^{--}$ , however, appears to be mainly influenced by the relative impermeability of the cell membrane to this anion. In dilute solutions of electrolytes, the potential difference due to the Donnan equilibrium is to be regarded as positive when the cataphoretic charge of the cell due to the medium is negative. This discrepancy in sign may be explained by the existence at an "outer phase-boundary" of a second Donnan equilibrium, the nature of which is determined by the ionisation of the protein of the cell membrane. O. O.

**Theory of Dialysis.** A. and H. BETHE and Y. TERADE (*Z. physikal. Chem.*, 1924, **112**, 250—269).—Dialysis through a thin membrane against water, with good stirring, should proceed according to the equation  $k = \{-m \log (1 - c_2/Cm)\}/t$ , where  $k$  is a constant,  $m$  the ratio of the initial volume of liquid to the total volume in the inner and outer vessels,  $C$  the initial concentration of the solution, and  $c_2$  the concentration after time  $t$ . Experiments with non-electrolytes (sugars and carbamide) diffusing through a parchment-paper membrane gave results in agreement with this formula. Electrolytes showed deviations greater than the experimental error,  $k$  varying in a characteristic manner for certain groups of electrolytes. Dialysis without stirring gave similar results. The increase in the diffusion coefficient for hydrochloric acid and sodium hydroxide at

temperatures up to 61° is proportional to the square of the temperature increment. S. S.

**Hydrodiffusion Experiments.** I. H. VON EULER and E. ERIKSON (*Ark. Kemi, Min., Geol.*, 1924, **9**, No. 11, 1—9; cf. A., 1920, ii, 595).—The rate of diffusion of acetic acid into an aqueous solution of aniline (0.32*N*) is approximately 35% less than the rate for diffusion into pure water. The observed difference is due to salt formation, which causes a reduction in the osmotic pressure of the free acid and also affects the viscosity, possibly as a consequence of a difference in the degree of hydration of the acetic acid when this is converted into the ionic form. T. H. P.

**Calculation of Gaseous Equilibrium Constants.** S. W. SAUNDERS (*J. Physical Chem.*, 1924, **28**, 1151—1166).—The mean molecular heats of gases at constant pressure, between 0° K. and *T*° K. have been calculated from experimental data for the range 273°—*T*° (K.). These have been employed in the calculation of various equilibrium constants. The reactions include the synthesis of water, hydrogen cyanide, methane, acetylene, cyanogen, ammonia, and nitric oxide; the oxidation of carbon monoxide; the reduction of carbon dioxide by carbon, and the reaction  $\text{H}_2 + \text{CO}_2 = \text{H}_2\text{O} + \text{CO}$ . The results obtained agree well with experiment, except in the case of the synthesis of ammonia. M. B. D.

**Ammonium Carbamate Equilibrium.** T. R. BRIGGS and V. MIGRDICHIAN (*J. Physical Chem.*, 1924, **28**, 1121—1135).—The dissociation of ammonium carbamate, alone and in the presence of excess of ammonia or carbon dioxide, has been examined at eight temperatures between 10° and 45°. The results, with the exception of those at 10°, agree with the mass law equation  $p_{\text{NH}_3}^2 \cdot p_{\text{CO}_2} = K_p$  within the limits of experimental error. Previous results by Horstmann and Isambert are inaccurate. M. B. D.

**Reaction between Ferric Chloride and Arsenious Acid.** K. JELLINEK and L. WINOGRADOFF (*Z. Elektrochem.*, 1924, **30**, 477—490).—The reaction  $2\text{FeCl}_3 + \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{FeCl}_2 + \text{H}_3\text{AsO}_4 + 2\text{HCl}$  has been studied in presence of free hydrochloric acid (1.5*N* to 4*N*) at 107° and 127° in sealed tubes. Analyses were carried out by precipitating ferrous iron by means of potassium ferricyanide and iodometric determination of arsenious acid in the filtrate. At 107°, the constant  $[\text{H}_3\text{AsO}_3] \cdot [\text{FeCl}_3]^2 / [\text{H}_3\text{AsO}_4][\text{FeCl}_2]^2[\text{HCl}]^2$  is  $3.54 \times 10^{-2}$ ; at 127°, it is  $1.17 \times 10^{-1}$ . The thermal value of the ( $\rightarrow$ ) reaction is +18,000 cal. Both reactions appear to be termolecular, and are strongly catalysed by hydrochloric acid. W. A. C.

**Complexity of some Metal Tartrate Ions and the Solubility Products of certain Metallic Hydroxides and Sulphides.** K. JELLINEK and H. GORDON (*Z. physikal. Chem.*, 1924, **112**, 207—249).—The constitution of complex tartrate ions of the more noble metals has been studied by means of *E.M.F.* measurements of an

electrode of the metal in a tartrate solution of small hydrogen-ion concentration containing a small amount of the metal salt. For less noble metals, alkali was added until a precipitate of hydroxide was just formed; the hydroxyl-ion content of the solution was then measured, and from this and the solubility product of the oxide the concentration of metal ion was obtained. New determinations have been made of certain normal potentials and solubility products. Recorded values of potentials (hydrogen scale) at summer temperature are  $\text{Ag}|\text{Ag}^+$ , +0.808 v.;  $\text{Cu}|\text{Cu}^+$ , +0.343 v.;  $\text{Pb}|\text{Pb}^{++}$ , -0.103 v.;  $\text{Sb}|\text{Sb}^{+++}$ , +0.244 v. Solubility products (g.-mol. per litre) at 15–20° are  $[\text{Ag}^+][\text{OH}']$ ,  $6 \cdot 10 \times 10^{-9}$ ;  $[\text{Cu}^{++}][\text{OH}']^2$ ,  $1 \cdot 7 \times 10^{-13}$ ;  $[\text{Fe}^{+++}][\text{OH}']^3$ ,  $1 \times 10^{-38}$ ;  $[\text{Fe}^{+++}]^2[\text{S}']^3$ ,  $1 \times 10^{-88}$ . The solubility product of silver hydroxide at 40° is  $1 \cdot 4 \times 10^{-8}$ , whence the heat of solution is -1650 cal.

In acid solutions, copper and tartrate ions react to form a complex ion,  $\text{COO}'\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{COO}' + \text{Cu}^{++} \rightleftharpoons \text{COO}'\cdot\text{CH}-\underset{\text{O}-\text{Cu}-\text{O}}{\text{CH}}\cdot\text{COO}'$

+2H'. In moderately alkaline solutions, the sodium salt of this complex ion is formed, whilst in strongly alkaline solutions the salt  $\text{Cu}[\text{O}\cdot\text{CH}(\text{CO}_2\text{Na})\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{Na}]_2$  is formed. Lead behaves in the same manner as copper, whilst antimony gives the ion  $\text{COO}'\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}_2(\text{SbO})$ . Chromium and iron give more complex tartrates, probably of the formula  $\text{X}_2\text{T}_3$ , where X is the metal and T the tartrate ion. S. S.

**Graphical Determinations of Chemical Equilibria.** O. SCHWARTZKOPFF (*Z. anorg. Chem.*, 1924, **138**, 233–248).—Theoretical. A method is described whereby, if the relation between two quantities is of the form  $y=f(x)$  and can be plotted in the form of a graph, it is possible, by a simple geometrical construction alone, to construct the integration curve  $z=\int f(x) \cdot dx$ , and also more complicated derived integration curves such as  $y=\int f(x)/x^2 \cdot dx$ . The method is applied to an investigation of the reaction  $2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2$ , the initial data being the relations between the temperature and molecular heats of the gases concerned. These are plotted graphically and curves for the equilibrium constant and energy of reaction as functions of the temperature are derived. W. H.-R.

**Systems: Sodium Chloride–Sodium Hydroxide–Water and Potassium Chloride–Potassium Hydroxide–Water.** A. VON ANTROPOFF (*Z. Elektrochem.*, 1924, **30**, 457–467).—Both systems have been examined at temperatures ranging from the cryohydratic to the boiling temperatures. Full numerical data and numerous diagrams are given. Allowing for the wide difference between the binary systems hydroxide–water and chloride–water at higher temperatures, the ternary systems present no abnormalities.

W. A. C.

**Sparingly Soluble Salts, readily obtained from Hot Solutions of Reacting Substances.** I. K. P. CHATTERJEE and N. R. DHAR (*J. Physical Chem.*, 1924, **28**, 1009–1028).—The solubility of the citrates of calcium and strontium and of the oxalates

and tartrates of copper, zinc, magnesium, manganese, cobalt, nickel, iron (ferrous), and thorium has been determined at temperatures up to 100°. Calcium citrate forms four different hydrates,  $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 16\text{H}_2\text{O}$ ,  $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , but in most cases, the same hydrate is precipitated from hot and cold solutions, the solubility increasing with rise of temperature. The influence of temperature on the rate of precipitation is found to depend on whether the reaction mixture is agitated or not.

L. L. B.

### Selective Solvent Action by the Constituents of Aqueous Alcohol. III. Effect of some Water-soluble Semi-solutes.

R. WRIGHT (*J. Chem. Soc.*, 1924, 125, 2068—2069).—A semi-solute dissolved in aqueous alcohol lowers the vapour pressure of the constituent in which it is soluble and raises the vapour pressure of the other constituent. Experiments with potassium, sodium, and ammonium salts show that sulphates and carbonates have the greatest effect and nitrates and bromides the least; the effects of sodium and potassium salts of the same acid are almost identical and are slightly greater than the effect of the ammonium salt. The data are not conclusive enough to say that each ion produces its own independent effect.

S. K. T.

### Theory of Thermodynamical Phase Boundary Potentials.

E. ABEL (*Z. physikal. Chem.*, 1924, 112, 206).—A correction to a previous paper (*ibid.*, 110, 587).

S. S.

**Application of Phase Rule to Galvanic Cells.** J. A. BEATTIE (*J. Amer. Chem. Soc.*, 1924, 46, 2211—2223).—A general method of deriving the phase rule is described. The method is applied to galvanic cells, the phase rule being deduced in the form:  $V = n + 2 - P + R - S + (\pi - 1)$ , where  $V$  is the number of independent variables and  $n$  is the number of components distributed in  $P$  phases separated by  $S$  surfaces with electrical potentials corresponding with  $\pi$  different pressures,  $R$  being the number of arbitrary restrictions imposed (*e.g.*, pressure, temperature). The number of energy equations it is necessary to write for a given cell represents the number of phases. Detailed application is made to three typical cells. When the calculated number of independent variables is greater than is expected, the system is not in equilibrium, either because it is not correctly divided into phases, or because some irreversibility between the phases exists and additional restrictions are necessary to remove it, or else because the system can never be in equilibrium. A cell with two electrodes in the same solution must, for the purposes of the rule, be considered as having two liquid phases separated by a surface at which there is a potential difference.

S. K. T.

**Electrochemical Polarisation.** E. SPITALSKY (*Z. Elektrochem.*, 1924, 30, 491—492).—An improved rotating commutator for the study of polarisation phenomena is described.

W. A. C.

**Preparation of Chromium by Electrolysis.** J. SIGRIST, P. WINKLER, and M. WANTZ.—(See ii, 864.)

**Electrolytic Deposition of Tungsten.** B. NEUMANN and H. RICHTER (*Z. Elektrochem.*, 1924, 30, 474—477).—From aqueous solutions of double cyanides and oxalates of tungsten no metallic tungsten is obtainable under any conditions, the utmost effect being reduction to  $\text{WO}_2$ . Acetone and pyridine solutions of  $\text{WCl}_6$  also gave negative results. From glycerol solutions of the hexachloride, small quantities of metal are deposited, but there is considerable decomposition of the solvent, and conduction ceases after a short time.  
W. A. C.

**Reduction Potentials of Quinones. II. Potentials of certain Derivatives of Benzoquinone, Naphthaquinone, and Anthraquinone.** J. B. CONANT and L. F. FIESER (*J. Amer. Chem. Soc.*, 1924, 46, 1858—1881; cf. A., 1923, ii, 9, 727).—The reduction potentials of 35 additional derivatives of the above quinones have been determined in acid alcoholic solution. The reduction potential as determined is a direct measure of the free energy of reduction of the quinone by hydrogen in the particular solvent employed. Some of the quinones were sufficiently soluble in water to allow of measurements being made in aqueous solution. The reduction potential of unsubstituted *o*-quinones is considerably higher than that of the corresponding *p*-quinones, and in the case of the unsubstituted benzoquinones and naphthaquinones the difference appears to be nearly constant. The attachment of a phenylene group to a quinonoid nucleus (whether ortho or para) lowers the reduction potential, this lowering being about 220 mv. for one phenylene group, but much greater (about 338 mv.) for a second attached to a *p*-quinone, and much less (108 mv.) for a second if joined to an *o*-quinone. The phenylene group has more effect than two alkyl groups. The reduction potential is lowered on introducing a hydroxyl group into the molecule, the effect being greatest when this group is attached to the quinonoid nucleus; the methoxyl and ethoxyl groups are nearly equal in their influence, which is a little less than that of the hydroxyl group. The reduction potentials of chloro- and bromo-anilic acids are very markedly affected by the concentration of the acid employed, whereas those of the other quinones are essentially the same for the different strengths employed. This is connected with the fact that these compounds are acids of strength comparable with the mineral acids. The results obtained with certain so-called hydroxy-*p*-quinones give additional support to the *p*-quinonoid structure of these substances. Chlorine and bromine produce very nearly the same result. Substitution of hydrogen by chlorine increases the potential in all the series, but no satisfactory correlation can be made between the position of the substituent atom and the magnitude of its effect. The carboxyl, carbalkoxyl, or sulphonic acid group, when introduced into anthraquinone and naphthaquinone, raises the potential greatly. The following compounds were incidentally prepared. *Methyl anthraquinone-2-carboxylate*, m. p. 165°. *2-Chloromethylanthraquin-*

one, pale yellow, shining plates, m. p.  $164.5^{\circ}$ , was made by chlorinating  $\beta$ -methylantraquinone in chlorobenzene. In nitrobenzene, it is formed as a by-product along with anthraquinone- $\beta$ -carboxylic acid. Contrary to the statement that all  $\omega$ -halogenated methylantraquinones are decomposed by sulphuric acid, it is not affected by heating with concentrated sulphuric acid for an hour at  $100^{\circ}$ . A. C.

**Electrometric Studies on Azo and Hydrazo Compounds.** E. BILLMANN and J. H. BLOM.—(See i, 1353.)

**Electrolysis of Soda-Lime Glass. I. Evolution of Gas and its Relation to Sorption and Conductivity.** J. W. REBBECK and J. B. FERGUSON (*J. Amer. Chem. Soc.*, 1924, **46**, 1991—2002).—The electrolysis of soda-lime glass has been investigated by filling bulbs with mercury, immersing them in dilute sodium hydroxide solution, and passing a current in one direction or the other. When the mercury is the cathode, the gases evolved consist of oxygen mixed with excess of hydrogen. The gas evolution may be prevented by heating the tubes in a vacuum for long periods at  $350^{\circ}$ , but the power of evolving gas is regained if the tube is exposed to water or water vapour. Any gas evolved may be made to disappear by reversing the potential, and no gas is produced if the mercury is made the anode. The formation of gas is due to the action of sodium on sorbed water, and simultaneous electrolysis of the sodium hydroxide thus formed; noticeable gas evolution occurs at potentials as low as 1.3 volts. The sorption of water does not affect the resistance of soda-lime glass, but the resistance is greatly increased by heating in a vacuum owing to causes which are to be dealt with in a later paper. Immersion in an acid solution gives rise to greater gas evolution than immersion in alkaline solution; this is possibly due to the adsorption of hydrogen ions in the former case.

W. H.-R.

**Chemical Action Produced by Niton.** S. C. LIND and D. C. BARDWELL (*J. Amer. Chem. Soc.*, 1924, **46**, 2003—2009; cf. this vol., ii, 11).—The velocity coefficients of the reaction which occurs when electrolytic gas is acted on by niton show an abnormal increase at low pressures. The action is caused by both  $\alpha$ -rays and recoil atoms, but if the latter are cut off by enclosing the radon in a thin  $\alpha$ -ray bulb, the velocity coefficient is normal. In a bulb 1 cm. in diameter, the  $\alpha$ -ray effect equals the recoil-atom effect at 117 mm. pressure. When allowance is made for the effect of the recoil atoms, the product of the velocity coefficient for the  $\alpha$ -ray effect (expressed in terms of millimetres of pressure change per curie of radon) by the square of the diameter of the reaction sphere is constant=84.1.

W. H.-R.

**Thermal Decomposition of Methane.** R. C. CANTELO (*J. Physical Chem.*, 1924, **28**, 1036—1048).—The influence of various catalysts, CaO, bone-black, Cu-CuO, Ni-NiO,  $\text{Fe}_2\text{O}_3$ -Fe,  $\text{MnO}_2$ , and silica gel, on the thermal decomposition of methane has been studied at various temperatures. Most of these exert some influence

on the reaction; the action of Ni-NiO is especially noticeable, complete equilibrium probably being obtained at 780° with this material.

Methane may decompose according to any one of the following equations: (1)  $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ ; (2)  $2\text{CH}_4 \rightleftharpoons \text{C}_2\text{H}_4 + 2\text{H}_2$ ; (3)  $2\text{CH}_4 \rightleftharpoons \text{C}_2\text{H}_2 + 3\text{H}_2$ . Equilibrium constants calculated from Nernst's formula show that only negligible amounts of ethylene and acetylene are to be expected.

L. L. B.

**Autoxidation and Antioxygenising Action. Catalytic Properties of Sulphur and its Compounds: Generalisation of the Phenomenon.** C. MOUREU, C. DUFRAISSE, and M. BADOCHÉ (*Compt. rend.*, 1924, 179, 237—243).—A list of 71 sulphur compounds which act catalytically is given. It is suggested that the mode of combination of the sulphur in the molecule may be a factor in determining the nature and intensity of the observed catalytic action. Oxidisable substances studied include benzaldehyde, acetaldehyde, styrene, turpentine, linseed oil, and sodium sulphite.

H. J. E.

**Hydrolysis of Amino-acids in Presence of Charcoal.** K. WUNDERLY (*Z. physikal. Chem.*, 1924, 112, 175—198).—Glycine, alanine, aspartic acid, and leucine in aqueous solution undergo slow hydrolysis in the presence of charcoal. Bone-black and animal charcoal are the most effective; blood charcoal is less active, whilst linden charcoal and bone-black treated with iron oxide have no action. It was not found possible to detect the glycollic acid from glycine, but the lactic acid from alanine and the malic acid from aspartic acid were isolated and identified, and methods devised for their determination. The reaction is unimolecular and non-reversible and reaches a limit for a certain concentration of the amino-acid. This limiting concentration depends on the amount of amino-acid and hydroxy-acid present as required by the mass-action law. The velocity measurements show, however, that the reaction does not proceed according to the equation  $dx/dt = k\{(a-x) - bx^2\}$ , but corresponds with a reversible reaction in accordance with the unimolecular equation  $dx/dt = k_1(a-x-\xi)$ , where  $\xi$  is the limiting concentration of amino-acid.

S. S.

**One-sided Equilibrium.** E. BAUR (*Z. physikal. Chem.*, 1924, 112, 199—205).—A theoretical discussion of the work of Wunderly (preceding abstract), which is regarded as dealing with a case of an equilibrium which can be approached with finite velocity from one side only.

S. S.

**Combination of Hydrogen and Oxygen in the Presence of Activated Mercury.** R. G. DICKINSON (*Proc. Nat. Acad. Sci.*, 1924, 10, 409—410).—Hydrogen and oxygen in contact with mercury combine to form water at 45° or even at room temperature, when illuminated by light from a quartz mercury-arc lamp cooled by an air blast. This is due to dissociation of the hydrogen by "collisions of the second kind" with mercury atoms excited by absorption of the mercury line 2537 Å. (cf. Cario and Franck, A.,

1922, ii, 809). In the absence of any one of the three substances, or of the exciting radiation, no reaction takes place. M. S. B.

**Velocity of Hydrolysis of Ethyl Orthoacetate.** A. SKRABAL and M. BALTADSCHEWA (*Monatsh.*, 1924, **45**, 19—24; cf. A., 1921, ii, 581).—In preparing ethyl orthoacetate (Reitter and Hess, A., 1907, i, 667), a second product is formed, b. p. 77.5—78° (ketene acetal?). The kinetics of hydrolysis of the ester,  $\text{CMe}(\text{OEt})_3 + \text{H}_2\text{O} = \text{CH}_3 \cdot \text{CO}_2\text{Et} + 2\text{Et} \cdot \text{OH}$ , correspond with the equation  $dx/dt = k_w(a-x) + k_a[\text{H}^+](a-x)$ . The constant  $k_w$  is determined in the presence of sodium hydroxide, whereas  $k_a$  is measured by acid hydrolysis in the presence of a mixture of potassium dihydrogen and disodium hydrogen phosphates; the values  $k_w = 5.7 \times 10^{-4}$  and  $k_a = 1.0 \times 10^6$  are recorded at 25°. F. M. H.

**Velocity of Hydrolysis of Ethyl Ether.** A. SKRABAL and H. AIROLDI (*Monatsh.*, 1924, **45**, 13—18; cf. A., 1921, ii, 581; 1922, ii, 134).—The hydrolysis of ether to alcohol in presence of benzenesulphonic acid as catalyst was carried out in closed tubes at 98°, when practically no ethylene was formed. It is an acid hydrolysis. With minutes as units,  $k = 9 \times 10^{-5}$ . The velocity coefficients for related substances vary widely, and run parallel with variations in general reactivity.

To determine the alcohol formed, the reaction mixture was made alkaline and distilled; water was then removed by calcium oxide in presence of pyridine, and the alcohol esterified with acetic anhydride. After neutralisation of the acetic acid, the ethyl acetate was hydrolysed with barium hydroxide, and the mixture titrated with hydrochloric acid. F. M. H.

**Inversion of Sucrose and Determination of Hydrogen-ion Concentration.** M. DUBOUX (*Helv. Chim. Acta*, 1924, **7**, 849—854).—When the equation  $k = k_{\text{H}}[\text{H}^+] + k_{\text{M}}(C - [\text{H}^+])$ , in which  $k$  is the observed velocity coefficient,  $k_{\text{H}}$ ,  $k_{\text{M}}$  are the coefficients for the hydrogen ion and the non-ionised acid, and  $C$  is the total concentration of the acid catalyst, is applied to the inversion of sucrose,  $k_{\text{H}}$  is found to vary, not only with different acids, but also with change of concentration of the same acid. This difficulty is surmounted by giving  $k_{\text{H}}$  the constant value found for it when sucrose is inverted by 0.002*N*-hydrochloric acid, which is regarded as completely ionised. W. E. E.

**Kinetics of Catalytic Decomposition of Bromocamphorcarboxylic Acid.** W. PASTANOGOV (*Z. physikal. Chem.*, 1924, **112**, 448—460).—Measurements have been made of the rate at which carbon dioxide is split off from bromocamphorcarboxylic acid dissolved in acetophenone and *o*-nitrotoluene under the catalytic influence of aniline and quinidine. When the base is in excess, the reaction is unimolecular. With excess of acid, the velocity increases as the reaction proceeds, and the initial velocity is smaller the higher the concentration of the acid. No matter what the initial concentration, however, the velocity has the same value when



the same concentration of acid is reached, other conditions being equal. With the optically active base, the rates of decomposition of the *d*- and *l*-acids are different, but the value for the inactive acid is less than the calculated mean, and the difference increases as the reaction proceeds. This is probably due to the difference in distribution of the catalyst between the two acids when the quantities have become unequal, thus reducing the rate of decomposition of the more rapidly decomposed acid. It is unlikely that racemate formation has more than a secondary influence.

M. S. B.

**Catalytic Activity of Carbons from Aromatic Hydrocarbons and some Derivatives.** W. FARMER and J. B. FIRTH (*J. Physical Chem.*, 1924, 28, 1136—1146).—Determinations of the activity of carbons prepared from 22 aromatic hydrocarbons, with regard to the evolution of oxygen from hydrogen peroxide, have been made after (1) activation at 900° in a vacuum from 3 minutes to 4 hours, and (2) subsequent treatment with iodine in chloroform, heating to drive off the iodine, digesting in alcoholic potassium hydroxide, washing, and finally heating as in (1). Samples of carbon derived from amines show the highest activity and those from phenolic substances the least activity. The cause of the variation has not been disclosed. The effect of the iodine treatment is to increase the activity of the carbon in every case.

M. B. D.

**Catalytic Action of Copper. IV. Periodic Variation of the Activity with Temperature of Reduction.** W. G. PALMER and F. H. CONSTABLE (*Proc. Roy. Soc.*, 1924, A, 106, 250—268).—The relation between the catalytic activity of copper and the temperature of its reduction from the oxide has been examined in experiments on the decomposition of ethyl and propyl alcohols (cf. A., 1922, ii, 437). The breaks which occur in the reaction-velocity-temperature curves at about 280° (A., 1921, ii, 542) are shown to be due to the progressive covering of the catalyst with the polymerisation products of the corresponding aldehydes. For rising and falling temperatures, these curves coincide only when the reaction temperature does not exceed 280°.

The reaction velocity when plotted against the temperature of reduction (200—400°) shows three maxima, which are less pronounced when the reduction temperature reaches 420°, the reduced copper then undergoing a change in structure, accompanied by a permanent increase in activity. The more active the catalyst, the smaller is its temperature coefficient. The heat of activation of the alcohol molecule appears to vary periodically with the reduction temperature of the catalyst and to depend very largely both on the atomic arrangement in the adsorbing surface and on the change in the area of this surface exposed.

S. K. T.

**Mechanism of the Catalytic Decomposition of Ethyl Acetate by Nickel at Various Elevated Temperatures.** J. N. PEARCE and C. N. OTT (*J. Physical Chem.*, 1924, 28, 1201—1210).—Ethyl acetate begins to decompose at a temperature slightly below 300°.

The products of the catalytic decomposition of ethyl acetate by nickel, prepared by reducing the oxide obtained by heating nickel nitrate, have been examined at 300—450°. The proportions of carbon dioxide and methane in the decomposition products increase with rise in temperature; those of hydrogen and carbon monoxide decrease. Traces of ethane, but neither higher hydrocarbons nor free acid, are formed. The addition of hydrogen to the vapour before passing it over the nickel produces little change in the nature of the decomposition products. The activity of the catalyst is altered by some of the products of decomposition. The mechanism suggested is the primary decomposition into acetone, ether, and carbon dioxide.

M. B. D.

**Catalytic Decomposition of Formic Acid.** E. MÜLLER and F. MÜLLER (*Z. Elektrochem.*, 1924, **30**, 493—497).—In the form of finely-divided metal, osmium causes a steady reaction in the sense  $\text{H}\cdot\text{CO}_2\text{H}=\text{H}_2+\text{CO}_2$ , whilst the other members of the platinum group effect a trifling decomposition and rapidly become inactive. In the form of colloidal solutions, however (*e.g.*, when a salt of the metal is added instead of the metal itself), all the platinum metals show considerable catalytic activities. Thus where platinum black evolves 1—2 c.c. of gas, colloidal platinum evolves more than 200 c.c. Osmium and ruthenium, under these conditions, remain as dark, colloidal solutions; the other metals are rapidly coagulated, but continue to act catalytically. The phenomena indicate that catalytic activity is associated with particles of a definite range of magnitude and is independent of the nature of the metal.

W. A. C.

**Irreversible Reduction and Catalytic Hydrogenation.** J. B. CONANT and H. B. CUTTER (*J. Physical Chem.*, 1924, **28**, 1096—1107).—Where the oxidised and reduced forms of a compound can exist in mobile equilibrium, the behaviour towards oxidising and reducing agents is conditioned by the oxidation–reduction potential. In the absence of such equilibrium, oxidation–reduction potentials cannot be measured, but it is possible to characterise compounds of this type by determining the potential of the weakest reducing agent which will cause reduction. The authors use the term “apparent reduction potential,” and employ an electrochemical device for detecting when reduction occurs. The results of experiments with seventy-five compounds of different types show that, if the solvent and, in particular, the hydron concentration be specified, then the potential of the reducing agent employed determines whether or not appreciable reduction will take place. A table of apparent reduction potentials for seven substances in the different solvents is given. Maleic acid ( $-0.25\pm0.10$  v.) is not affected by vanadous chloride ( $-0.15$  v.), but in 0.2*N*-hydrochloric acid is immediately reduced by hydrogen and colloidal platinum ( $-0.05$  v.). Similar experiments with dimethylacrylic acid show that the process of catalytic hydrogenation cannot be formulated electrochemically, but consists in the direct addition of activated hydrogen atoms. Experiments in which (1) dimethyl-

acrylic acid, (2) maleic acid was added to an equimolecular mixture of anthraquinol-2 : 7-disulphonate and anthraquinone-2 : 7-disulphonate in 0.1*N*-hydrochloric acid (+0.17 v.), in the presence of a platinum catalyst, showed no reduction, although the catalyst was not poisoned.

The authors discuss in detail the possible differences between the mechanism of soluble reducing agents and catalytic hydrogenation. If soluble oxidising and reducing agents are assumed to be unable to add or remove hydrogen atoms to the carbon linking, but only to the oxygen atoms at the end of a doubly conjugated system, an explanation for the reversible reduction of quinones and the irreversible reduction of maleic acid is possible.

Alternative views for the formulation of electrochemical equations for reversible oxidation and reduction are discussed, and the authors decide in favour of electron transfer as a basis of representation.

L. L. B.

**Catalytic Dehydration of Alcohols.** A. B. BROWN and E. E. REID (*J. Physical Chem.*, 1924, **28**, 1077—1081).—The authors have studied the catalytic decomposition of ethyl and butyl alcohols between 220° and 500°, using the dehydrating catalysts thoria, alumina, blue oxide of tungsten, and silica gel. From ethyl alcohol, ethane and methane are formed, and from butyl alcohol, butane and propane, the amounts of ethane and butane being particularly large with silica gel as catalyst. Alumina and the oxide of tungsten are the best catalysts for the formation of ethylene and butylene, both for high yield and absence of side reactions. The ratio of unsaturated hydrocarbon to aldehyde is considerably higher for butyl than for ethyl alcohol, but decreases with rise of temperature with all catalysts. Butyl alcohol is in every case decomposed at a lower temperature than ethyl alcohol.

L. L. B.

**Catalytic Alkylation of Ammonia.** A. B. BROWN and E. E. REID (*J. Physical Chem.*, 1924, **28**, 1067—1076).—A quantitative study of the alkylation of ammonia by methyl, ethyl, *n*-propyl, and *n*-butyl alcohols, by passing the alcohols mixed with ammonia over various catalytic oxides at 300—500°, using the apparatus described by Kramer and Reid (*A.*, 1921, i, 389).

The following catalysts, arranged in order of ascending effectiveness, have been studied: blue oxide of tungsten, commercial silica gel, alumina, silica gel impregnated with nickel oxide, zirconia, silica gel impregnated with thoria, and a silica gel specially prepared by the authors. For high activity, long life, and absence of side reactions, the special silica gel is much the best. It is prepared by adding a sodium silicate solution (4.5% Na<sub>2</sub>O) to an equal volume of 10% pure hydrochloric acid. The resulting gel is broken into large fragments, suspended in running water for several days, and then dried at temperatures rising in stages to 180°. The optimum temperatures, percentages of alcohol converted into amines, and the ratios of primary, secondary, and tertiary amines formed, using this catalyst, are as follows: methyl, 480°, 56%,

5:12:3; ethyl, 465°, 39.5%, 2:5:3; *n*-propyl, 415°, 49%, 10:11:18; *n*-butyl, 430°, 25%, 11:11:3. L. L. B.

**Action of Light on Dissolved Silver Salts in the Presence of Zinc Oxide.** E. BAUR and A. PERRET.—(See ii, 857.)

**Photochemical Union of Hydrogen and Sulphur.** R. G. W. NORRISH and E. K. RIDEAL.—(See ii, 848.)

**Tap Plug.** E. T. LEEMANS (*Chem.-Ztg.*, 1924, **90**, 526).—To avoid loss of liquid which may occur in the bore of the plug of the ordinary tap, *e.g.*, in separating funnels, the plug is ground away on one side sufficiently to allow liquid to flow, instead of boring a central hole. On turning the plug at right angles the portion ground away now becomes part of the funnel. H. T.

**Micro-distillation Apparatus.** H. LEFFMANN (*Amer. J. Pharm.*, 1924, **96**, 506—507).—A simple trap, inserted between the distilling flask and the upright air condenser, prevents the condensed liquid from running back into the flask. Provision is made for removing the liquid periodically from the trap. H. T.

**Combined Fractionating Column and Condenser.** W. J. GOODERHAM (*J. Chem. Soc.*, 1924, **125**, 2197).—An ordinary glass-disc fractionating column and jacket is sealed at the lower end into the centre tube of a Liebig condenser, at the bottom of which a side-tube is fitted. The vapour ascends the column and is condensed in the annular space between the jacket of the column and the condenser tube, and the liquid is collected from the side-tube. The apparatus may also be used as a double-surface reflux condenser. S. K. T.

**Sublimation Apparatus.** A. GUTBIER and T. PAYER (*Chem.-Ztg.*, 1924, **48**, 807—808).—The apparatus consists of a hard glass distillation flask with a protective covering of asbestos sheet around the lower half and a wide side-tube containing a cylinder of thin platinum foil. The flask is supported within a metallic covering which serves to maintain an even heat throughout its length, and a small burner is employed to heat the side-tube. This is connected to a spherical receiver with two openings, the second being connected through a Liebig condenser to a second similar receiver which, in turn, is connected to the vacuum pump. A stream of purified gas is passed through the apparatus during the course of an experiment. The apparatus may be used, for example, for the purification of selenium dioxide by subliming the crude preparation, after drying at 120°, in a current of oxygen; the product in the first receiver consists of snow-white crystals of selenium dioxide free from moisture and oxides of nitrogen.

A. R. P.

**Apparatus for the Viscosimetric Determination of Transition Points.** N. H. HARTSHORNE (*J. Chem. Soc.*, 1924, **125**, 2096—2099).—The solubility tube is fitted with a stirrer the stem of which consists in part of a capillary tube surmounted by a bulb

of about 20 c.c. capacity. The results of experiments with saturated solutions of sodium sulphate, disodium phosphate, and nickel sulphate are recorded.

S. K. T.

**Transformations of Elements.** A. SMITS (*Nature*, 1924, 114, 609—610).—Description of a vacuum lamp constructed for the use of lead instead of mercury, and intended for experiments on the transmutation of elements.

A. A. E.

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## Inorganic Chemistry.

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**Chloro-perbromide Equilibria.** E. A. DANCATER (*J. Chem. Soc.*, 1924, **125**, 2038—2043).—The decomposition of chloro-perbromides has been investigated by shaking aqueous solutions of the chlorides with a concentrated solution of bromine in carbon tetrachloride, followed by the analysis of each layer (cf. Jakowkin, A., 1894, ii, 271; 1896, ii, 514). The chloro-perbromides of copper, calcium, strontium, barium, magnesium, and aluminium all behave normally, giving at 25° a dissociation constant  $K_1$ , agreeing approximately with that obtained by Jakowkin (*loc. cit.*) for the compound  $KCl, Br_2$  (about 0.73). The chlorides of cadmium and mercury behave abnormally, giving a much higher value of  $K_1$  which also increases considerably with increasing concentration. These abnormalities are due to the existence of complex molecules and ions in solution, and, using the method of Name and Brown (A., 1917, ii, 455), it is shown that, in a pure solution of cadmium or mercury chloride, the percentage of simple molecules and ions increases with the dilution. W. H.-R.

**Viscosity and Surface Tension of Solutions of Iodine and Potassium Iodide.** E. A. DANCATER (*J. Chem. Soc.*, 1924, **125**, 2036—2037).—Using viscosimeters of the Ostwald type and the surface tension method of Sugden (T., 1922, **121**, 858), determinations have been made at 25.6° (1) for aqueous-ethyl alcoholic solutions of iodine and potassium iodide, in which the alcohol was 70% by volume, and the sum of the iodine and iodide 0.1 g.-equiv. per litre; and (2) for pure methyl-alcoholic solutions in which the sum of iodine and iodide was 1.0 g.-equiv. per litre. Neither the viscosity nor the surface tension shows any appreciable variation, although the compound  $KI_3$  is undoubtedly formed. The density, viscosity, and surface tension of pure methyl alcohol were also determined; the values found were:  $d^{25.6}$  0.7874;  $\eta^{25.6}$  0.005613;  $\gamma^{25.6}$  22.58. W. H.-R.

**Preparation of Fluorine.** J. SIMONS (*J. Amer. Chem. Soc.*, 1924, **46**, 2175—2179).—The second fluorine generator described by Argo, Mathers, Humiston, and Anderson (A., 1919, ii, 333) is improved. A large, vertical, delivery tube is attached to the anode compartment and is occasionally heated to prevent choking. The

electrolyte (potassium hydrogen fluoride) is replenished by heating to a liquid state with aqueous hydrofluoric acid in a separate copper cell, the water being removed by electrolysis and the liquid salt decanted from the solid copper fluoride. Short-circuiting between the anode and the diaphragm is prevented by sealing the former into the latter with Portland cement. The improved generator, with a *P.D.* of 10 volts, yields 4 litres of fluorine per hour for 20 to 30 hours.

S. K. T.

**Preparation, Freezing Point, and Vapour Pressure of Hydrogen Fluoride.** J. SIMONS (*J. Amer. Chem. Soc.*, 1924, **46**, 2179—2183).—Anhydrous, air-free hydrogen fluoride, prepared by heating anhydrous potassium hydrogen fluoride (cf. preceding abstract) in a special copper retort, freezes at  $-83^{\circ}$ . The vapour pressure,  $p$ , in mm. of mercury is given by  $\log p = 7.37 - 1315/T$ , which holds between  $236^{\circ}$  and  $320^{\circ}$  Abs.

S. K. T.

**Density and Molecular Complexity of Gaseous Hydrogen Fluoride.** J. SIMONS and J. H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1924, **46**, 2183—2191).—The vapour density of hydrogen fluoride at temperatures below its b. p. was determined by a dynamical method. The results, together with the data of Thorpe and Hambly at higher temperatures (cf. T., 1889, **55**, 163), may be closely calculated on the assumption that the vapour consists of an equilibrium mixture of HF and  $(\text{HF})_6$ , the heat of association being 6670 cal. per mol.

S. K. T.

**Comparison of Molecular Volume Numbers [of Oxygen and Nitrous Oxide].** R. LORENZ and W. HERZ.—(See ii, 823.)

**Conditions of Reaction of Hydrogen with Sulphur. V. Photochemical Union.** R. G. W. NORRISH and E. K. RIDEAL (*J. Chem. Soc.*, 1924, **125**, 2070—2081; cf. T., 1923, **123**, 3202).—The absorption spectrum of sulphur vapour contains a band with maximum absorption at  $2750 \text{ \AA}$ ., in good agreement with the earlier work of Graham (A., 1910, ii, 1015). This corresponds with a critical increment of activation,  $q = 51,670$  cal. per g.-atom, in agreement with the value previously found (*loc. cit.*) for the critical increment of activation of the (dark) gaseous reaction between hydrogen and sulphur, 51,400 cal., and also with the heat of dissociation of the  $\text{S}_2$  molecule, 50,000 cal. Conversely, ultra-violet radiation of wave-length about  $2700 \text{ \AA}$ . is photochemically active in initiating a gaseous reaction between hydrogen and sulphur vapour, proportional to the pressure of the sulphur vapour. In the gaseous state, reactions between hydrogen and sulphur can take place only between sulphur atoms, which are produced both by collisions and by photochemical dissociation. In addition, a reaction at the surface takes place between hydrogen and activated  $\text{S}_8$  molecules, and is not affected by ultra-violet radiation, the activation being entirely caused by collisions. In all cases, whether the activation takes place in the gaseous state or at the surface, by radiation or by collision, the energy of activation is constant, indicating that, in activation by collisions, the Newtonian laws of

inelastic impact do not apply, but that the process obeys the laws of quantum dynamics, the same amount of energy being extracted from the colliding molecules, whatever the force of their impact, providing this exceeds a certain magnitude. In these reactions, activation of the sulphur molecule, whether  $S_2$  or  $S_8$ , is synonymous with the dissociation of one valency "bond." W. H.-R.

**Crystal Structures of some Sulphides, Selenides, and Tellurides.** M. L. HUGGINS (*Physical Rev.*, 1923, **21**, 211—212).—It is assumed that in crystals of the sulphides, selenides, and tellurides of zinc, cadmium, mercury (bivalent), copper (univalent), silver, and gold, each metallic atom is surrounded by four negative atoms at tetrahedron corners, and each sulphur, selenium, or tellurium atom by four or eight electropositive atoms at tetrahedron or cube corners. The available crystallographic data are in accord with the necessary structures, and the latter also receive confirmation from a consideration of inter-atomic distances calculated from the corresponding densities. A. A. E.

**Change of Conductance of Selenium due to Electronic Bombardment.** R. DE L. KRONIG (*Physical Rev.*, 1924, **24**, 377—382).—The increase in conductance,  $\Delta C$ , with current  $I$  and voltage  $V$  is in good agreement with the expression,  $\Delta C/C = \sqrt{1 + kIV} - 1$ , derived from the free electron theory of metallic conduction;  $k = 98.5$ . A. A. E.

**Crystal Structure of "Metallic" Selenium and Tellurium.** M. K. SLATTERY (*Physical Rev.*, 1923, **21**, 378—379).—Both elements crystallise in a simple triangular lattice with 3 atoms associated with each point of the lattice. For selenium and tellurium, respectively, the side,  $a$ , of the basal triangle is 4.34, 4.44 Å., and the axial ratio,  $c$ , 1.14, 1.33. A. A. E.

**Principal Optical Constants of Isolated Tellurium Crystals.** L. P. SIEG and G. D. VAN DYKE (*Physical Rev.*, 1923, **21**, 206).—For tellurium crystals, ranges of the principal optical constants in the visible spectrum were determined as follows: Principal reflecting powers (when the light falling on one of the hexagonal faces is polarised with the electric vector respectively parallel and perpendicular to the principal crystalline axis),  $R_1$  0.28—0.34,  $R_2$  0.26—0.30; refractive indices,  $n_1$  2.50—3.44,  $n_2$  2.05—2.68; principal absorption constants,  $k_1$  0.40—0.56,  $k_2$  0.54—0.67. A. A. E.

**Direct Determination of the Principal Reflecting Powers of Isolated Tellurium Crystals.** L. P. SIEG (*Physical Rev.*, 1923, **21**, 211; cf. preceding abstract).—By a direct method, the values of  $R_1$  0.28—0.34 and  $R_2$  0.22—0.32 have been obtained for tellurium. A. A. E.

**Ammonia, Carbon, Hydrogen Cyanide, Hydrogen Equilibrium, and the Free Energy of Hydrogen Cyanide.** R. M. BADGER (*J. Amer. Chem. Soc.*, 1924, **46**, 2166—2172).—The equilibrium  $NH_3 + C \rightleftharpoons HCN + H_2$  is investigated by a continuous flow method. No side reactions take place; the mean value of



$K(=p_{\text{H}_2} \cdot p_{\text{HCN}}/p_{\text{NH}_3})$  is  $5.8 \times 10^{-6}$ , corrected to  $800^\circ$  Abs. The free energy increase attending the reaction is 19,200 cal. With the help of previously published data, the free energy of hydrogen cyanide, in cal., is shown to be given by  $F=30,600+0.607 \log_e T-0.00068T^2+0.000000117T^3-6.3T$ . The value at  $800^\circ$  Abs. is 28,400 cal. [Cf. *B.*, 1924, 940.] S. K. T.

### Explosion of Ammonia with Electrolytic Gas and Oxygen.

J. R. PARTINGTON and A. J. PRINCE (*J. Chem. Soc.*, 1924, 125, 2018—2025).—Carefully dried mixtures of ammonia with electrolytic gas ( $2\text{H}_2+\text{O}_2$ ) in varying proportions were exploded with the mixture initially at  $85^\circ$ , and 380 mm. pressure so that no steam could condense. The mixture becomes explosive when the ratio of electrolytic gas to ammonia is just above 1, when 79% of the ammonia is decomposed. When the ratio is just above 3, the decomposition is complete, the sole products being steam, hydrogen, and nitrogen. When ammonia is exploded with a deficiency of oxygen, the excess of ammonia is completely decomposed into nitrogen and hydrogen, and oxides of nitrogen are formed only if the ratio of ammonia to oxygen is less than 1.6; the maximum oxidation of nitrogen is 16% with the ratio 1.22. The commencement of oxidation of nitrogen is marked by colour changes in the flame, which changes from yellow to green, violet, and white as the oxidation of nitrogen increases. When ammonia is exploded with oxygen, the amount of nitrogen oxidised is greater than in the explosion of a corresponding mixture of nitrogen, hydrogen, and oxygen. W. H.-R.

**Hyponitrites.** L. W. JONES and A. W. SCOTT (*J. Amer. Chem. Soc.*, 1924, 46, 2172—2175).—Hyponitrous acid may be regarded as the hydroximic acid of nitrous acid. Sodium hyponitrite, therefore, may be prepared by mixing alcoholic solutions of sodium ethoxide (corresponding with 6.62 g. of sodium) and of hydroxylamine hydrochloride (20 g.), cooling, filtering, adding sodium ethoxide solution (corresponding with 15.4 g. of sodium) to the filtrate, cooling again, and distilling the calculated amount of ethyl nitrite directly into the mixture. The sodium salt is precipitated (yield about 13.5%). S. K. T.

**Systems of Acids, Bases, and Salts.** E. C. FRANKLIN (*J. Amer. Chem. Soc.*, 1924, 46, 2137—2151).—By classifying compounds as acids, bases, or salts of the "water," "hydrogen sulphide," "ammonia," "hydrogen fluoride," or "methane" systems, and by comparing the chemical properties of the corresponding members of each system, it is shown that sulphur, nitrogen, the halogens, and to a certain degree carbon, are acid-, base-, and salt-forming elements in the sense applied by Lavoisier to oxygen. Thus, the action of potassamide on solutions of metallic salts in liquid ammonia is exactly analogous to the action of potassium hydroxide on the same salts in aqueous solution. Azoimide is regarded as "ammononitric" acid, comparable with "aquonitric," or ordinary

nitric, acid; thus a mixture of azoimide and hydrochloric acid dissolves gold and platinum, and potassium azide is a "nitridising" agent, potassium nitrate being an oxidising agent. Many acid amides etc. belong to both the water and the ammonia systems, *i.e.*, are "mixed compounds" and experimental evidence is cited in support of this point of view. S. K. T.

**Solid Arsenic Hydrides.** L. MOSER and A. BRUKL (*Monatsh.*, 1924, 45, 25—37).—In seeking a better method of preparing  $\text{As}_2\text{H}_2$ , a new solid arsenic hydride was discovered and was shown to be  $\text{As}_4\text{H}_2$ .

Reckleben and Scheiber's preparation of solid  $\text{As}_2\text{H}_2$ , by the action of water on sodium arsenide (A., 1911, ii, 390), was repeated and their analyses were confirmed (*cf.* also Janovsky, A., 1873, 842; 1876, i, 681). Its impurity (arsenic) is ascribed to the action of sodium hydroxide on arsenic trihydride, but it is obtained pure, in small yield, by atmospheric oxidation of aqueous arsenic trihydride. Interaction of arsenic trihydride and phosphorus pentachloride (Janovsky, *loc. cit.*) in carbon tetrachloride solution did not give  $\text{As}_2\text{H}_2$ .

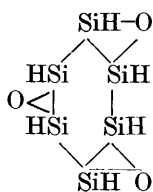
Oxidation of arsenic trihydride with stannic chloride in the presence of hydrochloric acid gave a red, amorphous, insoluble hydride,  $\text{As}_4\text{H}_2$ . It is decomposed by heat into arsenic, the trihydride, and hydrogen; the hydrogen was determined volumetrically by first measuring the total volume of free hydrogen + arsenic trihydride, and subsequently absorbing the latter with silver nitrate. To determine the arsenic, the hydride was dissolved in nitric acid, the solution reduced with iron, and the arsenic ion titrated with potassium bromate after distillation with hydrochloric acid and potassium bromide. The compound is more stable than  $\text{As}_2\text{H}_2$ , but gradually forms arsenic, especially if damp. It is unchanged by boiling water or hydrochloric acid but forms arsenic with boiling concentrated (or fused) alkali. With nitric acid, bromine, or hydrogen peroxide it gives arsenic acid. F. M. H.

**Equilibrium of the Reaction between Arsenious Acid and Bromine, and between Arsenic Acid and Hydrogen Bromide.**

W. MANCHOT and F. OBERHAUSER (*Z. anorg. Chem.*, 1924, 138, 357—367).—The reduction of disodium arsenate by hydrobromic acid and by mixtures of hydrochloric acid and potassium bromide and the oxidation of arsenious acid by bromine are indicated by the scheme:  $\text{As}_2\text{O}_5 + 4\text{HBr} \rightleftharpoons \text{As}_2\text{O}_3 + 4\text{Br} + 2\text{H}_2\text{O}$ . If the concentration of the hydrochloric acid is less than 24%, the reaction proceeds entirely from right to left; under these conditions, arsenious acid may be accurately titrated with bromine, the end-point of the titration being unaffected by the exact concentration of hydrochloric acid. The reverse reaction, however, may take place if the concentration of hydrochloric acid exceeds 24%; the equilibrium conditions depend on the concentrations of arsenate, bromide, and hydrochloric acid, and these effects have been studied qualitatively.

W. H.-R.

**Constitution of Siloxen.** H. KAUTZKY and G. HERZBERG (*Ber.*, 1924, 57, [B], 1665—1670).—Further examination of oxydisilin,  $\text{Si}_2\text{H}\cdot\text{OH}$  (Kautzky, A., 1921, ii, 505) has led the authors to assign to it the annexed constitution; the designation "siloxen" is suggested.



Siloxen is converted by gentle treatment with iodine solution into the compound,  $\text{Si}_6\text{H}_5\text{O}_3\text{I}$ , the composition of which is deduced from its analyses and from determination of the hydrogen evolved by the action of potassium hydroxide; by the action of hydrogen bromide on siloxen an analogously constituted *bromide*,  $\text{Si}_6\text{H}_5\text{O}_3\text{Br}$ , is obtained. The action of iodine dissolved in glacial acetic acid on siloxen yields a *tri-iodo* derivative,  $\text{Si}_6\text{H}_3\text{O}_3\text{I}_3$ , the properties of which are very similar to those of silical bromide,  $\text{Si}_2\text{OHBr}$  (*loc. cit.*), which is therefore considered to be tribromosiloxen,  $\text{Si}_6\text{H}_3\text{O}_3\text{Br}_3$ . If the latter substance is treated with the requisite quantity of bromine (dissolved in boiling glacial acetic acid) for the production of hexabromosiloxen, the halogen is absorbed completely, with the formation of a yellow compound which gives the reactions characteristic of halogenated siloxens and is readily hydrolysed to an intensely black hydroxy derivative. With greater proportions of bromine, reaction occurs slowly; the products, however, are colourless and do not yield coloured compounds when hydrolysed. The hydrogen atoms in siloxen must therefore be united similarly to silicon atoms. The mode of linking of the oxygen atoms is deduced from the observation that siloxen is converted by exhaustive chlorination into hexachlorodisiloxan,  $\text{SiCl}_3\cdot\text{O}\cdot\text{SiCl}_3$ , and by treatment with methyl alcohol in the presence of ammonia into *hexamethoxydisiloxan*,  $\text{O}[\text{Si}(\text{OMe})_3]_2$ ; since the group  $\text{Si}\cdot\text{O}\cdot\text{Si}$  is present in each of these compounds obtained in widely differing ways, it is assumed to be present in siloxen. The action of ammonia on tribromosiloxen gives *triaminosiloxen*, a red substance which is much more sensitive towards light and moisture than the corresponding hydroxy or halogeno derivatives.

Since siloxen and its derivatives retain the finely-lamellated structure of the calcium silicide from which they are derived, it is very remarkable that the reactions proceed quantitatively and with almost titrimetric rapidity and definiteness.

H. W.

**Equilibrium Diagram of Carbon.** J. A. M. VAN LIEMPT (*Chem. Weekblad*, 1924, 21, 517—524).—A critical discussion of recent attempts to obtain liquid carbon. The formula of Kohn (A., 1921, ii, 302) connecting the vapour pressure with the temperature of the positive electrode in the carbon arc cannot be correct, since the vapour pressures calculated from it for the conditions of the ordinary carbon filament lamp are found to be impossibly high. Laar's formula  $\log p(\text{atm.}) = -47120/T + 9.4$  (A., 1921, ii, 17), which is in very close agreement with that of Jedrzejewski and Wertenstein (*Z. Physik*, 1923, 19, 20), indicates values for the triple point, critical temperature, and critical pressure of  $3900^\circ$ ,  $7800^\circ$ , and 1500 atm., respectively; taking the atomic heat of

fusion at Debye's value, 8.8, however, these results give a density of 0.0003 for liquid carbon, and are obviously untrustworthy. The conclusion is reached that trustworthy results cannot be obtained unless all the experiments are performed with uniform specific material.

S. I. L.

**Action of Heat and Vacuum on Artificial Graphite.** P. LEBEAU and M. PICON (*Compt. rend.*, 1924, **179**, 264—266).—On heating three specimens of artificial graphite in a vacuum, similar results were obtained in each case. At 1000°, the gas evolved consisted of methane, carbon monoxide, and hydrogen, the percentages being 43.5, 20.5, and 36, respectively; at higher temperatures, methane was not observed, and the percentage of carbon monoxide increased with temperature, reaching 95.8 at 2400°. On allowing dry air to come into contact with previously heated graphite and subsequently reheating this graphite in a vacuum, larger quantities of gas were obtained, but methane was absent. Volatilisation of the carbon was observed at 2300°; it became rapid at 2400°.

H. J. E.

**Behaviour of Aqueous and Ethyl-alcoholic Solutions of Mercuric Chloride towards Different Adsorbents.** II. M. A. RAKUZIN and A. N. NESMEJANOV (*Münch. med. Woch.*, 1924, **71**, 429—430; from *Chem. Zentr.*, 1924, i, 2892; cf. this vol., ii, 461).—Dry activated charcoal adsorbs ethyl alcohol. The adsorption decreases with increasing concentration and ceases at a concentration of 40%.

G. W. R.

**Reaction between Carbon Monoxide and Iodic Acid in Aqueous Sulphuric Acid.** A. B. LAMB, A. W. PHILLIPS, and R. K. CARLETON (*J. Amer. Chem. Soc.*, 1924, **46**, 2017—2026).—Solutions of iodic acid in aqueous sulphuric acid react with carbon monoxide at the ordinary temperature with liberation of iodine, the reaction being greatly accelerated by increasing concentration of the sulphuric acid. With a given concentration of sulphuric acid, the iodic acid, in the presence of a large excess of carbon monoxide, reacts unimolecularly. On the other hand, the velocity of the reaction is practically unaffected by the concentration of the carbon monoxide whether the latter is present as gas or entirely in solution, and it is only when the carbon monoxide is almost entirely used up that the reaction velocity decreases. The velocity of the reaction is nearly proportional to the activity of the undissociated sulphuric acid molecules. These results may be due to the reaction between carbon monoxide and iodic acid, or iodate ion, taking place unimolecularly in two successive reactions of approximately the same speed, and hypothetical equations are given.

W. H.-R.

**Thermal Dissociation of certain Carbonates.** G. MAZZETTI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 46—50).—Results are given of an investigation of the thermal dissociation of various carbonates by the ordinary method of thermal analysis and by means

of a device which traces on a photographic plate the curve connecting loss of weight with the temperature.

By the former method, the initial decomposition temperature of silver carbonate is found to be  $218^{\circ}$  (Joulin gave  $225^{\circ}$  and Nernst's approximate formula gives  $275^{\circ}$ ), and the temperature at which the oxide decomposes in a current of carbon dioxide,  $414^{\circ}$ . The second method reveals two distinct arrests at  $168^{\circ}$  and  $389^{\circ}$ , respectively. For cadmium carbonate, the two methods indicate  $332^{\circ}$  and  $355^{\circ}$ , respectively, as the temperature of initial decomposition, Nernst's theorem giving  $346^{\circ}$ . With lead carbonate, the thermal curve shows a distinct change of direction at  $346^{\circ}$ . Colson gave  $302^{\circ}$  as the temperature of decomposition, and Nernst's theorem indicates  $337^{\circ}$ . In none of the above cases is any sign of the formation of a basic carbonate obtained.

T. H. P.

**Attempts to Prepare a Fluocarbonate: Bearing on the Co-ordination Number of Carbon.** J. H. HILDEBRAND, H. B. MERRILL, and J. SIMONS (*J. Amer. Chem. Soc.*, 1924, **46**, 2225—2226).—Unsuccessful attempts were made to prepare caesium fluocarbonate by the combination of carbon tetrafluoride and caesium fluoride under various conditions, and by the action of fluorine on caesium carbonate. Liquid hydrogen fluoride and liquid carbon tetrafluoride, which are not appreciably soluble in one another, also show no tendency to combine. Since caesium fluocarbonate is, theoretically, the most likely compound to show carbon with a co-ordination number exceeding four, it appears improbable that carbon can have a co-ordination number greater than this.

S. K. T.

**Magnetic Susceptibility of Helium, Neon, Argon, and Nitrogen.** L. G. HECTOR (*Physical Rev.*, 1924, **24**, 418—425).—The magnetic susceptibilities are ( $\times 10^{-10}, \pm 2\%$ ):—helium,  $-0.780$ ; neon,  $-2.77$ ; argon,  $-7.52$ ; nitrogen,  $-4.91$ , at  $20^{\circ}$  and 760 mm. There is satisfactory agreement between the experimental values and the orders of magnitude predicted by Pauli (A., 1921, ii, 161) and by Joos (*Z. Physik*, 1923, **19**, 347). A. A. E.

**Rare Gases of Volcanic Exhalations.** A. PIUTTI and E. BOGGIO-LERA (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], **30**, 92—99).—The results are given of analyses of a number of gaseous mixtures of volcanic origin. In all cases, the ratio between the proportions of argon and nitrogen present is less than in ordinary air, whereas the ratios (He+Ne):N and (He+Ne):A vary within wide limits and in some instances are greater than is the case in air. In one and the same volcanic region, the contents of helium and neon together in different exhalations vary inversely with the temperatures at which they issue.

T. H. P.

**Pressure of Saturated Vapour of Mixtures of Potassium and Sodium Chlorides.** L. HACKSPILL and R. GRANDADAM (*Compt. rend.*, 1924, **179**, 464—467).—The vapour pressure of fused potassium chloride rises from 1 mm. of mercury at  $830^{\circ}$  to 10.8 mm. at  $994^{\circ}$ ; the experimental values are thus a little lower

than those calculated by Jackson and Morgan (A., 1921, ii, 260). Similar measurements were made in the case of mixtures of potassium and sodium chlorides of different composition over the same temperature range, and the results are shown graphically, together with the composition of the vapour corresponding with a pressure of 3.49 mm. A specimen of silvinit containing 65% of potassium chloride gave results from which the conclusion is drawn that separation of the two chlorides by fractional distillation is practicable.

H. J. E.

**Marine Salt Deposits. Polytherms of the Four-salt Points in the Potassium Chloride Region of Quinary Systems.** SEROWY (*Kali*, 1924, 17, 289—296, 305—309, 320—324, 333—335, 345—350; from *Chem. Zentr.*, 1924, i, 2773).—The author has investigated the equilibria of solutions saturated with carnallite, potassium chloride, sodium chloride, and kieserite. The different equilibrium intervals lie close together in the direction of low sulphate concentrations. The ionic concentrations are shown in solubility curves as functions of temperature. The concentration of magnesium chloride shows a regular increase, which becomes more pronounced at higher temperatures. The curve for magnesium sulphate is similar. The polytherms for sodium chloride and potassium chloride are abnormal. Above 72°, the absolute amount of potassium chloride remains always above that of sodium chloride, but at higher temperatures the relative solubility of sodium chloride increases. At high temperatures, the behaviour of the solutions examined is not in agreement with the Wilson rule. The densities of the different equilibrium solutions are given in tabular form.

G. W. R.

**Effect of X-Rays on Halite and Sylvite.** P. L. BAYLEY (*Physical Rev.*, 1923, 21, 716).—Halite, which on exposure to X-rays assumes a dark brownish-yellow colour, becomes colourless after several days' exposure to bright daylight. The purple colour assumed by sylvite fades in a few minutes in daylight. Halite has a very broad absorption band at the edge of the violet extending far into the ultra-violet and visible green; sylvite has a broad absorption band in the yellow and green. During fading, the peaks of the absorption curves are unchanged. Halite fades most rapidly in the bluish-green portion of the spectrum, and sylvite in the orange. The results possess analytical utility.

A. A. E.

**Study of Secondary Valency by X-Rays.** G. L. CLARK and W. DUANE (*Physical Rev.*, 1923, 21, 380).—Potassium iodide is simple cubic, with the length of unit edge 3.532 Å.; potassium tri-iodide is monoclinic,  $d\ 4.68\text{ Å.}$  Cæsium iodide is cube-centred, with a distance between planes containing like atoms of 4.562 Å. In the unit parallelepiped containing 1 mol. of cæsium tri-iodide, the distances between planes bearing cæsium atoms are 4.49 Å. (100), 6.50 Å. (010), and 7.04 Å. (001); the iodine planes are one-quarter as far apart, so that one iodine atom is at the centre of the parallelepiped and the other two so-called secondary valency atoms are

equidistant on both sides along the body diagonal. The compound  $\text{CsIBr}_2$  has a similar structure with corresponding distances 4.26, 5.91, and 6.90 Å.

A. A. E.

**Metaphosphates. III.** P. PASCAL (*Bull. Soc. chim.*, 1924, [iv], **35**, 1131—1141; cf. this vol., ii, 39, 171, 605).—When potassium trimetaphosphate is heated the corresponding tetrametaphosphate is formed and finally Kurrol's insoluble salt; the rate of formation of the latter increases with the temperature much more rapidly than the rate for the tetrametaphosphate. A hexametaphosphate is produced on fusion. Viscosity measurements show that the transition points of Kurrol's three salts are  $420^\circ$  and  $505^\circ$ ; a sharp transition at  $320^\circ$  corresponds with the formation of higher condensation products of potassium trimetaphosphate. Potassium hexametaphosphate is prepared as a viscous, hygroscopic mass from the corresponding sodium salt through the lead salt. This process may cause self-condensation of the molecules of the potassium salt. The insoluble salt of Kurrol is formed by heating the hexametaphosphate to below  $660^\circ$ ; at this temperature, there is a momentary fusion, after which the salt only melts at  $960^\circ$ . The presence of a trace of the lead salt greatly accelerates these changes.

S. K. T.

**Sodium Hypochlorite [Hydrates].** A. SANFOURCHE and L. GARDENT (*Bull. Soc. chim.*, 1924, [iv], **35**, 1088—1093).—By cooling a very concentrated solution of sodium hypochlorite, deliquescent crystals of the pentahydrate were prepared, m. p.  $24.5 \pm 0.5^\circ$ . The crystals decompose slowly below  $25^\circ$ , yielding, in the absence of carbon dioxide, chlorate, chloride, and oxygen; they oxidise organic matter energetically, but do not attack metals (iron, tin, zinc). A study of the solution of the crystals revealed the existence of two other hydrates,  $\text{NaClO} \cdot 2.5\text{H}_2\text{O}$  (m.p.  $57.5^\circ$ ) and  $\text{NaClO} \cdot \text{H}_2\text{O}$  (decomp. on melting); no indication of the existence of Applebey's heptahydrate was observed (T., 1919, **115**, 1106).

S. K. T.

**Kinetics of the Decomposition of Sodium Hypochlorite Solutions.** F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], **30**, 107—114; cf. A., 1920, ii, 488).—The decomposition of sodium hypochlorite takes place in accordance with the equations (i)  $3\text{NaOCl} = \text{NaClO}_3 + 2\text{NaCl}$  and (ii)  $2\text{NaOCl} = 2\text{NaCl} + \text{O}_2$ . If  $a$  is the initial quantity of hypochlorite chlorine, that is, one-half of the active chlorine per unit volume of solution,  $x$  the quantity decomposed after the lapse of time  $t$ , and  $y$  and  $z$  the respective quantities of chlorate chlorine and chloride chlorine formed in the same time,  $x = 3y + z$ ;  $dy/dt = k_1(a-x)^3$  and  $dz/dt = k_2(a-x)^2$ . By the use of finite increments, an expression is obtained which, when applied to the experimental results furnished at  $30^\circ$ , gives the mean value 0.004153 for  $1/t \cdot x/a(a-x)$  and the mean value 0.0154 for  $k_1:k_2$ . The decomposition proceeds, indeed, as though it were a reaction of the second order, whereas actually it consists of two collateral reactions of the second and third orders, respectively.

T. H. P.

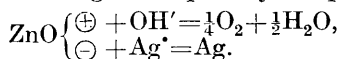
**Thermal Decomposition of Sodium, Barium, and Cadmium Dithionates in Aqueous Solution.** J. CORNOG and W. E. HENDERSON (*J. Amer. Chem. Soc.*, 1924, **46**, 1978—1980).—*N*-Solutions of the above dithionates are not decomposed by prolonged boiling, but, when heated in closed tubes at 150°, complete decomposition occurs within 6 hours. In the presence of excess of air the final reaction is  $\text{MS}_2\text{O}_6 + \text{H}_2\text{O} + \text{O} = \text{MSO}_4 + \text{H}_2\text{SO}_4$ , but in an inert atmosphere the reaction is more complex. Decomposition is favoured by increasing concentration and low pressure, and is accelerated by the initial presence of sulphur dioxide. The primary decomposition probably results in the formation of metallic sulphate and sulphur dioxide, and is followed by secondary reactions in which sulphur or sulphuric acid are formed. W. H.-R.

**Ammonium as a Reducing Agent.** H. H. SCHLUBACH and H. MIEDEL.—(See i, 1295.)

**Observations of the Course of Recrystallisation [of Silver] by Means of X-Rays.** R. GLOCKER and E. KAUPP (*Z. Metallk.*, 1924, **16**, 377—379).—X-Ray photographs show that severely rolled sheets of silver do not undergo complete recrystallisation at 150° in the sense that the new crystallites are not regularly oriented even after prolonged annealing. At 700°, complete recrystallisation takes many hours, but it is effected in 10 minutes at 850°. The rate of recrystallisation at the lower temperatures is greater the severer the deformation which the metal has undergone. [Cf. B., 1924, 1016.] A. R. P.

**Hall Effect and Specific Resistance of Evaporated Films of Silver, Copper, and Iron.** J. C. STEINBERG (*Physical Rev.*, 1923, **21**, 196).—Films obtained by evaporating a metallic filament in a vacuum are crystalline, but in a very finely-divided state. In the cases of silver, copper, and iron, the specific resistance is ten times as great as that of the bulk metal. The Hall coefficients of the diamagnetic metals are not altered, but that of evaporated iron is six times as great as for the bulk metal. A. A. E.

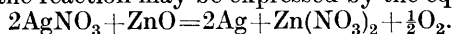
**Action of Light on Dissolved Silver Salts in the Presence of Zinc Oxide.** E. BAUR and A. PERRET (*Helv. Chim. Acta*, 1924, **7**, 910—915).—It is supposed that after being activated by the ultra-violet waves, zinc oxide can “electrolyse” a surrounding solution of silver nitrate or sulphate. Thus, after receiving one quantum of energy, a molecule of zinc oxide can discharge both a hydroxyl and a silver ion of the aqueous silver nitrate solution in contact with it according to the photolytic equation,



In support of the supposed analogy between photolysis and electrolysis, it is proved that silver peroxide is formed just as it is at the anode in ordinary electrolysis. A mixture of zinc oxide with silver nitrate solution was exposed to sunlight in a revolving evacuated tube; the combined silver present in the solid phase



after exposure was found to increase and decrease with the peroxide content. When, however, all the peroxide had disappeared and there was also practically no silver ion in the solution, there was still combined silver in the solid phase, probably in the form of oxide. It is imagined that the photolytic oxygen mostly adds on to the silver salt or silver oxide which the solution presents to it. The peroxide compound afterwards dissociates thermally, leaving silver oxide, which either passes into solution again by double decomposition with the zinc salt, or else is itself photolytically decomposed into silver and oxygen. This succession of reactions, which is influenced in many ways, especially by temperature, excludes the possibility of there being any relation between the amounts of combined and metallic silver in the solid phase. On the other hand, the total photolytic oxygen (gas evolved plus gas dissolved in liquid phase plus gas fixed as peroxide) is in that stoichiometric relation with the metallic silver produced which is required by the photolytic equation previously given. Thus, as a whole, the reaction may be expressed by the equation :



W. E. E.

**Crystalline Structure of Calcium Oxide, Sulphide, and Selenide.** W. P. DAVEY (*Physical Rev.*, 1923, **21**, 213).—Using the method previously described (*ibid.*, 1922, **19**, 538), results were obtained for the diffraction pattern, ionic lattice, and side of unit cube, respectively, as follows :—calcium oxide, face-centred cube, simple cube,  $2.395 \pm 0.002$ ; calcium sulphide, simple cube, simple cube,  $2.843 \pm 0.003$ ; calcium selenide, face-centred cube, simple cube,  $2.957 \pm 0.003$ . On heating calcium with selenium in an evacuated tube, reaction took place with explosive violence; a brown scale of CaSe, found on the fragments, was formed during the instant of the explosion, but was sufficiently crystalline to give a diffraction pattern.

A. A. E.

**Thermal Decomposition of Calcium Hydrogen Carbonate in Aqueous Solution.** R. STUMPER (*Compt. rend.*, 1924, **179**, 266—268).—Solutions of calcium hydrogen carbonate were kept at 70°, 80°, and the b. p. and were also boiled rapidly, the proportion of undecomposed hydrogen carbonate being determined from time to time. The values obtained indicate that the reaction is unimolecular, although the reaction velocity is somewhat greater at the outset and finally less than the theoretical values. H. J. E.

**Rôle of Water in Reactions in the Solid State. III.** D. BALAREV (*Z. anorg. Chem.*, 1924, **138**, 349—356).—The reaction between calcium oxide and silica has been studied at temperatures up to 930° in atmospheres of dry air, hydrogen, and carbon dioxide, and also in steam. The velocity of the reaction and the temperature at which it begins to take place with measurable speed depend on the atmosphere, the accelerating effect of water being the greatest. Traces of hydrogen chloride or hydrogen sulphide greatly accelerate the reaction owing to the formation of surface films of calcium

chloride or sulphide which liquefy. In other cases, the gas is adsorbed on the surface and the adsorbed layer produces a loosening of the surface molecules of the solid which is comparable with a softening or melting. When two solids are stirred together, a loosening of the molecules occurs at the points of contact and a slight reaction occurs. Whether the action proceeds further depends on the temperature, compression, heat of reaction, and the water or gas content. The reaction is greatly accelerated if a liquid or fused layer can be formed, and this may be caused either by action of the atmosphere or by the thermal effect of the first small reaction. Thus reactions between calcium oxide and other solids above the temperature of dissociation of calcium hydroxide are comparatively slow unless the other solid can form a fused or liquid layer, as in the systems  $\text{CaO-MoO}_3$  or  $\text{CaO-Ag}_4\text{P}_2\text{O}_7$ . The greater reactivity attributed by Hedvall and Heuberg (this vol., ii, 484) to solids in the region of their transition points may also be due to the effect of fused or liquefied surface layers (cf. this vol., ii, 483, 611). Silver pyrophosphate,  $\text{Ag}_4\text{P}_2\text{O}_7$ , melts at  $565 \pm 2^\circ$ ; white silver sodium pyrophosphate,  $\text{Ag}_3\text{NaP}_2\text{O}_7$ , becomes yellow at  $235 \pm 3^\circ$  and melts at  $400-450^\circ$ .  
W. H.-R.

#### Crystalline Structure of Barium and Strontium Selenides.

M. K. SLATTERY (*Physical Rev.*, 1923, **21**, 213).—X-Ray examination by Davey's method (*ibid.*, 1922, **19**, 538) shows barium and strontium selenides to have a simple cubic structure of ions,  $d = 3.308$  and  $3.117 \text{ \AA.}$  ( $\pm 0.003 \text{ \AA.}$ ), respectively. A. A. E.

#### Combining Weight of Lead from Vesuvian Cotunnite. A.

PIUTTI and D. MIGLIACCI (*Gazzetta*, 1924, **54**, 605—610).—Lead tetraphenyl, prepared from cotunnite which made its appearance in Vesuvius during the eruption of 1906, has the same m. p.,  $223.6^\circ$ , as the compound prepared from ordinary lead, and exhibits scarcely any radioactivity, the residues from the phenylation being far more radioactive than the original material in consequence of the accumulation of radium-*D*. Lead tetraphenyl may be obtained perfectly pure by alternate crystallisations from benzene and chloroform and by treatment with absolute alcohol, provided that sufficiently pure lead chloride is used in its preparation. The action of bromine vapour converts lead tetraphenyl quantitatively into lead bromide, the ratio between the weights of the two compounds thus furnishing a means of calculating the combining weight of lead. Ordinary lead gave values lying between 207.170 and 207.216, the mean being 207.192, whereas lead from the Vesuvian cotunnite gave numbers ranging from 207.025 to 207.079, the mean being 207.050, which corresponds with a mixture of ordinary lead and urano-lead containing about 12% of the latter.  
T. H. P.

( $\alpha + \gamma$ ) **Eutectoid in Brass.** W. HEIKE and K. LEDEBUR (*Z. Metallk.*, 1924, **16**, 380—381).— $\beta$ -Brass undergoes a transformation at  $470^\circ$  which is accompanied by an evolution of heat, but not by a visible change in the microstructure, so that some doubt has been thrown on the theory that this is due to the decom-

position of the  $\beta$  constituent into the  $\alpha + \gamma$  eutectoid. If about 15% of manganese is added to the alloy, however, the change from  $\beta$  into a coarse eutectoidal structure of  $\alpha + \gamma$  is very marked and, as manganese forms only solid solutions with both copper and zinc, this appears to indicate that the change at  $470^\circ$  in the pure brass is really a eutectoid transformation. [Cf. *B.*, 1924, 1016.]

A. R. P.

**Crystal Structure and Density of Cuprous Selenide and Zinc Selenide.** W. P. DAVEY (*Physical Rev.*, 1923, **21**, 380).—Cuprous selenide crystals are composed of three interpenetrating face-centred cubic lattices, two of copper and one of selenium, giving a crystal structure similar to that of calcium fluoride. The side of each of the face-centred cubes is  $5.751 \pm 0.007 \text{ \AA}$ . Zinc selenide, similarly to zinc sulphide, is composed of two interpenetrating face-centred cubes of side  $5.651 \pm 0.007 \text{ \AA}$ . The calculated densities are : cuprous selenide, 7.154; zinc selenide, 5.283.

A. A. E.

**Crystallographic Identity of the Two Forms of Mercuric Oxide.** G. R. LEVI (*Gazzetta*, 1924, **54**, 709—712).—Results are given of an X-ray examination of yellow and red mercuric oxide by the method of crystalline powders irregularly oriented, use being made of an anti-cathode of pure copper and of preparations 1.5 mm. in diameter. The two photograms are virtually identical, a constant displacement of the interferences amounting to about 0.8 mm. being explainable by the difference between the apparent specific gravities of the two modifications. The latter are therefore crystallographically identical and the symmetry appears to be trimetric or even of a higher order, although Moses A., 1904, ii, 46) and Hillebrand and Schaller (A., 1907, ii, 788) agree that the natural mercuric oxide, montroydite, crystallises in the orthorhombic system.

T. H. P.

**Revision of the Atomic Weight of Yttrium. Analysis of Yttrium Chloride.** I. O. HONIGSCHMID and A. MEUWSEN (*Z. anorg. Chem.*, 1924, **140**, 341—356).—Pure yttria was prepared from two different sources by fractional precipitation with ammonia followed by fractionation of yttrium bromate. Holmium was very difficult to separate from yttrium by either process, but the latter separated the material into less soluble fractions containing holmium, and more soluble fractions containing erbium, which could be readily separated by repetition of the ammonia fractionation. The yttria thus obtained was further purified by double precipitation of the chloride by saturating its solution with hydrogen chloride at  $0^\circ$ . The yttrium chloride was dried over potassium hydroxide, heated at  $350^\circ$  in a current of hydrogen chloride, and the ratios  $\text{YCl}_3 : 3\text{AgCl} : 3\text{Ag}$  were determined with this material. The purest fraction gave a mean atomic weight of  $\text{Y} = 88.950 \pm 0.010$  and spectroscopic examination showed only the faintest trace of erbium to be present. Two others specimens of yttrium chloride containing about 0.05—0.1% of other rare earths, chiefly holmium and

dysprosium, gave results for the atomic weight of just above 89. These figures are in agreement with Aston's conclusion that yttrium is a single element of atomic weight 89. A. R. P.

**Separation of Yttrium from the other Elements of Gadolinite.** L. ROLLA, V. CUTTICA, and L. FERNANDES (*Gazzetta*, 1924, 54, 617—622).—Not only is yttrium sulphate less soluble than the sulphates of the other metals accompanying yttrium in gadolinite, but the differences in solubility are still more marked with the double sulphates formed with thallous sulphate. Fractional crystallisation of the double sulphates hence serves as a good method for the preparation of pure yttrium salt. T. H. P.

**Fractionation of the Cerium Earths and Separation of the Various Groups of Rare Earths.** L. FERNANDES (*Gazzetta*, 1924, 54, 623—628).—Fractional crystallisation of the double sulphates formed with thallous sulphate (cf. preceding abstract) serves as a means of separating the cerium metals. Cerium thallous sulphate has the formula,  $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{Tl}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , but the presence of excess of thallous sulphate may lead to the precipitation of the salt,  $\text{Ce}_2(\text{SO}_4)_3 \cdot 3\text{Tl}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . The lanthanum salts of analogous formulæ have also been prepared. A convenient method for determining the atomic weight of the metal of any fraction in order to follow the course of the separation consists in converting the oxide into sulphate, crystallising the latter, washing it with water and dehydrating it, precipitating the sulphate as barium sulphate, and determining the ratio between the weights of the anhydrous sulphate and the barium sulphate. This procedure obviates the troublesome elimination of traces of carbonate from the oxide.

T. H. P.

**Crystal Structures of Alumina, Ferric Oxide, and Chromic Oxide.** W. P. DAVEY (*Physical Rev.*, 1923, 21, 716).—For alumina, ferric oxide, and chromic oxide, respectively, the side of unit triangle is 4.745, 5.035, 4.932 Å.; axial ratio, 2.726, 2.726, 2.754; computed density, 4.001, 5.243, 5.256. In all three cases there are 3 mols. per unit prism. A hexahedral molecule is assumed, consisting of an equilateral triangle of oxygen with a metal atom immediately above and below the centre of the triangle. The oxides are "valency compounds" and should not be decomposed by an electric field while molten.

A. A. E.

**Reactions in Carbonyl Chloride Solutions. II. Formation of Chloroaluminates.** A. O. GERMANN and K. GAGOS (*J. Physical Chem.*, 1924, 28, 965—972).—Carbonyl chloride solutions of aluminium chloride react with many metals, and vigorously with magnesium and calcium. This is due to the production of double salts, which in the case of magnesium and calcium are soluble in carbonyl chloride and hence do not impede the attack of the metal. The compound  $\text{CaCl}_2 \cdot 2\text{AlCl}_3 \cdot 2\text{COCl}_2$  has been isolated. This readily loses carbonyl chloride (dissociation pressure at  $19.5^\circ = 25$  mm.) and the product when heated loses aluminium chloride, giving the compound  $3\text{CaCl}_2 \cdot 4\text{AlCl}_3$ , previously obtained

by Baud by fusing together the anhydrous salts. Magnesium reacts in a similar manner, but on cooling the product a two-liquid system is formed which has not been further investigated. S. S.

**New Types of Ter- and Quadri-valent Compounds of Manganese.** F. OLSSON.—(See i, 1298.)

**Crystal Lattice of Manganous Oxide.** G. R. LEVI (*Gazzetta*, 1924, **54**, 704—708).—Investigation by the Debye and Scherrer method shows that the crystal lattice of manganous oxide is cubical and of exactly the same type as that of sodium chloride, the value of  $a$  being 4.40 Å. The calculated density is 5.46, which agrees well with the value, 5.432, found for the oxide after fusion in the Tammann furnace; for the artificial product Rammelsberg (*Ann. Phys. Chem.*, 1865, [ii], **124**, 513) and Playfair and Joule (*T.*, 1846, **3**, 57) gave the value 5.091, and for the mineral the latter authors gave 5.18. Laue's method gave for magnesium oxide the value  $a=4.22$  Å. (cf. Gerlach, *Z. Physik*, 1922, **3**, 184). T. H. P.

**Crystal Structure of Manganese Dioxide.** A. ST. JOHN (*Physical Rev.*, 1923, **21**, 389).—Polianite is a body-centred tetragonal array of  $\text{MnO}_2$  groups having an axial ratio 0.651, edge 4.44 Å., and  $d$  5.043. The oxygen atoms lie on a face-centred tetrahedral lattice and the manganese on a body-centred lattice, a manganese atom being at the centre of alternate tetrahedra of oxygen atoms. Since the pattern of pyrolusite is similar, any external form leading to its classification as orthorhombic is due to pseudomorphism. A. A. E.

**Solubility Product of Barium Manganate and the Equilibrium between Manganate and Permanganate Ions.** H. I. SCHLESINGER and H. B. SIEMS (*J. Amer. Chem. Soc.*, 1924, **46**, 1965—1978).—Barium manganate may be prepared by the cautious addition of a saturated solution of potassium permanganate to a boiling saturated solution of barium hydroxide, carbon dioxide being excluded. The bluish-black barium manganate is washed by decantation, separated, dried at 110°, and then in a vacuum desiccator over phosphorus pentoxide. It may be analysed by suspension in excess of phosphoric acid, when it is decomposed thus:  $3\text{BaMnO}_4 + 4\text{H}_3\text{PO}_4 = 2\text{Ba}(\text{H}_2\text{PO}_4)_2 + \text{Ba}(\text{MnO}_4)_2 + \text{MnO}_2 + 2\text{H}_2\text{O}$ . The resulting mixture is treated with excess of a standard solution of ferrous phosphate, which reacts with both manganese dioxide and permanganate, and the unchanged ferrous salt titrated with standard permanganate solution. In this way, the total oxidising power of the mixture is obtained. A similar determination is carried out in which the manganese dioxide is filtered off, and the permanganate determined alone. From these titrations the quantity of manganate originally present can be calculated, the double determination being necessary to allow for manganese dioxide present as impurity. The solubility product of barium manganate determined by measuring equilibrium concentrations in the reaction  $\text{BaMnO}_4 + \text{K}_2\text{CO}_3 \rightleftharpoons \text{BaCO}_3 + \text{K}_2\text{MnO}_4$ , is  $2.46 \times 10^{-10}$  on the assumption that potassium carbonate and manganate are equally ionised under the equilibrium

conditions. The equilibrium constant for the reaction between manganate and permanganate ions is  $K_{eq} = [\text{MnO}_4']^2[\text{OH}']^4/[\text{MnO}_4'']^3 = 16 \pm 7$  at  $25^\circ$ . An apparatus is described for the accurate determination, by conductivity measurements, of the end-point of the titration of very small quantities of alkali in the presence of permanganate.

W. H.-R.

**Crystal Structure of Hard Steel.** K. HEINDLHOFFER (*Physical Rev.*, 1924, **24**, 426—438).—By the use of the ionisation chamber method, the X-ray spectrum and its intensity distribution have been observed for iron practically free from carbon and for iron containing respectively C, 0.80, 1.31%; Cr, 0.14, 0.12%; Mn, 0.35, 0.24%; Si, 0.19, 0.17%, in both the fine and coarse martensitic condition. Martensite shows the same lines as pure iron, but less intense, somewhat broader, and slightly shifted, the amount of shift being approximately the same for different carbon contents. The space lattice of martensite, like that of  $\alpha$ -iron, is a body-centred cube, but contracted by 0.4%. From considerations of density, martensite is believed to be a mixture in varying proportions of (a) a solid solution of carbon in  $\alpha$ -iron, the carbon atoms replacing the iron atoms, and (b) finely-dispersed cementite. The solid solution is unstable even at the ordinary temperature. At  $260^\circ$ , the lattice distortion of martensite largely disappears in 30 minutes, although only part of the carbon is precipitated, and the hardness is still far above that of the annealed state. The cementite also contributes to the hardness by reason of its fine grained condition. [Cf. *B.*, 1924, 1015.]

A. A. E.

**Metallographic Heat Etching.** F. SAUERWALD, W. SCHULTZE, and G. JACKWIRTH (*Z. anorg. Chem.*, 1924, **140**, 384—390).—Annealing polished metallic specimens in a vacuum develops the grain structure in the same way as "heat etching" them in a fused salt bath or in an indifferent gas, showing that the "etching" is not due to chemical action, but to recrystallisation phenomena on the surface of the specimen and to volume changes during heating. The characteristic double network that often develops during "heat etching" is due, not to polymorphic changes, but to this surface recrystallisation, which is induced by the cold work the specimen has undergone during polishing. Tests carried out on steels by heating in a vacuum indicate that the grain structure of the stable phase at high temperatures can be determined by slow cooling only when the composition of the steel is near the eutectoidal point and that, in other cases, quenching is essential for the development of the grain structure.

A. R. P.

**Crystal Structure of Iron-Nickel Alloys.** L. W. MCKEEHAN (*Physical Rev.*, 1923, **21**, 380).—The body-centred cubic lattice of iron has  $a = 2.872 \times 10^{-8}$  cm., corresponding with  $d$  7.775; the face-centred cubic lattice of nickel has  $a = 3.510 \times 10^{-8}$  cm., corresponding with  $d$  8.953. The variation of the lattices with composition of alloys has been followed.

A. A. E.

**Preparation of Chromium by Electrolysis.** J. SIGRIST, P. WINKLER, and M. WANTZ (*Helv. Chim. Acta*, 1924, **7**, 968—972).—In order to obtain a deposit of chromium from a chromic acid solution, it is necessary to add another electrolyte; a mixture of 0.3% of chromic sulphate and 24.5% of chromium trioxide was studied (cf. Sargent, *Trans. Amer. Electrochem. Soc.*, 1920, **37**, 479). Below 3.4 volts, only hydrogen is evolved. There is rapid increase of yield with rise of current density, the maximum being obtained at 160 amp./dm.<sup>2</sup> At small current density the deposit is soft, and at high values arborescence is marked, but with a rotating cathode current densities of more than 160 amp./dm.<sup>2</sup> give satisfactory results. The best results are given at the ordinary temperature (the yield at 50° being one-fourth that at 20°) and with a silver cathode: 0.17 g./amp. hour at  $\Delta=186$  amp./dm.<sup>2</sup> (52% of theory). The duration of the electrolysis has no effect on the quality or yield of metal. Experiments on pure chromium trioxide gave negative results; hence it is suggested that all the deposit of chromium is due to the electrolysis of chromic sulphate.

In the electrolysis of solutions of chromium salts, the use of a diaphragm is necessary and the yield depends on the  $p_H$  and chromium concentration of the electrolyte; a solution obtained by dissolving the sulphate (green spangles) in the warm, containing 161 g./litre of chromium, gave the best yield: 0.16 g./amp. hr. at  $\Delta=73.7$  amp./dm.<sup>2</sup>. Generally the deposit is arborescent, consisting of black needles of doubtful purity. Even the best deposits were inferior to those obtained from chromic acid and the yields were poor throughout.

W. E. E.

**Quinquevalent Chromium.** F. OLSSON.—(See i, 1299.)

**Chlorides of Bivalent Molybdenum, Tungsten, and Tantalum. IV. Derivatives of Tritungsten Hexachloride ["Tungsten Dichloride"].** K. LINDNER and A. KÖHLER (*Z. anorg. Chem.*, 1924, **140**, 357—367; cf. this vol., ii, 192).—Tungsten hexachloride is reduced to the "dichloride" by heating with magnesium, lead, zinc, or, preferably, aluminium powder mixed with quartz. The chloro-acid, obtained as previously described (A., 1922, ii, 509), crystallises in yellow needles of the composition  $H[W_3Cl_7, H_2O]_{aq}$ . The complex anion is not nearly so stable as the corresponding molybdenum and tantalum compounds; in alcoholic solution or on gentle heating, 1 mol. of hydrogen chloride is lost, leaving an insoluble yellow residue of  $[W_3Cl_6, H_2O]$ . With concentrated sulphuric acid, hydrogen chloride is evolved and the compound  $W_3Cl_4(SO_4)$  formed, whereas alkali hydroxides dissolve the chloro-acid with the evolution of hydrogen and the formation of the corresponding alkali tungstate. Hydrolysis with a small quantity of water yields the compound  $[W_3Cl_4, 2H_2O]Cl_2$ , whereas much water causes complete oxidation to tungstic acid. The following salts of the chloro-acid are described: (a) from alcoholic solution:  $C_5H_5N, H[W_3Cl_7, H_2O]$ , pearly yellow leaflets;  $(C_5H_5N)_3, H_3[W_3Cl_9]$ , yellow octahedra; (b) from aqueous solution:

$C_5H_5N, H[W_3Cl_7], 3H_2O$ , which loses  $3H_2O$  at  $36^\circ$ ;

$C_2H_4(NH_2)_2, H_2[W_3Cl_7], 2H_2O$ , which loses  $2H_2O$  at  $140^\circ$ ; (c) from pyridine solution after addition of ether:  $C_5H_5N, H[W_3Cl_7(C_5H_5N)], 2Et_2O$ , which loses ether at  $78^\circ$ .

From solutions of the chloro-acid in hot, concentrated hydrobromic acid, thin, yellow leaflets of  $H[W_3Br_4Cl_3, H_2O], 9H_2O$  are obtained on cooling; they yield with hydrobromic acid and pyridinium bromide light yellow crystals of  $(C_5H_5N)_3, H_3[W_3Br_6Cl_3]$ , which are converted into  $C_5H_5N, H[W_3Br_4Cl_3]$  with the loss of 2 mols. of pyridinium bromide on heating at the b. p. of xylene. Molecular-weight determinations of some of the above compounds by the cryoscopic method in nitrobenzene showed that the above formulæ are correct.

A. R. P.

**Pyrocatechol Compounds of Sexa- and Quinque-valent Molybdenum.** R. WEINLAND and P. HUTHMANN.—(See i, 1306.)

**Atomic Heats of Tungsten and Carbon at Incandescence Temperatures.** A. G. WORTHING (*Bull. Nela Res. Lab.*, 1922, 1, 349).—From the total radiation of a filament,  $F(T)$ , the relation between its resistance and the temperature,  $R=R(T)$ , and the rate of increase of temperature  $T=T(t)$ , the heat capacity at constant pressure,  $C_p$ , can be calculated  $E.I=F(T)+C_p(dT/dt)$ .  $F(T)$  and  $R(T)$  were determined in the ordinary way. By measuring the resistance at various time intervals after switching on the heating current, the increase in  $R$ , and thus the temperature are obtained. In the case of tungsten, the atomic heat was lower than that given by Pirano and Corbino. At high temperatures, however, it lies considerably above the theoretical value,  $3Nk$ . The value for carbon lies between 5 and 6, in good agreement with the prolongation to  $1000^\circ$  of a curve on graphite measured by Weber. It is stated that the assumption of the contribution of electron vibration to the magnitude of specific heats at high temperatures as explanation of their exceeding the theoretical value does not suffice.

CHEMICAL ABSTRACTS.

**Synthesis of Carnotite.** G. CANNERI and V. PESTELLI (*Gazzetta*, 1924, 54, 641—646).—The analytical data referring to carnotite (cf. Friedel and Cumenge, A., 1899, ii, 434) are unsatisfactory, owing partly to the difficulty of obtaining an amorphous or microcrystalline mineral free from impurities, and partly to the difficulties attending the separation of vanadium from uranium. By adding uranic anhydride in the form of ammonium pyrouanate to fused potassium (or sodium) metavanadate, microscopic, rectangular, fluorescent plates, apparently of the rhombic system and of the composition  $K[or Na](UO_2)VO_4$ , are obtained. These artificial carnotites are analogous in composition to the uranylphosphates obtainable either in solution or by the igneous method, and also to various natural uranylphosphates, and may be regarded as derivatives of the relatively stable uranylvandic acid,  $[V^{UO_3}]H$ . Evidence of this stability is furnished by the fact that, unlike the



vanadates, the carnotites do not alter in colour when treated with acids.

A method of separating vanadium from uranium by means of "cupferron" is described. [Cf. *B.*, 1924, 979.] T. H. P.

**Change in the Thermoelectric Power of Tin at the M. P.** T. R. HARRISON and P. D. FOOTE (*Physical Rev.*, 1923, **21**, 196—197).—The thermoelectric power of a solid tin-liquid tin thermocouple at the m. p. is 1.2 microvolts/degree, the liquid tin being at the higher potential. The Peltier *E.M.F.* is computed to be 0.6 millivolt. Both results are opposite in sign to those predicted by the simple electron theory. A. A. E.

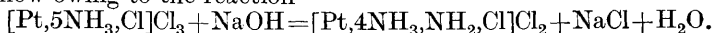
**Crystal Structures of some Tetragonal Crystals.** M. L. HUGGINS (*Physical Rev.*, 1923, **21**, 719—720).—In anatase and rutile ( $\text{TiO}_2$ ), each titanium atom is surrounded by four equidistant oxygen atoms, and each oxygen by two equidistant titanium atoms, all at tetrahedron corners. The compounds  $\text{SnO}_2$ ,  $\text{PbO}_2$ ,  $\text{MnO}_2$ ,  $\text{MoO}_2$ ,  $\text{RuO}_2$ ,  $\text{ZrSiO}_4$ ,  $\text{ThSiO}_4$ ,  $\text{YPO}_2$ , and  $\text{MgF}_2$  are like rutile; probably also  $\text{ZrO}_2$  and  $\text{SiO}_2$  (cristobalite). The compound  $\text{Mn}_3\text{O}_4$  has one of two structures, in both of which each manganese atom is surrounded by four oxygen atoms and each oxygen by three manganese atoms, at tetrahedron corners. In calcium tungstate, the oxygen atoms are each surrounded by two calcium and two tungsten atoms, at tetrahedron corners, each calcium or tungsten atom being surrounded by eight oxygen atoms. Lead molybdate is similar. Tetragonal mercuric iodide may be similar to anatase or to calcium tungstate. A. A. E.

**Isomorphism of Compounds of Thorium with those of Quadrivalent Cerium.** V. CUTTICA and A. TOCCHI (*Gazzetta*, 1924, **54**, 628—633; cf. this vol., ii, 112).—The compounds  $\text{Th}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{Th}(\text{NO}_3)_6$ , and  $\text{NiTh}(\text{NO}_3)_6 \cdot 8\text{H}_2\text{O}$ , are miscible in the solid state with the analogous ceric compounds in proportions varying over a moderately wide range, support being thus furnished to the view that cerium should be placed in the same sub-group as thorium (cf. Zambonini, A., 1923, ii, 499).

T. H. P.

**Substitutes for Platinum.** A. GAWALOWSKI (*Z. anal. Chem.*, 1924, **64**, 473).—Alloys of silver and aluminium, of silver, aluminium, and platinum, and of nickel and platinum, known technically as alargan, platalargan, and platnik, respectively, may be used as substitutes for platinum in analytical operations. W. H.-R.

**Theory of Indicators.** A. GRÜNBERG (*Z. anorg. Chem.*, 1924, **138**, 333—348).—A solution of chloropentammineplatinic chloride is colourless, but shows an absorption band in the ultra-violet. On gradual addition of a solution of sodium hydroxide, the absorption band moves sharply to the visible region of the spectrum at the point where 1 mol. of sodium hydroxide is present to every 1 mol. of chloropentammine salt. The mixture becomes pale yellow owing to the reaction



A similar change occurs when sodium hydroxide is added to a solution of hexammineplatinic chloride owing to the reaction  $[\text{Pt}, 6\text{NH}_3]\text{Cl}_4 + \text{NaOH} = [\text{Pt}, 5\text{NH}_3, \text{NH}_2]\text{Cl}_3 + \text{NaCl} + \text{H}_2\text{O}$ , but the absorption band, whilst undergoing a sharp change, does not move into the visible spectrum. When the colourless aqueous solution of the compound  $[\text{Pt}, 2\text{NH}_3, \text{C}_5\text{H}_5\text{N}, \text{NO}_2, \text{Cl}_2]\text{Cl}$  is treated with sodium hydroxide, the solution becomes yellow owing to the formation of the compound  $[\text{Pt}, \text{NH}_3, \text{NH}_2, \text{C}_5\text{H}_5\text{N}, \text{NO}_2, \text{Cl}_2]$ . These colour changes are reversible in the presence of hydrogen ions, and are examples of indicator action due to purely chemical reactions. They support the chemical theory of indicators of Stieglitz (A., 1904, ii, 17; 1908, i, 726) as opposed to the classical dissociation theory of Ostwald. The colour changes are due to the rearrangement of the inner co-ordination sphere.

W. H.-R.

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## Mineralogical Chemistry.

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**"Bitumen" in Meteorites.** P. E. SPIELMANN (*Nature*, 1924, 114, 276).—Evidence is adduced to show that the presence of a hydrocarbon in meteorites is due to the action of water on carbide after the arrival of the meteorite on the earth. A. A. E.

**Felspathic Sandstones of the Hercynian Chain and the Products of Permo-Triassic Evaporation.** L. CAYEUX (*Compt. rend.*, 1924, 178, 2103—2106).—The sandstones which occur in the Hercynian chain contain large masses of feldspars, which, however, represent much greater deposits reduced in quantity by erosion and decomposition. The part played by such felspathic sandstones in the carboniferous period was that of a source of potassium, sodium, magnesium, and calcium in water. The evaporation of such masses of water containing salts of these metals has given rise to salt deposits, notably those of Stassfurt. H. J. E.

**Datolite from Rigollo (Parma Province).** T. NOCCA (*Atti R. Accad. Lincei*, 1924, [v], 33, i, 444—447).—Analysis of crystals of this mineral,  $d^{18}$  2.995,  $n_D$  1.62—1.67, gave:  $H_2O$ , 6.09;  $SiO_2$ , 37.35,  $CaO$ , 35.27,  $B_2O_3$ , (21.29), these results agreeing well with the formula  $HCaBSiO_5$ . The results of crystallographic measurements are given. T. H. P.

**Presence of the Compound,  $K_2Mn_2(SO_4)_3$ , among the Products of the Present Activity of Vesuvius.** F. ZAMBONINI and G. CAROBBI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [III], 30, 123—126).—Stalactites of the laval cupola formed on Vesuvius during the activity of September—October 1922 contain small pink tetrahedra, sometimes united to groups, of the composition  $K_2Mn_2(SO_4)_3$ . The name manganolangbeinite is proposed for this mineral. T. H. P.

**Composition of Thomsonite.** S. G. GORDON (*Proc. Acad. Nat. Sci. Philadelphia*, 1924, **76**, 103—107).—From the previously published analyses of thomsonite, which give values for the ratio of lime to soda varying from 1 : 1 to 6 : 1, the graphs of the (lime + soda) content against the silica, and against the water contents, are plotted, and, by extrapolation, it is shown that the analysed minerals belong to a series (thomsonite series) which can be interpreted as mixed crystals of the end members :  $\text{CaO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2, 3\text{H}_2\text{O}$  (calciorthomsonite) and  $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 3\text{SiO}_2, \text{H}_2\text{O}$  (natrolite with  $1\text{H}_2\text{O}$ ), the latter component being only able to enter the mixed crystals to the extent of 50%.  
S. K. T.

**Content of Hafnium in Vesuvian Zircon.** A. PIUTTI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [III], **30**, 122—123).—In a private communication from von Hevesy, it is stated that Vesuvian zircon contains 1% of hafnium.  
T. H. P.

**Sklodowskite, a New Radioactive Mineral.** A. SCHOEP (*Compt. rend.*, 1924, **179**, 413—415).—The mineral occurs at Chinkolobwe (Belgian Congo) in the form of pale yellow crystals,  $d\ 3.54$ , associated with kasolite. It is a hydrated magnesium uranium silicate of the formula  $\text{MgO}, 2\text{UO}_3, 2\text{SiO}_2, 7\text{H}_2\text{O}$  containing small quantities of sodium, potassium, nickel, and telluric acid. It exhibits more marked dispersion and birefringence than chinkolobwite.  
H. J. E.

**Rare Gases of Volcanic Exhalations.** A. PIUTTI and E. BOGGIO-LERA.—(See ii, 854.)

**Combining Weight of Lead from Vesuvian Cotunnite.** A. PIUTTI and D. MIGLIACCI.—(See ii, 859.)

**Synthesis of Carnotite.** G. CANNERI and V. PESTELLI.—(See 865.)

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### Analytical Chemistry.

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**Apparatus for Identifying a Gas.** J. F. DURAND (*Bull. Soc. chim.*, 1924, [iv], **35**, 1207—1208).—A short glass tube, drawn out at one end to a capillary and closed at the other by a rubber tube with a glass rod inserted, is filled with the reagent for identifying the gas. A few drops of reagent are expelled by pressure and the tube lowered into the gas; on releasing the pressure, a portion of the gas bubbles up through the reagent. S. K. T.

**Colorimeter for Corrosive Gases.** E. C. WHITE and R. C. TOLMAN (*Physical Rev.*, 1923, **22**, 207).—An all-glass colorimeter for measuring low concentrations of bromine, iodine, nitrogen dioxide, etc., consists of a connected system of standard tubes on a rotating cylindrical frame, which are compared with the longer

sample tube and a very short tube containing gas of high enough concentration to be susceptible of direct measurement. A. A. E.

**Analysis of Volatile Organic Substances by Combustion in an Open Tube.** M. E. CARRIÈRE and C. LEENHARDT (*Bull. Soc. chim.*, 1924, [iv], **35**, 1206—1207).—The vapour of the volatile organic liquid is carried into the combustion tube by a stream of warm oxygen, the vaporisation taking place in a simple apparatus which can be attached to the end of the tube. S. K. T.

**Measurement of Hydrogen-ion Concentrations with Glass Electrodes.** W. E. L. BROWN (*J. Sci. Instruments*, 1924, **2**, 12—17).—A glass bulb filled with a solution of known hydrogen-ion concentration is immersed in the unknown solution. By means of capillary tubes, both solutions are connected with calomel electrodes, which, in turn, are connected with the electrometer and through a potentiometer to earth, respectively. The potentiometer is adjusted to balance nearly the whole *E.M.F.*, and the small remainder of a few millivolts is read off on the electrometer. The bulb of the glass electrode is 2 cm. in diameter and the walls are 0.03 mm. thick. The best results are obtained with soft glass; Jena glass behaves as a hydrogen electrode in acid solutions and as a sodium electrode in alkaline solutions. The results are calculated from the formula  $E=0.058 \cdot \log (C_1/C_2)$  volts, where *E* is the observed *E.M.F.*, and *C*<sub>1</sub> and *C*<sub>2</sub> are the hydrogen-ion concentrations of the two solutions. By the use of this apparatus, it has been shown directly that oxyhæmoglobin is a stronger acid than hæmoglobin. A. R. P.

**Acidosis. XX. Colorimetric Determination of Blood *p*<sub>H</sub> at Body Temperature without Buffer Standards.** A. B. HASTINGS and J. SENDROY, jun. (*J. Biol. Chem.*, 1924, **61**, 695—710).—By the use of a comparator and two tubes, one containing 0.01*N*-sodium hydroxide and the other 0.0001*N*-hydrochloric acid, into which are introduced varying amounts of phenol-sulphonephthalein, it is possible to obtain a colour corresponding with any given value of *p*<sub>H</sub>; the employment of standard buffer solutions can be avoided, and the *p*<sub>H</sub> of blood-serum determined to within  $\pm 0.02$ . If both determinations are carried out at the same temperature, the results obtained by electrometric and colorimetric methods agree within the limits of experimental error; by performing the colorimetric determination at body temperature, it is therefore possible to dispense with the correction proposed by Cullen (A., 1922, ii, 672). C. R. H.

**Use of Sodium Chloride as Standard in Analyses of Sea-water.** Y. MÉNAGER (*Compt. rend.*, 1924, **179**, 195—198).—The fourth International Congress of Chemistry has proposed the adoption of sodium chloride solution as standard, in the analysis of sea-water, instead of the normal sea-water from the hydrographic laboratory at Copenhagen. If this proposal be accepted, measurements should be referred to a certain volume of the standard solution, and not to a certain weight, owing to differences in density between the standard solution and sea-water of the same chlorine

content from different sources. In addition, new hydrographic tables should be drawn up, because of the difficulty of applying a uniform correction when passing from the old to the new system.

M. S. B.

**Replacement of Iodine by Ferric Chloride in Quantitative Analysis.** I. M. KOLTHOFF and O. TOMICEK (*Pharm. Weekblad*, 1924, **61**, 1205—1209).—The method of titration with ferric chloride proposed by Jellinek and Winogradoff (A., 1923, ii, 871; this vol., ii, 703) does not under any conditions give accurate results. The most suitable indicator was found to be meconic acid, in presence of a cupric salt as catalyst, but the highest degree of accuracy attained was 0.5%.

S. I. L.

**Standardisation of Thiosulphate Solution by the Permanganate-Iodide and Dichromate-Iodide Methods.** W. C. BRAY and H. E. MILLER (*J. Amer. Chem. Soc.*, 1924, **46**, 2204—2211).—The permanganate-iodide and the dichromate-iodide methods of standardising sodium thiosulphate give results agreeing to within 0.1%, the slight difference probably being due to a small oxygen error in the latter method. No side reactions occur in the permanganate method, but when dichromate is used this is only true within the narrow concentration range given by Vosburgh (A., 1922, ii, 863), and then only when the iodide is the last reagent added. When the dichromate is added last, too much iodine is liberated, probably due to an oxygen error. It is suggested that an intermediate compound is formed by the interaction of oxygen and the iodide and dichromate ions which reacts with the iodide in presence of acid to form iodine and with the dichromate to form oxygen, the latter causing the error.

S. K. T.

**Thomas Test for Ammonia.** B. H. BUTCHER (*Abstracts Bact.*, 1924, **8**, 32—33).—Thomas' test for ammonia, using phenol and sodium hypochlorite, is affected by peptone (0.05%), sodium caseinate (0.2%), milk (0.15%), acetic acid (0.25%), butyric acid (0.25%), lactic acid (0.35%), acetaldehyde (0.05%), dextrose (0.05%), lactose (0.1%). Formaldehyde (2%) did not interfere. Aliphatic amines produce a blue coloration identical with that given by ammonia.

A. A. E.

**Volumetric Determination of Ammonium Salts.** S. LÖVGREN (*Z. anal. Chem.*, 1924, **64**, 457—470).—In the presence of sufficient alcohol, ammonium salts may be determined by direct titration with sodium hydroxide, using thymolphthalein as indicator. In aqueous solution, ammonia gives a blue colour with thymolphthalein, but in the presence of alcohol, the equilibrium constants are altered so that the  $p_H$  curve of the ammonia is below the transformation line of the indicator. The concentration of the alcohol should be at least 50%, and the volume at the end of the titration should not exceed 10 c.c., concentrated solutions of sodium hydroxide being used if the quantity of ammonium salt is large. The method is applicable to ammonium salts of both weak and strong acids. In the absence of alcohol, it is possible to titrate ammonium salts

with sodium hydroxide with thymolphthalein as indicator, a comparison solution being used to estimate the exact colour produced when the equivalent quantity of sodium hydroxide has been added. W. H.-R.

**Direct Nesslerisation Micro-Kjeldahl Method and a Modification of the Nessler-Folin Reagent for Ammonia.** F. C. KOCH and T. L. McMEEKIN (*J. Amer. Chem. Soc.*, 1924, **46**, 2066—2069).—A rapid micro-Kjeldahl method is described which involves the addition to the sulphuric acid mixture of 30% hydrogen peroxide; it is also recommended for macro-Kjeldahl determinations on substances rich in carbohydrates and fats, since troublesome foaming is avoided.

After dilution, the acid liquid is nesslerised, using a modified reagent; the volume employed requires careful control, since variation in alkalinity affects the intensity of the colour. The modified Nessler-Folin reagent is prepared by dissolving 22.5 g. of iodine in 20 c.c. of water and 30 g. of potassium iodide, and shaking the solution, with cooling, with 30 g. of mercury until the yellow supernatant liquid has lost its yellow colour due to iodine. The aqueous solution is decanted and a few drops of iodine solution (prepared as before) are added until a slight excess of iodine can be detected by the starch test. The solution is diluted to 200 c.c., added to 975 c.c. of 10% sodium hydroxide solution, and well mixed. This reagent does not cause the turbidity common with the Folin-Denis procedure (A., 1916, ii, 573). R. B.

**Volumetric Analysis of Hydrazine by the Iodine, Bromate, Iodate, and Permanganate Methods.** I. M. KOLTHOFF (*J. Amer. Chem. Soc.*, 1924, **46**, 2009—2016; cf. Bray and Cuy, this vol., ii, 423).—The determination of hydrazine by direct titration with iodine according to the method of Stollé (A., 1903, i, 119; ii, 100) gives accurate results when less than 1 g. of sodium hydrogen carbonate to 25 c.c. of 0.1N-hydrazine sulphate is added. Starch should not be used as an indicator, but the iodine solution should be added until a yellow colour persists for 2 minutes.

Using methyl-red or indigo as indicator, hydrazine may be directly titrated with bromate if sufficient hydrochloric acid is present; the use of a particular indicator involves a small constant error in the volume of bromate used. In the direct titration of hydrazine by iodate by the method of Jamieson (A., 1912, ii, 487), accurate results are obtained if sufficient hydrochloric acid is present, whilst carbon tetrachloride may be substituted for chloroform. In the presence of sufficient hydrochloric acid, a boiling solution of hydrazine may be titrated directly with permanganate, whilst in alkaline solution hydrazine may be determined by oxidation with excess of permanganate, the unchanged excess being determined iodometrically. [Cf. B., 1924, 941.] W. H.-R.

**Comparative Susceptibility of Natural Phosphates towards Acids and its Determination with Citric Acid.** G. ANDRÉ and H. COPAUX (*Bull. Soc. chim.*, 1924, [iv], **35**, 1113—1115).—The fertility of a soil is shown to be measured by the ratio : phosphoric



acid soluble in 2% citric acid solution/total phosphoric acid. This ratio increased with the calcium carbonate content in four specimens of natural phosphates, but in the case of fluorapatite, from which limestone is absent, it was very low; it is concluded that phosphoric acid is assimilated from this mineral only with difficulty.

S. K. T.

**Comparative Susceptibility of Natural Phosphates towards Acids and its Potentiometric Determination.** H. COPAUX and J. DARIC (*Bull. Soc. chim.*, 1924, [iv], 35, 1115—1119).—A method is outlined whereby the fertilising powers of natural phosphates are compared by potentiometric measurements of the solution formed by shaking the mineral (previously freed from carbonate by boiling with ammonium chloride solution) with progressively increasing quantities of 0.1N-hydrochloric acid, filtering, and adding a slight excess of quinhydrone. The higher the "citric acid ratio" (preceding abstract), the smaller is the potential of a hydrogen electrode in the solution.

S. K. T.

**Micro-determination of Silicon and its Concentration in certain Organs.** G. BERTRAND (*Bull. Soc. Chim. biol.*, 1924, 6, 656—658).—The method of Isaacs (this vol., ii, 499) for the colorimetric determination of small amounts of silicon, and the conclusions of this author regarding the silicon content of the brain are criticised on the ground of the disturbing effect on his method of the presence of phosphates.

C. R. H.

**Critical Studies on Methods of Analysis. XIII. Carbon.** L. A. CONGDON, F. J. BROWN, and R. K. FRIEDEL (*Chem. News*, 1924, 129, 253—257).—The carbon content of a standard steel has been determined by wet and dry combustion methods both with and without previous separation of the iron by means of potassium copper chloride solution, and by the colorimetric method. Although there are great variations in the figures obtained in the individual tests, the authors conclude that direct combustion in oxygen of the separated carbon gives the most accurate results. [Cf. *B.*, 1924, 984.]

A. R. P.

**Determination of Gases in Blood and Other Solutions by Vacuum Extraction and Manometric Measurement.** I. D. D. VAN SLYKE and J. M. NEILL. II. C. R. HARRINGTON and D. D. VAN SLYKE (*J. Biol. Chem.*, 1924, 61, 523—573, 575—584).—I.—A pipette is provided at its upper end with a stopcock inlet and connected at its lower end with a levelling bulb and manometer system; the gases are liberated by shaking the liquid in a Torricellian vacuum as in Slyke and Stadie's method (*A.*, 1922, ii, 78). The pressure of total gases is then determined at a marked constant volume; the gas to be determined is then absorbed, and the residual pressure measured at the same volume, whence the amount of gas absorbed can be calculated. Correction must be introduced for the volume of fluid introduced during absorption and for reabsorption of a certain amount of gas in the process of running the solution up to the constant volume mark. The apparatus has been applied

to the determination of oxygen, carbon dioxide, and carbon monoxide in blood, both separately, or, by a combined method, on one sample.

II.—A modified pipette for the above apparatus is provided with a trap and 2-way stopcock at the bottom; thus blood and reagents can be removed, and the gas analysed over a non-absorbent solution of equal parts of glycerol and saturated sodium chloride. No correction for reabsorption is needed; moreover, carbon monoxide can then be determined by absorption with cuprous chloride. Gasometric analyses, in the modified apparatus, of hydrogen peroxide free from dissolved air agreed with titrimetric analyses by means of potassium permanganate constantly to within 0.1 millimol.

C. R. H.

**Determination of Carbon Dioxide in Serum in Presence of Ether.** J. H. AUSTIN (*J. Biol. Chem.*, 1924, **61**, 345—353).—A modification of the manometric method of Van Slyke and Neill (preceding abstract) is described by which it is possible to avoid the error introduced by the presence of ethyl ether due to the reabsorption of the latter in the process of absorption of carbon dioxide.

C. R. H.

**Detection of Carbonate in Sodium Hydrogen Carbonate by means of Phenolphthalein.** V. MACRI (*Boll. Chim. Farm.*, 1924, **63**, 531—533).—The results of Sabalitschka and Kubisch (*Schweiz. Apoth. Ztg.*, 1923, 161—179; cf. also this vol., ii, 500) are discussed. [Cf. *B.*, 1924, 940.]

T. H. P.

**Detection of Metals as Double Halides with Pyridine, Antipyrine, Pyramidone, or Aniline.** I. M. KOLTHOFF and H. HAMER (*Pharm. Weekblad*, 1924, **61**, 1222—1227).—The pyridine-thiocyanate compounds of the general formula  $M(CNS)_2(C_5H_5N)_2$  (Spacu, A., 1923, i, 96; ii, 34, 40, 41, 580, 585, 699, 879) are obtained with all the common heavy metals in concentrations of 100 mg. per litre. With antipyrine the action is more specific, zinc being detectable in presence of cadmium; with pyramidone 1 mg. of copper per litre gives a violet coloration. Using the bromides with pyridine, 5 mg. of cadmium or zinc per litre give crystalline precipitates readily differentiated under the microscope.

S. I. L.

**Lead. XI. Rapid Determination of Lead in Urine.** L. T. FAIRHALL (*J. Biol. Chem.*, 1924, **60**, 485—488).—The freshly-collected urine is made strongly alkaline with ammonia and kept overnight. The precipitate of alkaline-earth phosphates, which contains the whole of the lead, is then filtered, ashed, and the lead determined volumetrically by the chromate method. (A., 1922, ii, 659.)

E. S.

**Determination of Copper as Sulphide.** M. LEO (*Chem.-Ztg.*, 1924, **48**, 841).—In the method for the determination of copper as cuprous sulphide by ignition of cupric sulphide in hydrogen, coal gas may advantageously replace the hydrogen.

A. R. P.

**Separation of Mercury and Arsenic.** P. WENGER and M. SCHILT (*Helv. Chim. Acta*, 1924, **7**, 907—909).—From the mixed sulphides precipitated from hydrochloric acid solution, the arsenious

sulphide is dissolved out, in the first method, by ammonium hydroxide in the cold. The mercuric sulphide is washed with ammonium chloride solution, then with alcohol, and the free sulphur extracted by means of carbon disulphide. Finally, the sulphide is washed with alcohol and ether and dried. In the second method, the arsenious sulphide is removed by heating the mixed sulphides at  $100^{\circ}$  for 8 hours with saturated sodium hydrogen carbonate solution. The determination is then completed as in the first method. The results of both methods are about 0.5% high. W. E. E.

**Separation of Molybdic and Tungstic Acids.** I. KOPPEL (*Chem.-Ztg.*, 1924, **48**, 801—802).—The alkaline solution containing molybdate and tungstate is neutralised with formic acid, treated with a small quantity of ammonium sulphide solution, and acidified with formic acid. On warming, the brown colloidal precipitate of molybdenum sulphide coagulates; it is collected, dried, and calcined at a low temperature to molybdenum trioxide. Tungstic acid is recovered from the filtrate by evaporation with sulphuric acid and subsequent hydrolysis. [Cf. *B.*, 1924, Dec. 26.]

A. R. P.

**Quantitative Detection of Minute Quantities of Precious Metals in Mercury.** A. MIETHE and H. STAMMREICH (*Z. anorg. Chem.*, 1924, **140**, 368—370).—A large quantity of the mercury is distilled at the ordinary pressure until a few c.c. are left; this is distilled under reduced pressure until a small drop remains, which is then dissolved in nitric acid at the ordinary temperature. The resulting network of pure gold is fused under borax and the volume of the minute spherical bead determined by measuring its diameter under the microscope. The nitric acid solution is neutralised with ammonia and heated with hydrazine sulphate until the mercury-silver amalgam collects into a drop; this is washed and heated to expel the mercury. The resulting silver sponge is melted as before and its volume ascertained in a similar way; if it corresponds with a weight of more than 0.02 mg., the weight calculated from the volume will be too great and the bead should therefore be weighed directly. A. R. P.

**Detection of Ruthenium and Osmium.** L. WÖHLER and L. METZ (*Z. anorg. Chem.*, 1924, **138**, 368).—A blue colour is produced by the addition of thiocarbamide and hydrochloric acid to a solution containing complex chlorides of tervalent ruthenium, whilst, if thiocarbamilide is used, the blue-green solution can be extracted with ether, and as little as 0.0003 mg. of ruthenium per c.c. can be detected. With osmium, the addition of thiocarbamilide produces a red solution which can also be extracted with ether; this test is more sensitive than that with thiocarbamide (cf. Tschugaev, *A.*, 1918, ii, 335). The metals of the iron and platinum groups give characteristic colours with trithiocarbonates in the presence of hydrochloric acid, and unstable coloured solutions can be extracted with ether; nickel, platinum, and osmium give red, brown, and olive-green solutions, respectively. W. H.-R.

**Exact Gas-analytical Methods for the Analysis of Gaseous Fuels.** E. OTT (*Helv. Chim. Acta*, 1924, 7, 886—898; cf. A., 1920, ii, 767).—For the determination of heavy hydrocarbons in coal gas etc., 25% fuming sulphuric acid is preferable to bromine-water, since it absorbs benzene completely and ethylene better. The stationary pipette packed with glass rod gives more accurate results than the ordinary type, but the results are still affected by the physical solubilities of the constituents determined. Moreover, the absorption of heavy hydrocarbons is unsatisfactory. Much more than a trace of benzene (*e.g.*, up to 6%) or ethylene is necessary to suppress the absorption of oxygen by phosphorus. Improved methods are given for the absorption of carbon monoxide by ammoniacal cuprous chloride. The preparation of pure methane and ethylene is described. W. E. E.

**Modified Dichromate Method for the Determination of Glycerol. Hydration of Curd Fibres of Sodium Palmitate.** H. B. BENNETT (*J. Chem. Soc.*, 1924, 125, 1971—1975).—In the presence of sodium palmitate, glycerol may be determined as follows. A portion of the lye is diluted with water, warmed with 50% sulphuric acid, and allowed to cool, when a quantity of potassium dichromate, about 0.1 g. in excess of that required to oxidise the glycerol, is added, and the whole heated by boiling water under an air condenser for 2 hours. After cooling, the unchanged dichromate is determined by titration with sodium thiosulphate after the addition of potassium iodide. A slight error is introduced by partial oxidation of the surface layer of palmitic acid, but this can be determined and a correction applied. Using this method of analysis, it is shown that glycerol is negatively adsorbed by curd fibres of sodium palmitate at the ordinary temperature even in the absence of any salt. The curd fibres separating from an *N* (weight) anisotropic solution have the approximate composition  $\text{NaP}_4 \cdot 4 \cdot 3\text{H}_2\text{O}$  and are more soluble than those from ordinary (isotropic) 0.25*N*-solution which have the composition  $\text{NaP}_{10} \cdot 10\text{H}_2\text{O}$ . The degree of hydration slightly increases with age. W. H.-R.

**Determination of the Degree of Hydrolysis of Gallotannin by Tannase.** W. N. NICHOLSON and D. RHIND (*Analyst*, 1924, 49, 505—509).—The method of Freudenberg and Vollbrecht (A., 1922, i, 285) and various modifications thereof were found to be unsatisfactory. After hydrolysis with an extract of the mycelium of *Aspergillus niger*, the gallic acid was determined at intervals, subsequently to precipitation of the unchanged gallotannin with quinine hydrochloride, by a modification of Mitchell's method (A., 1923, ii, 188). D. G. H.

**Direct Determination of Dextrose and other Carbohydrates.** E. KNECHT and E. HIBBERT (*J. Chem. Soc.*, 1924, 125, 2009—2012).—Dextrose may be converted quantitatively into its osazone by heating its solution on a water-bath for 10 minutes with 4 times the theoretical amount of phenylhydrazine dissolved in acetic acid.

The resulting aqueous solution of phenylglucosazone is reduced with excess of titanous chloride in an atmosphere of carbon dioxide, followed by titration with crystal-scarlet to ascertain the unchanged excess of reducing agent. The amount of reducing agent required for 1 mol. of glucosazone is equivalent to 6H. The method is applicable to other carbohydrates which form osazones under similar conditions.

W. H.-R.

**Determination of Menthologlycuronic Acid in Urine.** A. J. QUICK (*J. Biol. Chem.*, 1924, **61**, 667—677).—The mentholglycuronic acid is separated from the urine by continuous extraction with ether after acidification with sulphuric acid; the residue from the ethereal extract is hydrolysed with hydrochloric acid and the glycuronic acid in the neutralised solution determined either by the method of Benedict (A., 1918, ii, 247) or of Folin and Wu (A., 1920, ii, 337).

C. R. H.

**Ethyl Ether. II. Determination of Peroxide as Contaminant.** A. W. ROWE and E. P. PHELPS (*J. Amer. Chem. Soc.*, 1924, **46**, 2078—2085).—The ether sample is added to an aqueous solution of cadmium potassium iodide, dilute sulphuric acid, and alcohol (purified with *m*-phenylenediamine hydrochloride by Girard and Cuniasse's method), and the iodine liberated is titrated with 0.1*N*-sodium thiosulphate solution, a control experiment being also performed. The time factor is extremely important, probably because of an equilibrium:  $\text{Et}_2\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Et}_2\text{O} + \text{H}_2\text{O}_2$ , the hydrogen peroxide reacting at once with hydriodic acid, whereas the diethyl peroxide may react slowly. A period of reaction of 1 hour is usually sufficient. The presence of acetaldehyde up to about 1% has a negligible effect on the titration, and acidification with sulphuric acid gives better results than acetic acid, trichloroacetic acid, or phosphoric acid. Ferrous sulphate appears to act as a negative catalyst for the peroxide reaction.

R. B.

**Determination of Acetaldehyde.** A. BEYTHIEN, H. HEMPEL, and C. WIESEMANN (*Z. Unters. Nahr. Genussm.*, 1924, **48**, 169—170).—The various methods of determining acetaldehyde were examined, very accurate results being obtained by Rieter's method of treating with sulphurous acid and titrating the aldehyde-sulphurous acid formed. A colorimetric method employing *m*-phenylenediamine is also described. [Cf. *B.*, 1924, 959.]

G. S. W.

**Pentose Metabolism. I. Colorimetric Determination of Furfuraldehyde.** G. E. YOUNGBURG and G. W. PUCHER (*J. Biol. Chem.*, 1924, **61**, 741—746).—The solution containing furfuraldehyde is treated with aniline and acetic acid and the red colour which develops is compared with that produced by a known amount of furfuraldehyde under the same conditions. The average error of the determination is  $\pm 2.5\%$ .

C. R. H.

## ERRATA.

## VOL. 126 (ABSTRACTS, 1924).

Page	Line	
i. 17	5*	for "HOUGOUNENQ" read "HUGOUNENQ."
i. 184	29	„ "mucus" read "mucous membrane."
i. 263	33	„ "small" read "large."
i. 515	16*	„ "this vol., i, 294" read "this vol., i, 288."
i. 537	14*	„ "-4-pyridine" read "-4-pyridone."
i. 603	11*	„ "trimethyl" read "trimethylene."
i. 661	8*	„ "thiophen-cocaine" read "thiophen-atropine."
i. 684	18*	„ "Stilzlobium" read "Stizolobium."
i. 944	30	„ "trimethyl- $\gamma$ -mannosides and tetramethyl- $\gamma$ -mannosides" read "trimethyl- $\gamma$ -methylmannosides and tetramethyl- $\gamma$ -methyl- mannosides."
i. 953	15*	„ "p-nitrophenyl thiocyanate" read "of mononitro deriva- tives."
i. 962	11*	„ "dibromocinnamic acid" read "cinnamic acid dibromide."
i. 967	18*	„ " $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ " read " $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ ."
i. 973	7*	„ "Sahina" read "Asahina."
i. 1054	8	„ " $\text{KTI}(\text{CN})_2\cdot\text{H}_2\text{O}$ " read " $\text{KTI}(\text{CN})_2$ ."
i. 1060	18	„ "3" read "2 or 3."
i. 1121	25	„ "triphenylmethylphosphorus dichloride" read "triphenyl- methoxyphosphorus dichloride."
i. 1121	7*	„ " $\text{PHCl}_2\cdot\text{OR} = \text{PCl}_2\text{R}\cdot\text{O} + \text{HCl}$ " read " $\text{PRCl}_2\cdot\text{OH} = \text{PRCl}_2\cdot\text{O} + \text{HCl}$ ."
i. 1246	15	„ "4-dimethylmethyleneamino-3-aminophenylarsinic acid" read "3-amino-4-isopropylideneaminophenylarsinic acid."
ii. 218	19*	„ " $k/(\lambda^2 - \lambda_0^2)$ " read " $k/(\lambda^2 - \lambda_0'^2)$ ."
ii. 299	5	„ "NORDOFF" read "NARDROFF."
ii. 355	11*	„ "solution, neutralised to phenolphthalein" read "alcoholic (formol-free) solution neutralised to thymolphthalein."
ii. 567	11*	The reagent used is cuprous oxide suspended in sulphuric acid, not the compound of cuprous sulphate and ethylene.
ii. 830	12*	for "SEDBERG" read "SVEDBERG."
ii. 913	12 col. i	for "Nordoff" read "Nardroff."
ii. 987	15	„ ii insert "Nardroff, R. von. See also B. Davis."
ii. 989	29	„ ii delete "Nordoff, R. von. See B. Davis."

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